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Analyse de la méthode projector augmented-wave pour les calculs de structure électronique en géométrie périodique

Analysis of the projector augmented-wave method for electronic structure calculations in periodic settings

Thèse dirigée par M. Xavier Blanc

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Abstract

Cette thèse est consacrée à l'étude de la méthode PAW (projector augmented-wave) et d'une de ses modifications, baptisée méthode PAW variationnelle (VPAW), pour le calcul de l'état fondamental d'Hamiltoniens en géométrie périodique. Ces méthodes visent à améliorer la vitesse de convergence des méthodes d'ondes planes (ou méthodes de Fourier) en appliquant une transformation inversible au problème aux valeurs propres initial agissant au voisinage de chaque site atomique. Cette transformation permet de capter une partie des difficultés dues aux singularités coulombiennes. La méthode VPAW est analysée pour un opérateur de Schrödinger unidimensionnel avec des potentiels de Dirac. Les fonctions propres de ce modèle comprennent des sauts de dérivées similaires aux cusps électroniques. Le saut de dérivée des fonctions propres du problème aux valeurs propres issu de la méthode VPAW est réduit de façon importante. Cela entraîne une accélération de convergence en ondes planes du calcul des valeurs propres corroborée par une étude numérique. Une étude de la méthode VPAW est conduite pour des Hamiltoniens 3D périodiques avec des singularités coulombiennes, parvenant à des conclusions similaires. Pour la méthode PAW, la transformation inversible comporte des sommes infinies qui sont tronquées en pratique. Ceci introduit une erreur, qui est rarement quantifiée en pratique. Elle est analysée dans le cas de l'opérateur de Schrödinger unidimensionnel avec des potentiels de Dirac. Des bornes sur la plus basse valeur propre en fonction des paramètres PAW sont prouvées conformes aux tests numériques.

Keywords: quantum chemistry, eigenvalue problems, plane-waves discretization, projector augmented-wave method

Abstract

This thesis is devoted to the study of the PAW method (projector augmented-wave) and of a variant called the variational PAW method (VPAW). These methods aim to accelerate the convergence of plane-wave methods in electronic structure calculations. They rely on an invertible transformation applied to the eigenvalue problem, which acts in a neighborhood of each atomic site. The transformation captures some difficulties caused by the Coulomb singularities. The VPAW method is applied to a periodic one-dimensional Schrödinger operator with Dirac potentials and analyzed in this setting. Eigenfunctions of this model have derivative jumps similar to the electronic cusps. The derivative jumps of eigenfunctions of the VPAW eigenvalue problem are significantly reduced. Hence, a smaller plane-wave cut-off is required for a given accuracy level. The study of the VPAW method is also carried out for 3D periodic Hamiltonians with Coulomb singularities yielding similar results. In the PAW method, the invertible transformation has infinite sums that are truncated in practice. The induced error is analyzed in the case of the periodic one-dimensional Schrödinger operator with Dirac potentials. Error bounds on the lowest eigenvalue are proved depending on the PAW parameters.

Keywords: quantum chemistry, eigenvalue problems, plane-waves discretization, projector augmented-wave method

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Préambule

Dans cette thèse, une modification de la méthode PAW (projector augmented-wave), baptisée méthode PAW variationnelle (VPAW), est proposée et analysée dans différents cadres. Les méthodes PAW et VPAW visent à réduire l'erreur de discrétisation en ondes planes dans les calculs de structure électronique.

Le premier chapitre est une introduction à l'approximation du cœur gelé et à la théorie des pseudopotentiels. Dans l'approximation du cœur gelé, les électrons sont séparés en électrons de cœur et de valence. Les électrons de cœur interagissent peu avec leur environnement. Leur comportement peut être décrit, en première approximation, par une fonction d'onde solution d'un Hamiltonien atomique. Les potentiels de Coulomb ainsi que les interactions avec les électrons de cœur sont alors remplacés par un potentiel régulier: le pseudopotentiel. De nombreux types de pseudopotentiels ont été proposés, reposant sur des motivations différentes. Les principales familles de pseudopotentiels sont exposées dans ce chapitre.

La méthode VPAW est présentée au Chapitre 2 dans le cadre d'Hamiltoniens de Kohn-Sham périodiques. Elle repose sur une transformation inversible du problème aux valeurs propres initial. La méthode VPAW est donc exacte puisqu'aucune approximation du problème aux valeurs propres initial n'est introduite, contrairement à la méthode PAW où les sommes infinies apparaissant dans les équations PAW doivent être tronquées en pratique. Un résumé des différentes contributions de cette thèse à l'analyse des méthodes PAW et VPAW est regroupé dans ce chapitre.

Le Chapitre 3 est consacré à l'étude de la méthode VPAW appliquée à un opérateur de Schrödinger périodique unidimensionnel avec des potentiels de Dirac. Les fonctions propres de ce modèle ont des sauts de dérivée similaires aux conditions de cusp de Kato de fonctions d'ondes électroniques. Le saut de dérivée des fonctions propres du problème aux valeurs propres issu de la méthode VPAW est réduit de façon importante. Cela entraîne une accélération de convergence des méthodes d'ondes planes, dont les estimations théoriques concordent avec les résultats numériques.

Au Chapitre 4, une analyse de l'erreur de troncature de la méthode PAW est fournie, pour la plus basse valeur propre du modèle unidimensionnel du chapitre précédent. Pour cela, la méthode PAW est interprétée comme une perturbation de la méthode VPAW qui est exacte. Les bornes obtenues sur la plus basse valeur propre PAW sont confirmées par les tests numériques.

Le dernier chapitre est dédié à l'étude de la méthode VPAW appliquée à des Hamiltoniens 3D périodiques. Les singularités des fonctions propres de ces Hamiltoniens sont connues précisément dans le cadre des espaces de Sobolev à poids. Grâce à cette caractérisation, il est possible de reproduire l'analyse faite pour le modèle unidimensionnel et montrer que les cusps des fonctions propres de la méthode VPAW sont réduits. Une estimation de l'accélération de convergence en ondes planes s'en suit, corroborée par des simulations numériques dans un modèle simple.

Preamble

In this thesis, a modification of the projector augmented-wave (PAW) method is proposed. It is called the variational PAW (VPAW) method and is studied in different settings. The PAW and VPAW methods aim to accelerate the convergence of plane-wave methods in electronic structure simulations.

The first chapter is an introduction to the frozen-core approximation and the pseudopotential theory. In the frozen-core approximation, the electrons are partitioned into core and valence electrons. The core electrons are not expected to be affected by the environment, therefore as a first approximation they can be described by an eigenfunction of an atomic Hamiltonian. Coulomb potentials and nonlinear interactions with core electrons are then replaced by a regular potential: the pseudopotential. A wide range of pseudopotentials has been proposed based on different motivations. Description of the main families of pseudopotentials is gathered in this chapter.

In Chapter 2, the VPAW method for periodic Kohn-Sham Hamiltonians is presented. It relies on an invertible transformation of the original eigenvalue problem. The VPAW method is an exact method, as no approximation of the original eigenvalue problem is introduced. This is not the case of the PAW method, where infinite sums appearing in the PAW equations need to be truncated in practice. A summary of the different contributions of this thesis on the PAW and VPAW method is regrouped in this chapter.

Chapter 3 is devoted to the analysis of the VPAW method applied to a periodic one-dimensional Schrödinger operator with Dirac potentials. The eigenfunctions of this operator have cusps that are similar to the Kato cusp of electronic wave functions. The study of the VPAW method shows that cusps of the eigenfunctions of the VPAW eigenvalue problem are significantly reduced. Estimates of the plane-wave convergence of the eigenvalues using the VPAW method are proved, fully corroborated by numerical simulations.

In Chapter 4, the PAW truncation error is analyzed by reinterpreting the PAW method as a perturbation of the VPAW method, which is exact. The analysis is restricted to the lowest eigenvalue of the one-dimensional Schrödinger operator considered in the previous chapter. Numerical tests are provided confirming the error bounds on the lowest PAW eigenvalue.

The last chapter is dedicated to the study of the VPAW method for periodic linear 3D Hamiltonians. Singularities of the molecular wave functions are accurately characterized using weighted Sobolev space. Using this characterization, as in the one-dimensional setting, it is possible to show that the eigenfunctions of the VPAW eigenvalue problem have reduced cusps resulting in an acceleration of convergence of plane-wave methods. The efficiency of the VPAW method is confirmed by numerical tests on a simple model.

List of publications

Here is a list of articles that were written during this thesis:

— [BCD17a] (with Xavier Blanc and Eric Cancès) *Variational projector augmented-wave method*, Comptes Rendus Mathématique, 355, (2017), pp. 665-670.

— [BCD17b] (with Xavier Blanc and Eric Cancès), *Variational projector augmented-wave method: theoretical analysis and preliminary numerical results*, submitted.

— [Dup17] *Projector augmented-wave method: analysis in a one-dimensional setting*, submitted.

— [Dup18] *The variational projector augmented-wave method for the plane-wave discretization of linear Schrödinger operators*, in preparation.

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CHAPTER 1

PSEUDOPOTENTIAL THEORY

For simplicity, the presentation is restricted to finite molecular systems, described by a non-relativistic Schrödinger equation.

1.1 The N-body Schrödinger equation and its one-body approximations

All the equations will be presented using atomic units, where the following physical constants are all set equal to 1: the electron mass m_e, the elementary charge e, the reduced Planck constant $\hbar$ and the Coulomb's constant $k_e = \frac{1}{4\pi\epsilon_0}$.

The molecular system considered contains

- $N_{\rm at}$ nuclei of charge $Z_1, \ldots, Z_{N_{\rm at}} > 0$ at positions $\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\rm at}} \in \mathbb{R}^3$;
- N electrons of charge -1 at positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$.

Spins of electrons are neglected.

Since a proton is roughly 1836 times heavier than an electron, in a first approximation, we can consider that electrons relax instantaneously to small variations of the positions of nuclei. Nuclei can thus be treated classically and their position will be a parameter in the stationary Schrödinger equation satisfied by the electronic wave function. This approximation is commonly called the Born-Oppenheimer approximation.

The electronic wave function is described by a function Ψ belonging to $\bigotimes_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C})$ where $\bigotimes$ denotes the tensor product. By the Pauli exclusion principle, since electrons are fermions, the electronic wave function Ψ is antisymmetric, *i.e.* for any permutations $\sigma \in \mathcal{S}_N$,

$$\Psi(\mathbf{r}_{\sigma(1)}, \ldots, \mathbf{r}_{\sigma(N)}) = (-1)^\sigma \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N).$$

Therefore, Ψ in fact belongs to the space $\bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C})$ which is the antisymmetrized product space

of $L^2(\mathbb{R}^3)$. This space is endowed with the inner product

$$\forall \Phi, \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C}),\ \langle \Phi | \Psi \rangle = \int_{\mathbb{R}^{3N}} \Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)^* \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N,$$

where Φ^* denotes the complex conjugate of Φ. The corresponding norm is denoted by $\| \cdot \|$. The quantity $|\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2$ is interpreted as the probability of finding the N electrons at positions $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Hence the norm of the electronic wave function is equal to 1:

$$\|\Psi\|^2 = \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2\, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N = 1.$$

Since the electrons in a molecular system are indistinguishable, it is often more interesting to study the electronic density ρ of a molecular system which represents the distribution of the N electrons:

$$\rho(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, \mathrm{d}\mathbf{r}_2 \ldots \mathrm{d}\mathbf{r}_N. \tag{1.1.1}$$

1.1.1 The Schrödinger model

The time-independent ground-state problem corresponds to the energy minimization

$$E_0^N(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}}) = \inf_{\Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C}), \|\Psi\|=1} \langle \Psi | H^N_{(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}})} | \Psi \rangle, \tag{1.1.2}$$

where $H^N_{(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}})}$ is the N-body Hamiltonian of the molecular system

$$H^N_{(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}})} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) + \sum_{\substack{i,j=1 \\ i<j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1.1.3}$$

The terms appearing in $H^N_{(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}})}$ have the following physical meaning

- $$-\frac{1}{2}\sum_{i=1}^{N} \Delta_i$$
  models the kinetic energy of the electrons;
- $$-\sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$
  models the Coulomb interaction between the electron i and the nuclei;

- $$\sum_{\substack{i,j=1\\ i<j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

  models the Coulomb interaction between the electrons.

The operator $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ acting on $\bigwedge_{i=1}^{N} L^2(\mathbb{R}^3,\mathbb{C})$ is a self-adjoint operator with domain $\bigwedge_{i=1}^{N} H^2(\mathbb{R}^3,\mathbb{C})$.

The ground-state can be identified with the bottom of the spectrum of H^N

$$E_0^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}}) = \inf \sigma(H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}).$$

The theoretical properties of the spectrum of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ are well-understood. Before stating the main theorems on the essential and discrete spectrum of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$, we define Σ^N the bottom of the essential spectrum

$$\Sigma^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}}) = \inf \sigma_{\rm ess}(H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}).$$

Theorem 1.1 (HVZ Theorem [Žis60, vW64, Hun66])**.** *We have*

$$\sigma_{\rm ess}(H^N) = [\Sigma^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}}), +\infty),$$

where

$$\Sigma^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}}) = E_0^{N-1}(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}}).$$

By this theorem, the essential spectrum of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ is an interval. To reach the energy $\Sigma^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})$, an electron escapes at infinity and is removed from the molecular system. The conditions to have a well-defined ground-state are given by the following theorem.

Theorem 1.2 (Discrete spectrum of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$)**.** *Let $Z = \sum_{I=1}^{N_{\rm at}} Z_I$ be the total charge of the system.*

1. *(Existence of a ground-state [Žis60, ŽS65]) If $N < Z+1$, $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ has an infinite number of eigenvalues E_k^N of finite multiplicity such that $E_k^N \underset{k\to\infty}{\longrightarrow} \Sigma^N(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})$.*
2. *(Spectrum of negatively charged systems [Jaf76, VŽ77, Sig82]) If $N \geq Z+1$, $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ has at most a finite number of eigenvalues below its essential spectrum.*
3. *(Non-existence when N is large [Rus82, Sig82, Sig84]) There is N_c such that if $N \geq N_c$ $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ has no eigenvalues below its essential spectrum.*

Theorem 1.2 states that for positively charged or neutral systems, the ground-state of the molecular system is well-defined. For too negatively charged systems, the molecule cannot bind all the electrons of the system. For the remainder of the section, we will consider only neutral or positively charged systems for which there is a ground-state. The wave function associated to this ground-state satisfies the Schrödinger equation

$$H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}\Psi = E_0^N\Psi. \tag{1.1.4}$$

The properties of the electronic ground-state wave function are well-known. The first work on the behavior of the electronic wave function close to a nucleus has been done by Kato in [Kat57]. He showed that the eigenfunctions of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ satisfy for $k = 1, \dots, N_{\rm at}$:

$$\forall \mathbf{r}_2, \dots, \mathbf{r}_N, \quad \left.\frac{\partial \overline{\Psi}}{\partial r}\right|_{r=0} = -Z_k \Psi(\mathbf{R}_k, \mathbf{r}_2, \dots, \mathbf{r}_N), \tag{1.1.5}$$

where

$$\overline{\Psi}(r, \mathbf{r}_2, \dots, \mathbf{r}_N) = \int_{S(0,1)} \Psi(r\hat{\mathbf{r}} + \mathbf{R}_k, \mathbf{r}_2, \dots, \mathbf{r}_N)\, \mathrm{d}\hat{\mathbf{r}}.$$

This is the so-called *Kato cusp* condition. When there is no ambiguity, for $\mathbf{r} \in \mathbb{R}^3$ we denote by $(r, \hat{\mathbf{r}})$, $r \geq 0$, $\hat{\mathbf{r}} \in S(0,1)$ its spherical coordinates.

Generalizations of the Kato cusp conditions have been studied in [HOHOS94, FHOHOS05, FHOHOS09]. More precisely, in [FHOHOS05], it is shown that the eigenfunctions of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$ can be written as a product of an explicit function, depending on the positions and the charge of the nuclei, and a smoother function.

Theorem 1.3 (Theorem 1.1 of [FHOHOS05]). *Let Ψ be an eigenfunction of $H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\rm at}})}$. Define $\mathbf{y}_{i,\alpha} = \mathbf{r}_i - \mathbf{R}_\alpha$, $i = 1, \dots, N$, $\alpha = 1, \dots, M$. Let*

$$\mathcal{F} = e^{F_2 + F_3}, \tag{1.1.6}$$

with

$$F_2(\mathbf{r}_1, \dots, \mathbf{r}_N) = -\sum_{\alpha=1}^{N_{\rm at}} \sum_{i=1}^{N} Z_\alpha |\mathbf{y}_{i,\alpha}| + \frac{1}{2} \sum_{1 \leq i < j \leq N} |\mathbf{r}_i - \mathbf{r}_j|,$$

and

$$F_3(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{2-\pi}{6} \sum_{\alpha=1}^{N_{\rm at}} \sum_{1 \leq i < j \leq N} Z_\alpha \mathbf{y}_{i,\alpha}^T \mathbf{y}_{j,\alpha} \log\left(|\mathbf{y}_{i,\alpha}|^2 + |\mathbf{y}_{j,\alpha}|^2\right).$$

Then

$$\Psi = \mathcal{F}\Phi,$$

and the function Φ is locally $C^{1,1}(\mathbb{R}^{3N})$.

In computational chemistry, the factor $\mathcal{F}$ is usually called a Jastrow factor and is commonly used in trial functions for quantum Monte-Carlo simulations [FMNR01, LRT02].

1.1.2 One-body approximations

The N-body Schrödinger equation (1.1.4) is numerically solvable only for small molecular systems. For example, for a system with N electrons and 10 discretization points per direction, the number of degrees of freedom is 10^{3N} which rapidly becomes unbearable even for supercomputers.

Different strategies have to be developed to reduce the cost of computing the ground-state.

The Hartree-Fock model

To reduce the dimension of the minimization space, the minimization problem (1.1.2) can be restricted to functions of the form

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i=1}^{N} \psi_i(\mathbf{r}_i).$$

However, such functions do not satisfy the Pauli exclusion principle, hence we are lead to consider an antisymmetric linear combination of such functions. This is the so-called Slater determinants

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_2) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

which are usually denoted by $\Psi = |\psi_1 \dots \psi_N\rangle$. The functions $\psi_i \in L^2(\mathbb{R}^3, \mathbb{R})$ are called orbitals and can be chosen orthonormal. The factor $\frac{1}{\sqrt{N!}}$ is a normalization factor. The energy minimization problem can be written as

$$E^0_{\mathrm{HF}} = \inf_{\Psi \in V_{\mathrm{HF}}} \left\langle \Psi | H^N | \Psi \right\rangle,$$

where H^N is the electronic Hamiltonian (1.1.3) and V_{HF} is the set of Slater determinants

$$V_{\mathrm{HF}} = \left\{ \Psi = |\psi_1 \dots \psi_N\rangle,\ \psi_i \in H^1(\mathbb{R}^3),\ \langle \psi_i | \psi_j \rangle = \delta_{ij} \right\}. \tag{1.1.7}$$

Since $V_{\mathrm{HF}} \subset \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C})$, the Hartree-Fock minimum energy E^0_{HF} is always higher than the exact ground state E^N_0.

For $\Psi = |\psi_1 \dots \psi_N\rangle$, the Hartree-Fock energy functional can be written as

$$\begin{aligned} \mathcal{E}^{\mathrm{HF}}(\Psi) = \langle \Psi | H^N | \Psi \rangle = \sum_{i=1}^{N} \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \psi_i|^2 + \int_{\mathbb{R}^3} V \rho_\Psi + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Psi(\mathbf{r}) \rho_\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \\ - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left| \sum_{j=1}^{N} \psi_j(\mathbf{r}) \psi_j(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}', \end{aligned} \tag{1.1.8}$$

where ρ_Ψ is the electronic density

$$\rho_\Psi(\mathbf{r}) = \sum_{i=1}^{N} |\psi_j(\mathbf{r})|^2,$$

and V is the nuclear potential

$$V(\mathbf{r}) = -\sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}.$$

For neutral or positively charged systems E^{HF} has a minimizer which satisfies the Euler-Lagrange

equations [Lio87]

$$\mathcal{F}[\Psi]\psi_j = \epsilon_j \psi_j, \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}, \tag{1.1.9}$$

where the eigenvalues $\epsilon_1 < \epsilon_2 \leq \cdots \leq \epsilon_N$ are the lowest eigenvalues of the Fock operator $\mathcal{F}[\Psi]$ defined by

$$\mathcal{F}[\Psi]g = -\frac{1}{2}\Delta g(\mathbf{r}) + V(\mathbf{r})g(\mathbf{r}) + \sum_{i=1}^{N} \int_{\mathbb{R}^3} \frac{|\psi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}'\; g(\mathbf{r}) - \sum_{i=1}^{N} \int_{\mathbb{R}^3} \frac{\psi_i(\mathbf{r}')g(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}'\; \psi_i(\mathbf{r}). \tag{1.1.10}$$

The Fock operator $\mathcal{F}[\Psi]$ depends on the orbitals $\psi_1, \ldots, \psi_N$: the eigenvalue problem (1.1.9) is nonlinear. However, in practice, it is easier to deal with a system of N nonlinear three dimensional eigenvalue problems than a linear eigenvalue problem in $\mathbb{R}^{3N}$.

Although the Hartree-Fock model captures 90% to 99% of the total ground-state energy (1.1.2) [Bac92], the missing energy, called the correlation energy, may hide important physical phenomena. Refinements of the Hartree-Fock theory have been developed to recover this missing correlation energy, relying on a converged Hartree-Fock calculation. Some of these methods are based on perturbation theory (Møller-Plesset perturbation theory). Other use an increased variational space V_{HF}, incorporating Slater-determinants with Hartree-Fock excited states orbitals (Configuration Interaction method) or using a different anzatz for the wave function (Coupled-Cluster method). These methods are usually very expensive and only affordable for small molecular systems. The interested reader may refer to [Dus17] for more information.

Density functional theory

The idea of the density functional theory is to express the minimization problem (1.1.2) using the electronic density ρ defined in (1.1.1) rather the full-electronic wave function Ψ. This theory has been first developed by Hohenberg-Kohn [HK64] and later on by Levy and Lieb [Lie83]. Let H_0^N be

$$H_0^N = -\frac{1}{2}\sum_{i=1}^{N} \Delta_i + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and V the nucleus-electron Coulomb potential

$$V(\mathbf{r}) = -\sum_{i=1}^{N}\sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}. \tag{1.1.11}$$

Hence, we have

$$H^N_{(\mathbf{R}_1,\ldots,\mathbf{R}_{N_{\mathrm{at}}})} = H_0^N - \sum_{i=1}^{N}\sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}.$$

In [Lie83], it is shown that the minimization problem (1.1.2) is equivalent to

$$E_0^N(\mathbf{R}_1, \ldots, \mathbf{R}_{N_{\mathrm{at}}}) = \inf_{\rho \in \mathcal{I}_N} \left(F_{LL}(\rho) + \int_{\mathbb{R}^3} V(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \right). \tag{1.1.12}$$

where

$$\mathcal{I}_N = \left\{ \rho \mid \exists \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \rho_\Psi = \rho \right\}.$$

The universal Levy-Lieb functional F_{LL} is defined by

$$F_{LL}(\rho) = \inf \left\{ \langle \Psi | H_0^N | \Psi \rangle, \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \|\Psi\| = 1, \rho_\Psi = \rho \right\}. \tag{1.1.13}$$

In [Lie83], the following characterization of $\mathcal{I}_N$ is proved

$$\mathcal{I}_N = \left\{ \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} = N \right\}.$$

The density functional theory seems to be a very promising practical approach since it is easier to approximate functions in $\mathcal{I}_N$ than in $\bigwedge_{i=1}^{N} L^2(\mathbb{R}^3)$. However, the analytic expression of the Levy-Lieb functional F_{LL} is unknown. Only qualitative criteria satisfied by F_{LL} are available. Approximations of the Levy-Lieb functional have been proposed, using exact formulas in very specific settings that are "close" to the molecular system under consideration. For Kohn-Sham models, the reference system is a system with N non-interacting electrons. The Kohn-Sham functional T_{KS} is obtained by replacing H_0^N in the definition of the Levy-Lieb functional (1.1.13) by the Hamiltonian

$$T_N = -\frac{1}{2} \sum_{i=1}^{N} \Delta_i.$$

The Kohn-Sham functional T_{KS} has a simple expression when ρ belongs to the space

$$\mathcal{R}_N = \left\{ \rho,\ \exists V \in L^{3/2} + L^\infty \text{ such that } \inf \left\{ \langle \Psi | - \frac{1}{2} \sum_{i=1}^{N} \Delta_i + V(\mathbf{r}_i) | \Psi \rangle, \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \|\Psi\| = 1 \right\} \right.$$
$$\left. \text{is reached for some } \Psi \text{ of density } \rho \right\}.$$

In that case, the expression of T_{KS} becomes

$$T_{KS}(\rho) = \inf \left\{ \frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i|^2,\ \phi_i \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij},\ \sum_{i=1}^{N} |\phi_i|^2 = \rho \right\}. \tag{1.1.14}$$

Introducing the Coulomb energy which represents the electrostatic energy of density ρ given by

$$J(\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{r},$$

and the exchange-correlation functional E_{xc}

$$E_{\text{xc}}(\rho) = F_{LL}(\rho) - T_{KS}(\rho) - J(\rho),$$

the Kohn-Sham minimization problem can be written as

$$\inf \left\{ \mathcal{E}^{\text{KS}}(\Psi),\ \Psi = (\psi_i)_{1\leq i\leq N} \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \psi_i\psi_j = \delta_{ij} \right\}, \tag{1.1.15}$$

with

$$\mathcal{E}^{\text{KS}}(\Psi) = \sum_{i=1}^{N} \frac{1}{2}\int_{\mathbb{R}^3} |\nabla\psi_i|^2 + \int_{\mathbb{R}^3} V\rho_\Psi + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\Psi(\mathbf{x})\rho_\Psi(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} + E_{\text{xc}}(\rho_\Psi).$$

Assuming the differentiabiliy of the exchange-correlation functional E_{xc}, the $(\psi_i)_{1\leq i\leq N}$ minimizing (1.1.15) satisfy the *Kohn-Sham* equations

$$\begin{cases} -\frac{1}{2}\Delta\psi_i + V\psi_i + \rho\star\frac{1}{|\cdot|}\psi_i + V_{\text{xc}}[\rho]\psi_i = \epsilon_i\psi_i \\ \int_{\mathbb{R}^3}\psi_i\psi_j = \delta_{ij}. \end{cases} \tag{1.1.16}$$

where $\epsilon_1 < \epsilon_2 \leq \cdots \leq \epsilon_N$ are the lowest eigenvalues of the Kohn-Sham operator.

Although solving (1.1.16) is more convenient than solving the N-body eigenvalue problem (1.1.4), minimizers of (1.1.12) do not necessarily belong to $\mathcal{R}_N$ (see [Lie83]) and the Kohn-Sham problem (1.1.15) is different from (1.1.12). This difficulty can be circumvented if mixed states are allowed and the Lieb functional is used (see [Lie83] for more details). An extended Kohn-Sham model arises using the Janak kinetic functional instead of the Kohn-Sham functional T_{KS} (see [CDK+03] Section 15).

The lack of knowledge of the Levy-Lieb functional F_{LL} is moved to the exchange-correlation functional E_{xc} which usually accounts for 10% of the total energy of the molecular system. Approximations of E_{xc} have been proposed among which the local density approximation (LDA):

$$E_{\text{xc}}[\rho] = \int_{\mathbb{R}^3} g(\rho(\mathbf{r}))\,\mathrm{d}\mathbf{r},$$

or the generalized gradient approximation (GGA):

$$E_{\text{xc}}[\rho] = \int_{\mathbb{R}^3} h(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))\,\mathrm{d}\mathbf{r}.$$

Existence of minimizers of extended Kohn-Sham model for these exchange-correlation functionals is proved in [AC09].

Some functionals mixing the Hartree-Fock exchange functional to the LDA exchange-correlation functional seem to be very efficient in practice (the B3LYP functional [Bec93] for example).

Numerical strategies to solve the Hartree-Fock or Kohn-Sham energy minimization

The Hartree-Fock or Kohn-Sham energy functionals are not convex, hence deterministic algorithms to find global minimium of (1.1.8) or (1.1.12) may not converge. In practice, the codes aim to solve the nonlinear eigenvalue problems (1.1.9) or (1.1.16) where the electronic density is obtained by taking the eigenfunctions associated to the lowest eigenvalues of the Fock or Kohn-Sham operator: this is the so-called *Aufbau principle*.

For the Hartree-Fock eigenvalue problem, usually one starts with an initial guess of the form $\Psi_0 = |\psi_1^{(0)}, \dots, \psi_n^{(0)}\rangle$ and compute the N lowest eigenvalue of the Fock operator $\mathcal{F}[\Psi_0]$. The associated eigenfunctions form the new set of orbitals and this step is repeated until self-consistency is reached, *i.e.* when $\|\Psi_{n+1} - \Psi_n\|$ is below a given tolerance. This fixed-point iteration is known as the *Roothaan algorithm* but sometimes fails even for basic molecular systems. A mathematical analysis of the behavior of the Roothaan algorithm is provided in [CLB00b]. New strategies have been proposed to solve (1.1.9), the level-shifting algorithm, which has also been analyzed in [CLB00b], the optimal damping algorithm [CLB00a] or the DIIS algorithm [Pul82].

1.2 General principle of pseudopotentials

The resolution of the Hartree-Fock or Kohn-Sham equations, although much simpler than the N-body Schrödinger eigenvalue problem, can still be too expensive especially in solid-state simulations. The difficulties are two-fold: first the Coulomb interaction with the nuclei gives rise to cusps that considerably impede the Fourier convergence rate, second, because of the orthogonality of the electronic wave functions, the valence electron wave functions have to oscillate near an atomic site. This behavior is hard to grasp with small plane-wave bases.

It is possible to simplify a bit more the setting. It is a common observation that only valence electrons are affected by the environment. Thus we can treat the core electrons as fixed in a first approximation. This approach reduces the number of electrons to consider. This is highly beneficial as the computational cost of standard methods in electronic structure calculations increases rapidly with the number of electrons. This approximation is the so-called *frozen-core approximation*.

In pseudopotential methods, also referred as effective-core potentials, the Coulomb interaction and the exchange-correlation potential generated by the core electrons are replaced by a smoother potential that approximates the original operator. The idea was first proposed by Hellmann [Hel35] as early as 1935 and since then a wide range of pseudopotentials have been designed: Troullier-Martins [TM91] and Kleinman-Bylander [KB82] norm conserving pseudopotentials, Vanderbilt [Van90] ultrasoft pseudopotentials and Goedecker [GTH96] pseudopotentials to name but a few.

Finally, pseudopotentials also enable one to include relativistic effects in the electronic Hamiltonian. Since the core electrons are localized close to the nucleus, their velocity compared to the light speed may not be negligible. The valence electrons are further away from the nucleus, thus a non-relativistic treatment is enough to compute their properties. However, since core electrons interact with the valence ones, it can be important to include some relativistic effects of the core electron wave functions in the Hamiltonian. This aspect will not be covered in this thesis.

A brief historical overview of the pseudopotentials is given below. For simplicity, the presentation

of the pseudopotential method is restricted to finite molecular systems. A detailed exposition of the pseudopotential theory for solid-state physics can be found in [Pic89].

1.2.1 Atomic Hamiltonian

Pseudopotentials begin with the design of regular eigenfunctions associated to the eigenfunctions of an atomic Hamiltonian. The pseudopotential is then obtained by calculating the potential of the atomic Schrödinger equation satisfied by the regular eigenfunction. In the quantum chemistry litterature, this is called *inverting the atomic Schrödinger equation*. Hence, it is important to state the properties of eigenfunctions of an atomic Hamiltonian.

The atomic Hamiltonian H^{AE} is an operator acting on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ modeling a single atom in vacuum:

$$H^{\mathrm{AE}} := -\frac{1}{2}\Delta - \frac{Z}{r} + V(r), \tag{1.2.1}$$

where V is a multiplicative potential which at first, will be considered smooth and bounded. The case where V is a Kohn-Sham potential will be covered later.

Since the atomic Hamiltonian is rotationally invariant, H^{AE} is block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ associated with the eigenspaces of the operator $\mathbf{L}^2$ (the square of the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (-i\nabla)$).

The eigenfunctions $\phi_{n\ell m}$ can be decomposed into a radial function $\frac{R_{n\ell}(r)}{r}$ and a real spherical harmonics $Y_{\ell m}$ (see [RS78] Section XIII.3.B for further details):

$$\phi_{n\ell m}(\mathbf{r}) = \frac{R_{n\ell}(r)}{r} Y_{\ell m}\left(\hat{\mathbf{r}}\right). \tag{1.2.2}$$

The radial functions $R_{n\ell}$ satisfies a radial Schrödinger equation on the half-line $(0, +\infty)$:

$$\mathfrak{h}_\ell^{\mathrm{AE}} R_{n\ell} := -\frac{1}{2} R''_{n\ell}(r) + \left(\frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} + V(r)\right) R_{n\ell}(r) = \epsilon_{n\ell} R_{n\ell}(r). \tag{1.2.3}$$

The number of square integrable eigenfunctions of $\mathfrak{h}_\ell^{\mathrm{AE}}$ is closely linked to the number of zeros of the eigenfunction $R_{n\ell}$. More precisely, denoting $N_\ell(\epsilon_{n\ell})$ the number of zeros of $R_{n\ell}$ different from $r = 0$, we have the following property ([RS78] Theorem XIII.8): if $\epsilon_{n\ell} \leq 0$, then $\mathfrak{h}_\ell^{AE}$ has exactly $N_\ell(\epsilon_{n\ell})$ eigenvalues below $\epsilon_{n\ell}$.

This property is central in the design of pseudopotential. In the pseudopotential theory, we are interested in defining a pseudopotential only giving valence states of the atomic operator. Indeed the pseudopotential already includes the effect of core states. Hence, the valence eigenvalue $\epsilon_{n\ell}$ should become the lowest eigenvalue of the atomic Hamiltonian with the pseudopotential. Hamiltonians with pseudopotentials are called *pseudo* or *pseudized* Hamiltonians.

Pseudopotentials are usually defined by inverting a radial Schrödinger equation satisfied by a chosen regular eigenfunction $\widetilde{R}_{n\ell}$. If this radial pseudo wave function $\widetilde{R}_{n\ell}$ is nodeless, by the previous characterization, $\epsilon_{n\ell}$ is indeed the ground-state of the radial pseudo Hamiltonian.

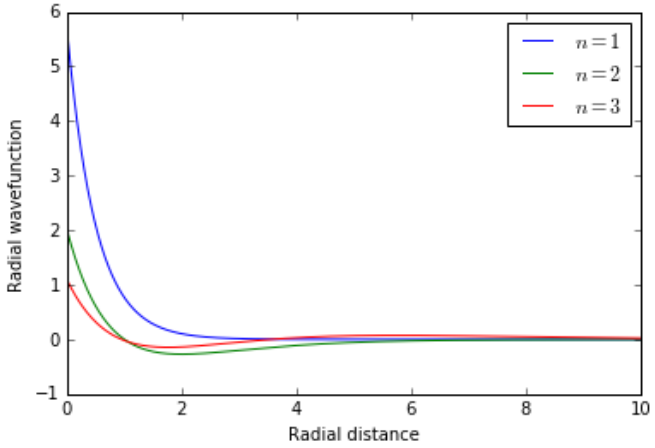


Figure 1.2.1 – Radial eigenfunctions R_{n0} of the hydrogenoid atom (*i.e.* $V = 0$ in (1.2.1)). The first eigenfunction R_{10} is nodeless, R_{20} has one node and R_{30} has two nodes.

When $V = \rho \star \frac{1}{|\cdot|} + V_{\mathrm{xc}}[\rho]$ is a Kohn-Sham potential, the all-electron operator H^{AE} is invariant under rotations around the atom if the electronc density ρ is radial. In the reduced Hartree-Fock model (*i.e.* $V_{\mathrm{xc}} = 0$), if the system is neutral or positively charged, it has been proved in [Sol91] that the electronic density ρ is radial. Thus, the eigenfunctions of the all-electrons operator H^{AE} satisfy a decomposition of the type (1.2.2).

For Kohn-Sham LDA models, there exists no result on the uniqueness of the atomic ground state. To the best of our knowledge, no numerical evidence has been published so far that the radial LDA ground state might not be unique.

In the remainder of this presentation, we will suppose that the LDA ground state is radial, hence that the eigenfunctions of the all-electron Hamiltonian satisfy a decomposition (1.2.2).

In the following, eigenfunctions of atomic Kohn-Sham LDA Hamiltonian are denoted by $\phi_{n\ell m}$, $n \in \mathbb{N}^*$, $\ell \in \mathbb{N}$, $|m| \leq \ell$. $\epsilon_{n\ell}$ is the eigenvalue associated to the eigenfunction $\phi_{n\ell m}$. $R_{n\ell}$ defined by the decomposition (1.2.2) will be called the *radial wave function*. The electronic density generated by the eigenfunctions associated to the lowest eigenvalues of the atomic Kohn-Sham LDA Hamiltonian is [1]

$$\rho(r) = \frac{2\ell + 1}{4\pi r^2} \sum_{\ell=0}^{\ell_{\max}} \sum_{n=1}^{n_\ell} |R_{n\ell}(r)|^2,$$

where $\ell_{\max}$ is the maximal angular momentum for which there is a wave function appearing in the electronic density. For simplicity, we have supposed that all the shells $0 \leq \ell \leq \ell_{\max}$ are fully occupied. This requirement can be lifted by introducing occupation numbers for each quantum state (see [CM14]).

For each angular momentum $0 \leq \ell \leq \ell_{\max}$ and $|m| \leq \ell$, $(\phi_{n\ell m})_{1 \leq n \leq n_\ell - 1}$ is the family of core wave functions for the angular momentum ℓ, m and $\phi_{n_\ell \ell m}$ is the valence wave function.

This yields a decomposition of the electronic density into:

1. the spherical harmonics satisfy for all $\ell \in \mathbb{N}$ and $\hat{\mathbf{r}} \in S(0,1)$, $\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\hat{\mathbf{r}})|^2 = \frac{2\ell+1}{4\pi}$.

- ρ_c the core electronic density

$$\rho_c(r) = \sum_{\ell=0}^{\ell_{\max}} \frac{2\ell+1}{4\pi r^2} \sum_{n=1}^{n_\ell - 1} |R_{n\ell}(r)|^2, \tag{1.2.4}$$

- ρ_v the valence electronic density

$$\rho_v(r) = \sum_{\ell=0}^{\ell_{\max}} \frac{2\ell+1}{4\pi r^2} |R_{n_\ell \ell}(r)|^2. \tag{1.2.5}$$

1.2.2 Frozen-core approximation

In the frozen-core approximation, a partition of the electrons between core and valence states is chosen. Although there is no rigorous definition of the partition between core and valence electrons, in practice, it is not hard to make such a decision. Proof of the assertions in this subsection are given in Appendix A.

In the following, the N electrons are split into n_c core electrons and n_v valence electrons:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N! n_c! n_v!}} \sum_{\sigma \in \mathcal{S}_N} \Phi_c(\mathbf{r}_{\sigma(1)}, \dots, \mathbf{r}_{\sigma(n_c)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \dots, \mathbf{r}_{\sigma(N)}),$$

where $\Phi_c \in \bigwedge_{i=1}^{n_c} L^2(\mathbb{R}^3)$ is a normalized wave function of the core electrons and $\Phi_v \in \bigwedge_{i=1}^{n_v} L^2(\mathbb{R}^3)$ is a normalized wave function of the valence electrons. The core and valence wave functions satisfy the orthogonality condition:

$$\forall \mathbf{x}_2, \dots, \mathbf{x}_{n_c}, \mathbf{y}_2, \dots, \mathbf{y}_{n_v} \in \mathbb{R}^3, \ \int_{\mathbb{R}^3} \Phi_c(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_{n_c}) \Phi_v(\mathbf{r}, \mathbf{y}_2, \dots, \mathbf{y}_{n_v}) \, \mathrm{d}\mathbf{r} = 0.$$

The core electrons are generally close to atomic core states. We thus suppose that the core electron wave function Φ_c is given by a Slater determinant

$$\Phi_c(\mathbf{r}_1, \dots, \mathbf{r}_{n_c}) = |\phi_1 \dots \phi_{n_c}\rangle,$$

with normalized $\phi_i \in L^2(\mathbb{R}^3)$ for $i = 1, \dots, n_c$. The functions $(\phi_i)_{1 \le i \le n_c}$ are orbitals of the atomic core states. The orthogonality condition between the core and valence electrons becomes

$$\forall \mathbf{r}_2, \dots, \mathbf{r}_{n_v} \in \mathbb{R}^3, \ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}_1) \Phi_v(\mathbf{r}_1, \dots, \mathbf{r}_{n_v}) \, \mathrm{d}\mathbf{r}_1 = 0, \quad \forall \, 1 \le i \le n_c, \tag{1.2.6}$$

The form of the total wave function is then:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N! n_v!}} \sum_{\sigma \in \mathcal{S}_N} (-1)^\sigma \phi_1(\mathbf{r}_{\sigma(1)}) \dots \phi_{n_c}(\mathbf{r}_{\sigma(n_c)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \dots, \mathbf{r}_{\sigma(N)}), \tag{1.2.7}$$

The core electronic density ρ_c is given by

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{n_c} |\phi_i(\mathbf{r})|^2 .$$

The frozen core energy functional is given by

$$\mathcal{E}^{\mathrm{FC}}(\Psi) = \langle \Psi | H^N_{(\mathbf{R}_1,\dots,\mathbf{R}_{N_{\mathrm{at}}})} | \Psi \rangle, \tag{1.2.8}$$

where Ψ is normalized and given by (1.2.7). The orthogonality between the core and valence electrons yields a new partition of the energy:

$$\mathcal{E}^{\mathrm{FC}}(\Psi) = \mathcal{E}_{CORE}(\phi_1,\dots,\phi_{n_c}) + \mathcal{E}_v^{\mathrm{FC}}(\phi_1,\dots,\phi_{n_c},\Phi_v), \tag{1.2.9}$$

where the core energy E_{CORE} is the Hartree-Fock energy of the core electrons

$$\mathcal{E}_{CORE}(\phi_1,\dots,\phi_{n_c}) = \sum_{i=1}^{n_c} \frac{1}{2}\int_{\mathbb{R}^3} |\nabla\phi_i|^2 - \int_{\mathbb{R}^3} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\rho_c(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\left|\sum_{j=1}^{n_c}\phi_j(\mathbf{r})\phi_j(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'.$$

and the valence energy functional $\mathcal{E}_v^{\mathrm{FC}}$ is

$$\begin{aligned}\mathcal{E}_v^{\mathrm{FC}}(\phi_1,\dots,\phi_{n_c},\Phi_v) &= \frac{1}{2}\int_{\mathbb{R}^{3n_v}} |\nabla\Phi_v|^2 - \sum_{i=1}^{n_v}\int_{\mathbb{R}^{3n_v}} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}|\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})|^2\,\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v} \\ &+ \sum_{1\le i<j\le n_v}\int_{\mathbb{R}^{3n_v}} \frac{|\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\,\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v} + \sum_{i=1}^{n_v}\int_{\mathbb{R}^{3n_v+3}} \frac{\rho_c(\mathbf{r}_0)|\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})|^2}{|\mathbf{r}_0-\mathbf{r}_i|}\,\mathrm{d}\mathbf{r}_0\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v} \\ &- \sum_{i=1}^{n_c}\sum_{j=1}^{n_v}\int_{\mathbb{R}^{3n_v+3}} \frac{\phi_i(\mathbf{r}_0)\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})\phi_i(\mathbf{r}_j)\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{j-1},\mathbf{r}_0,\mathbf{r}_{j+1},\dots,\mathbf{r}_{n_v})}{|\mathbf{r}_0-\mathbf{r}_j|}\,\mathrm{d}\mathbf{r}_0\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v}.\end{aligned}$$

In the frozen core approximation, the core wave functions $(\phi_i)_{1\le i\le n_c}$ are fixed and the energy is minimized over the set of the valence wave functions orthogonal to the core wave functions $(\phi_i)_{1\le i\le n_c}$:

$$E_v^{\mathrm{FC}} = \min_{\Phi_v\in V_{\mathrm{fc}}} \mathcal{E}_v^{\mathrm{FC}}(\phi_1,\dots,\phi_c,\Phi_v), \tag{1.2.10}$$

where V_{fc} is

$$V_{\mathrm{fc}} = \left\{ \Phi_v \in \bigwedge_{i=1}^{n_v} L^2(\mathbb{R}^3),\ \|\Phi_v\|_{L^2(\mathbb{R}^{3n_v})} = 1,\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}_1)\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})\,\mathrm{d}\mathbf{r}_1 = 0,\ \forall\, 1\le i\le n_c \right\}.$$

If the minimization problem (1.2.10) admits a minimizer, then the minimizing valence wave

function Φ_v satisfies the Euler-Lagrange equation

$$H_v \Phi_v = E_v^{\mathrm{FC}} \Phi_v, \tag{1.2.11}$$

where $\Phi_v \in V_{\mathrm{fc}}$ and the valence Hamiltonian H_v is given by

$$H_v = \sum_{j=1}^{n_v} \left(-\frac{1}{2}\Delta_j - \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|} + J_c(j) - K_c(j) \right) + \sum_{1 \le i < j \le n_v} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1.2.12}$$

$J_c(j)$ is the Coulomb operator with the core electrons

$$J_c(j)\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}) = \sum_{i=1}^{n_c} \int_{\mathbb{R}^3} \frac{|\phi_i(\mathbf{r}')|^2}{|\mathbf{r}_j - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \; \Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}), \tag{1.2.13}$$

and $K_c(j)$ the exchange operator with the core electrons

$$K_c(j)\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}) = \sum_{i=1}^{n_c} \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}')\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{j-1}, \mathbf{r}', \mathbf{r}_{j+1}, \ldots, \mathbf{r}_{n_v})}{|\mathbf{r}_j - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \phi_i(\mathbf{r}_j). \tag{1.2.14}$$

The validity of the frozen-core approximation is now well accepted in the theoretical chemistry community (see [VBG80] where it is shown with a bit of hand waving that the frozen-core approximation in a molecular system is correct up to second order in the difference between the exact electron core density and the approximated core density).

1.2.3 Phillips-Kleinman pseudopotentials

Generalized Phillips-Kleinman pseudopotentials

In solving the frozen-core minimization problem (1.2.10), the valence wave function Φ_v has to be explicitly orthogonalized to the core wave functions. This means that all the integrals of Equation (1.2.6) have to computed. It is possible to circumvent this difficulty by removing the constraint. Let $P(i)$ be the orthogonal projection onto the core space: for $f \in \bigotimes_{i=1}^{n_v} L^2(\mathbb{R}^3)$

$$P(i)f(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v}) = \sum_{j=1}^{n_c} \phi_j(\mathbf{r}_i) \int_{\mathbb{R}^3} \phi_j(\mathbf{r}_i) f(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v}) \, \mathrm{d}\mathbf{r}_i, \quad i = 1, \ldots, n_v. \tag{1.2.15}$$

The minimization problem (1.2.10) can be recasted as

$$E_v^{\mathrm{FC}} = \inf_{\Phi \in \bigwedge_{i=1}^{n_v} L^2(\mathbb{R}^3)} \left\{ \frac{\langle \Phi | \prod_{i=1}^{n_v} (\mathrm{Id} - P(i)) H_v \prod_{i=1}^{n_v} (\mathrm{Id} - P(i)) | \Phi \rangle}{\langle \Phi | \prod_{i=1}^{n_v} (\mathrm{Id} - P(i)) | \Phi \rangle} \right\}, \tag{1.2.16}$$

where H_v is defined in (1.2.12).

The wave function reaching E_v^{FC} written in this form satisfies the Euler-Lagrange equation

$$\prod_{i=1}^{n_v}(\mathrm{Id}-P(i))H_v\prod_{i=1}^{n_v}(\mathrm{Id}-P(i))\Phi = E_v^{\mathrm{FC}}\prod_{i=1}^{n_v}(\mathrm{Id}-P(i))\Phi,$$

or written differently:

$$\widetilde{H}\Phi = E_v^{\mathrm{FC}}\Phi,$$

with

$$\widetilde{H} = \prod_{i=1}^{n_v}(\mathrm{Id}-P(i))H_v\prod_{i=1}^{n_v}(\mathrm{Id}-P(i)) + E_v^{\mathrm{FC}}\left(\sum_{i=1}^{n_v}P(i) - \sum_{1\le i<j\le n_v}P(i)P(j)+\dots\right). \quad (1.2.17)$$

Unfortunately, expanding Equation (1.2.17) introduces many-electrons operators, hence it seems that no advantage is taken by this approach. Motivated by the desire to retain a Hamiltonian operator where at least the two-electron operators remain in standard form, one is led to consider an approximation of Equation (1.2.17) of the form:

$$\begin{aligned} H_{PK} &= \sum_{i=1}^{n_v}\left((\mathrm{Id}-P(i))h'(i)(\mathrm{Id}-P(i)) + E_v^{\mathrm{FC}}P(i)\right) + \sum_{1\le i<j\le n_v}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \\ &= \sum_{i=1}^{n_v}(h'(i)+U_i^{\mathrm{PK}}) + \sum_{1\le i<j\le n_v}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \end{aligned} \quad (1.2.18)$$

where $h'(i)$ is given by

$$h'(i) = -\frac{1}{2}\Delta_i - \sum_{I=1}^{N_{\mathrm{at}}}\frac{Z_I}{|\mathbf{R}_I-\mathbf{r}_i|} + J_c(i) - K_c(i)$$

with $J_c(i)$ and $K_c(i)$ respectively defined in (1.2.13) and (1.2.14) and

$$U_i^{\mathrm{PK}} = P(i)h'(i)P(i) - P(i)h'(i) - h'(i)P(i) + E_v^{\mathrm{FC}}P(i). \quad (1.2.19)$$

Potentials of this form are called *generalized Phillips-Kleinman* (PK) pseudopotentials [KBT76].

Suppose that there is a unique valence electron ($n_v = 1$). In that case, $H_{PK} = h' + U_i^{\mathrm{PK}}$ and h' is a Fock operator of n_c wave functions $(\phi_j)_{1\le j\le n_c}$. Let $(\phi_j)_{1\le j\le n_c}$ be the eigenfunctions associated to the lowest eigenvalues $(E_j)_{1\le j\le n_c}$ of the Fock operator h' with n_c electrons

$$h'\phi_j = E_j\phi_j, \quad j = 1,\dots,n_c.$$

These eigenfunctions exist since in that case, the system is positively charged [Lio87]. It is easy to see that the PK pseudopotential (1.2.19) can be simplified to (the index i is dropped since there is

only one valence wave function):

$$\forall \mathbf{r} \in \mathbb{R}^3,\ (U^{\mathrm{PK}} f)(\mathbf{r}) = \sum_{j=1}^{n_c} (E_v^{\mathrm{FC}} - E_j)\phi_j(\mathbf{r}) \int_{\mathbb{R}^3} \phi_j f. \tag{1.2.20}$$

This is the original form derived by Phillips and Kleinman in [PK59].

Let ϕ_v be a valence wave function minimizing the frozen core energy functional (1.2.10). Since there is only one valence electron, ϕ_v satisfies

$$H_v\phi_v = E_v^{\mathrm{FC}}\phi_v \iff h'\phi_v = E_v^{\mathrm{FC}}\phi_v, \quad \int_{\mathbb{R}^3} \phi_i\phi_v = 0.$$

Thus

$$H_{PK}\phi_v = h'\phi_v + U^{\mathrm{PK}}\phi_v = E_v^{\mathrm{FC}}\phi_v + \sum_{j=1}^{n_c} (E_v^{\mathrm{FC}} - E_j)\phi_j(\mathbf{r}) \int_{\mathbb{R}^3} \phi_j\phi_v = E_v^{\mathrm{FC}}\phi_v.$$

By choice of the core wave functions $(\phi_i)_{1\leq i\leq n_c}$, we have

$$H_{PK}\phi_i = h'\phi_i + U^{\mathrm{PK}}\phi_i = E_i\phi_i + \sum_{j=1}^{n_c} (E_v^{\mathrm{FC}} - E_j)\phi_j(\mathbf{r}) \int_{\mathbb{R}^3} \phi_j\phi_i = E_v^{\mathrm{FC}}\phi_v.$$

Hence any linear combinations of the form

$$\chi_v = C_v\phi_v + \sum_{i=1}^{n_v} a_{iv}\phi_i, \quad C_v, a_{iv} \in \mathbb{R}, \tag{1.2.21}$$

are eigenfunctions of the PK Hamiltonian (1.2.18)

$$H_{PK}\chi_v = h'\chi_v + U^{\mathrm{PK}}\chi_v = E_v\chi_v.$$

The lowest eigenvalue of the operator H_{PK} is the valence eigenvalue that we want to compute. Although this property is interesting from a computational point of view, construction of the PK pseudopotential (1.2.19) requires the knowledge of the valence eigenvalue E_v^{FC}. Hence, the generation of the PK pseudopotential is a nonlinear procedure.

Generation of PK pseudopotentials

In practice, the PK pseudopotentials are generated for atomic Hamiltonians and replace the interactions with the core electron wave function in molecular settings.

Consider the atomic Hamiltonian operator

$$H^{\mathrm{AE}} = -\frac{1}{2}\Delta - \frac{Z}{r} + \rho \star \frac{1}{|\cdot|} - V_{\mathrm{xc}}[\rho]. \tag{1.2.22}$$

Using the partition of core and valence states introduced in Section 1.2.1, for each angular momentum

$\ell \in [\![0, \ell_{\max}]\!]$, a radial pseudo wave function $\chi_{n_\ell \ell}$ is defined such that

$$\chi_{n_\ell \ell}(r) = C_\ell R_{n_\ell \ell}(r) + \sum_{n=1}^{n_\ell - 1} a_{n\ell} R_{n\ell}(r), \quad C_\ell, a_{n\ell} \in \mathbb{R}.$$

The radial functions $R_{n\ell}$, $n = 1, \ldots, n_\ell$ are the radial wave functions of the eigenfunctions of (1.2.22) given by the decomposition (1.2.2). The coefficients are chosen to satisfy the following properties

i) $\chi_{n_\ell \ell}$ is normalized thus $|C_\ell| < 1$ [2];

ii) $\chi_{n_\ell \ell}$ has no radial node (except at 0);

iii) $\chi_{n_\ell \ell}$ should have a minimal number of oscillations.

The pseudo valence density $\widetilde{\rho}_v$ is given by

$$\widetilde{\rho}_v(r) = \sum_{\ell=0}^{\ell_{\max}} \frac{2\ell + 1}{4\pi r^2} |\chi_{n_\ell \ell}(r)|^2.$$

The radial PK pseudopotential U_ℓ^{PK} for the angular momentum ℓ is obtained by

$$U_\ell^{\mathrm{PK}} = \epsilon_{n_\ell \ell} + \frac{1}{2} \frac{\Delta \chi_{n_\ell \ell}}{\chi_{n_\ell \ell}} + \frac{Z}{r} - \widetilde{\rho}_v \star \frac{1}{|\cdot|} - V_{\mathrm{xc}}[\widetilde{\rho}_v]. \tag{1.2.23}$$

The full PK pseudopotential is the operator

$$U^{\mathrm{PK}} = \sum_{\ell=0}^{\ell_{\max}} U_\ell^{\mathrm{PK}}(r) Y_{\ell m}(\hat{\mathbf{r}}) \langle Y_{\ell m}, \cdot \rangle. \tag{1.2.24}$$

A pseudopotential of the form (1.2.24) is called *semilocal* because it is a multiplicative operator for the radial coordinate but an integral operator of the spherical coordinates.

For $\ell \in [\![0, \ell_{\max}]\!]$, the functions $\mathbf{r} \mapsto \frac{\chi_{n_\ell \ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})$ are eigenfunctions for the eigenvalue $\epsilon_{n_\ell \ell}$ of the pseudo Hamiltonian

$$H^{\mathrm{PK}} = -\frac{1}{2}\Delta - \frac{Z}{r} + U^{\mathrm{PK}} + \widetilde{\rho}_v \star \frac{1}{|\cdot|} - V_{\mathrm{xc}}[\widetilde{\rho}_v].$$

Remark 1.4. *The pseudopotential U^{PK} can also be written*

$$U^{\mathrm{PK}} = U_{\ell_{\max}}^{\mathrm{PK}}(r) + \sum_{\ell=0}^{\ell_{\max}-1} (U_\ell^{\mathrm{PK}}(r) - U_{\ell_{\max}}^{\mathrm{PK}}(r)) Y_{\ell m}(\hat{\mathbf{r}}) \langle Y_{\ell m}, \cdot \rangle,$$

since $\mathbf{r} \mapsto \frac{\chi_{n_\ell \ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})$ are still eigenfunctions of H^{PK} for the eigenvalue $\epsilon_{n_\ell \ell}$. Pseudopotentials are usually given in this form.

2. If $|C_\ell| = 1$ the radial pseudo wave function $\chi_{n_\ell \ell}$ is simply the radial valence wave function $R_{n_\ell \ell}$ that we wish to "regularize". This case should be avoided in the pseudopotential construction

The PK pseudopotential, however, does not have the good long-range behaviour as pointed out in [CLP79]. Indeed, suppose that $V_{\mathrm{xc}} = 0$. For large r, the radial PK pseudopotential U_ℓ^{PK} should reproduce the Coulomb tail of the frozen core density

$$U_\ell(r) \approx \frac{n_c}{r}, \qquad r \gg 1.$$

The radial wave functions $R_{n_\ell \ell}$ are eigenfunctions of a radial Schrödinger operator

$$\forall\, r > 0,\ \mathfrak{h}_\ell^{\mathrm{AE}} R_{n_\ell \ell} = -\frac{1}{2} R''_{n_\ell \ell}(r) + \left(\frac{\ell(\ell+1)}{2r^2} + -\frac{Z}{r} + \rho \star \frac{1}{|\cdot|} \right) R_{n_\ell \ell}(r) = \epsilon_{n_\ell \ell} R_{n_\ell \ell}(r). \tag{1.2.25}$$

They decay exponentially fast as r goes to infinity. More precisely [BM77, HOHOS85], we know that for all $\varepsilon, \delta > 0$, there exists a positive constant C such that for $1 \leq n \leq n_\ell$ and r sufficiently large

$$C \exp\left(-(\sqrt{-|\epsilon_{n\ell}|} + \varepsilon) r \right) \leq R_{n\ell}(r) \leq C \exp\left(-(\sqrt{-|\epsilon_{n\ell}|} - \delta) r \right).$$

Thus, the core electrons wave functions decay much faster than the valence wave function, hence for sufficiently large r, we have

$$\chi_{n_\ell \ell}(r) \approx C_\ell R_{n_\ell \ell}(r).$$

Hence, using (1.2.25),

$$\frac{1}{2} \frac{\Delta \chi_{n_\ell \ell}}{\chi_{n_\ell \ell}} \approx -\frac{Z}{r} + (\rho_c + \rho_v) \star \frac{1}{|\cdot|} + \epsilon_{n_\ell \ell}.$$

Substituting this in Equation (1.2.23), we obtain

$$U_\ell^{\mathrm{PK}} \approx \rho_c \star \frac{1}{|\cdot|} + \rho_v \star \frac{1}{|\cdot|} - \widetilde{\rho}_v \star \frac{1}{|\cdot|}.$$

At first order in $\frac{1}{r}$, we can establish that

$$\rho_v \star \frac{1}{|\cdot|}(r) = \frac{1}{r} + \frac{1}{r} \sum_{\ell=0}^{\ell_{\max}} \int_{y>r} |R_{n_\ell \ell}(y)|^2 \left(\frac{r}{y} - 1 \right) \mathrm{d}y + \mathcal{O}\left(\frac{1}{r^2} \right),$$

and

$$\widetilde{\rho}_v \star \frac{1}{|\cdot|}(r) = \frac{1}{r} + \frac{1}{r} \sum_{\ell=0}^{\ell_{\max}} C_\ell^2 \int_{y>r} |R_{n_\ell \ell}(y)|^2 \left(\frac{r}{y} - 1 \right) \mathrm{d}y + \mathcal{O}\left(\frac{1}{r^2} \right).$$

By the normalization condition i) on $\chi_{n_\ell \ell}$, we necessarily have $|C_\ell| < 1$, hence U_ℓ^{PK} introduces a spurious negative contribution. This problem can be solved if $\chi_{n_\ell \ell}(r) = R_{n_\ell \ell}(r)$ for $r \geq r_c$ is imposed for some cut-off radius r_c. This paved the way to the theory of norm-conserving pseudopotentials.

1.2.4 Norm-conserving pseudopotentials

The norm-conserving pseudopotentials (NC pseudopotentials) have been introduced by Topp and Hopfield [TH73] in the context of empirical pseudopotentials. They have become a central feature in the generation of pseudopotential since the seminal paper by Hamann, Schlüter and

Chiang [HSC79] and later with the BHS pseudopotentials [BHS82].

Generation of the NC pseudopotentials

The generation of NC pseudopotentials is similar to the generation of the PK pseudopotentials. As in the PK pseudopotential generation, core electrons are frozen and for each angular momentum ℓ with a valence electron, we build a pseudopotential V_ℓ by inverting a radial Schrödinger equation.

For each $\ell \in [\![0, \ell_{\max}]\!]$, a radial NC pseudo wave function $\widetilde{R}_{n_\ell \ell}$ corresponding to the valence state of energy $\epsilon_{n_\ell \ell}$ is defined. $\widetilde{R}_{n_\ell \ell}$ satisfies the following essential conditions:

1. the radial pseudo wave function satisfies a radial Schrödinger equation with the *same* eigenvalue $\epsilon_{n_\ell \ell}$ as the radial wave function $R_{n_\ell \ell}$:

$$\forall\, r \in (0, +\infty),\ -\frac{1}{2}\widetilde{R}''_{n_\ell \ell}(r) + \frac{\ell(\ell+1)}{2r^2}\widetilde{R}_{n_\ell \ell}(r) + V_\ell(r)\widetilde{R}_{n_\ell \ell}(r) = \epsilon_{n_\ell \ell}\widetilde{R}_{n_\ell \ell}(r). \tag{1.2.26}$$

   The eigenvalue $\epsilon_{n_\ell \ell}$ is usually called the *atomic reference level* or *atomic reference energy*.

2. norm-conservation:

$$\int_0^{+\infty} |\widetilde{R}_{n_\ell \ell}(r)|^2 \,\mathrm{d}r = 1, \tag{1.2.27}$$

3. for a previously chosen cut-off radius $r_{c,\ell}$,

$$\widetilde{R}_{n_\ell \ell} = R_{n_\ell \ell} \quad \text{on } (r_{c,\ell}, +\infty) \text{ for some } 0 < r_{c,\ell} < r_c \tag{1.2.28}$$

4. the radial pseudo wave function has to be nodeless

$$\widetilde{R}_{n_\ell \ell} > 0, \quad \text{on } (0, +\infty). \tag{1.2.29}$$

By the Sturm oscillation theorem, if $\widetilde{R}_{n_\ell \ell}$ is nodeless and V_ℓ is a regular enough multiplicative potential, $\widetilde{R}_{n_\ell \ell}$ is an eigenfunction associated to the lowest eigenvalue of (1.2.26).

Existence of such pseudopotentials and topological properties of the set of NC pseudopotentials can be found in [CM15]. In particular, existence of optimal pseudopotentials *i.e.* with minimal oscillations is precisely stated.

There are many different ways to generate NC pseudopotentials satisfying (1.2.26) to (1.2.29) [HSC79, Ker80, BHS82, TM91] usually by specifying the shape of the radial NC pseudo wave function $\widetilde{R}_{n_\ell \ell}$. The screened potential V_ℓ is deduced by inverting the radial Schrödinger equation (1.2.26)

$$\forall\, r \in (0, r_c),\ V_\ell(r) = \epsilon_{n_\ell \ell} + \frac{1}{2}\frac{\widetilde{R}''_{n_\ell \ell}(r)}{\widetilde{R}_{n_\ell \ell}(r)} - \frac{\ell(\ell+1)}{2r^2}.$$

The local *ionic* pseudopotential is obtained by subtracting the Hartree and exchange-correlation potentials calculated from the valence pseudo wave functions. This step is called the *unscreening* of the pseudopotential:

$$V_{\mathrm{ion},\ell}(r) = V_\ell(r) - \widetilde{\rho}_v \star \frac{1}{|\cdot|} - V_{\mathrm{xc}}[\widetilde{\rho}_v], \tag{1.2.30}$$

with $\widetilde{\rho}_v$ the pseudo valence electronic density

$$\widetilde{\rho}(r) = \sum_{\ell=0}^{\ell_{\max}} \frac{2\ell+1}{4\pi r^2} |\widetilde{R}_{n_\ell \ell}(r)|^2.$$

The ionic pseudopotential is the semilocal operator $V_{\text{ion}}^{\text{NC}}$ given by

$$V_{\text{ion}}^{\text{NC}} = V_{\text{ion},\ell_{\max}}(r) + \sum_{\ell=0}^{\ell_{\max}-1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{\mathbf{r}})(V_{\text{ion},\ell}(r) - V_{\text{ion},\ell_{\max}}(r))\langle Y_{\ell m}, \cdot \rangle. \tag{1.2.31}$$

By definition of the radial pseudo wave functions $(\widetilde{R}_{n_\ell \ell})_{0 \le \ell \le \ell_{\max}}$ and of the NC pseudopotential $V_{\text{ion}}^{\text{NC}}$, it is easy to check that $\mathbf{r} \mapsto \frac{\widetilde{R}_{n_\ell \ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})$ is an eigenfunction of the operator

$$-\frac{1}{2}\Delta + V_{\text{ion}}^{\text{NC}} + \widetilde{\rho}_v \star \frac{1}{|\cdot|} + V_{\text{xc}}[\widetilde{\rho}_v],$$

for the eigenvalue $\epsilon_{n_\ell \ell}$.

If the exchange-correlation energy E_{xc} is not a linear functional with respect to the density ρ (which is usually the case for Kohn-Sham LDA models), the ionization step (1.2.30) involves an approximation. Indeed the radial wave function $\widetilde{R}_{n\ell}$ satisfies the following radial equation

$$-\frac{1}{2}\widetilde{R}''_{n\ell}(r) + \frac{\ell(\ell+1)}{2r^2}\widetilde{R}_{n\ell}(r) + \left(V_{\text{ion},\ell}^{\text{NC}}(r) + \widetilde{\rho}_v \star \frac{1}{|\cdot|} + V_{\text{xc}}[\widetilde{\rho}_v]\right)\widetilde{R}_{n\ell}(r) = \epsilon_{n\ell}\widetilde{R}_{n\ell}(r),$$

hence the total energy of the system is given by

$$E_0^{\text{NC}}[\rho] = T[\rho_c + \widetilde{\rho}_v] + E_H[\rho_c + \widetilde{\rho}_v] + E_{\text{xc}}[\rho_c] + E_{\text{xc}}[\widetilde{\rho}_v].$$

This approximation can be significant if the difference between $E_{\text{xc}}[\rho_c] + E_{\text{xc}}[\widetilde{\rho}_v]$ and $E_{\text{xc}}[\rho_c + \widetilde{\rho}_v]$ is important. This happens for example when the core density ρ_c and the pseudo valence density $\widetilde{\rho}_v$ overlap significantly. A proposed solution by Louie et al. [LFC82] (see also [FS99]) is to introduce a partial core density $\widetilde{\rho}_0^{\text{core}}$ in the unscreening step (1.2.30):

$$V_{\text{ion},\ell}(r) = V_\ell(r) - \widetilde{\rho}_v \star \frac{1}{|\cdot|} - V_{\text{xc}}[\widetilde{\rho}_v + \widetilde{\rho}_0^{\text{core}}], \tag{1.2.32}$$

where

$$\widetilde{\rho}_0^{\text{core}}(r) = \begin{cases} \rho_c(r) & \text{for } r \ge r^{\text{nlc}} \\ a\frac{\sin(br)}{r} & \text{for } r < r^{\text{nlc}} \end{cases}.$$

The coefficients a and b are determined so that $\widetilde{\rho}_0^{\text{core}}$ is C^1 at r^{nlc}. This procedure is called the *nonlinear core correction* and has to be used for atoms with few valence electrons (the alkali atoms). The core cut-off radius r^{nlc} is usually chosen such that the core density ρ_c drops below the pseudo valence density $\widetilde{\rho}_v$.

Troullier-Martins pseudopotentials

The Troulliers-Martins pseudopotentials [TM91] have become the most popular NC pseudopotential and are widely used in solid-state simulation codes. The exposition follows the usual notations introduced in [TM91]. For simplicity, the index ℓ on n_ℓ is dropped.

The Troullier-Martins radial pseudo wave functions are given by

$$\widetilde{R}_{n\ell}(r) = \begin{cases} R_{n\ell}(r) & \text{if } r > r_c \\ C_{n\ell} r^{\ell+1} e^{p(r)} & \text{if } r \leq r_c \end{cases} \tag{1.2.33}$$

where p is an even polynomial of degree 12:

$$p(r) = \sum_{k=0}^{6} c_{2k} r^{2k}. \tag{1.2.34}$$

Inverting the radial Schrödinger equation (1.2.26), the pseudopotential V_ℓ^{TM} is defined by:

$$V_\ell^{\mathrm{TM}} = \epsilon_{n\ell} + \frac{(\ell+1)p'(r)}{r} + \frac{p'(r)^2 + p''(r)}{2}. \tag{1.2.35}$$

The seven conditions to determine the coefficients $(c_{2k})_{0\leq k\leq 6}$ are:

1. **Norm conservation**
$$\int_0^{r_c} |\widetilde{R}_{n\ell}(r)|^2 \,\mathrm{d}r = \int_0^{r_c} |R_{n\ell}(r)|^2 \,\mathrm{d}r. \tag{1.2.36}$$
2. **continuity conditions**
$$\widetilde{R}_{n\ell}^{(k)}(r) = R_{n\ell}^{(k)}(r), \quad \text{for } 0 \leq k \leq 4. \tag{1.2.37}$$
3. **Smoothness of the pseudopotential** By construction, we already have $(V_{scr,\ell}^{\mathrm{TM}})'(0) = 0$. We can enforce $(V_{scr,\ell}^{\mathrm{TM}})''(0) = 0$ with
$$(2\ell+5)c_4 + c_2^2 = 0. \tag{1.2.38}$$

It is easy to see that the five equations imposed by the continuity conditions of the radial pseudo wave function are linear, then plugging (1.2.38) into (1.2.36) yield a non-linear equation of one variable which can be solved using a Newton method.

Kleynman-Bylander form of the pseudopotentials

So far the presentation of pseudopotentials has been restricted to finite molecular systems. They are however primarily used for solid-state calculations where plane-waves methods are the method of choice.

When solving numerically the eigenvalue problem of the pseudized Hamiltonian, it is not advised to store the whole Hamiltonian matrix. Instead, the eigenvalues are computed using iterative methods, for which, it is crucial to reduce the matrix-vector computational complexity.

In a basis of N_{pw} plane-waves, evaluating $V\widetilde{\psi}$ in the reciprocal space where V is a multiplicative potential costs $\mathcal{O}(N_{\mathrm{pw}} \log N_{\mathrm{pw}})$ operations (apply an inverse FFT to $\widetilde{\psi}$ to have its real space

representation, multiply pointwise by V and apply a FFT to the whole result).

The semilocal part associated to the angular momentum ℓ in (1.2.31)

$$\delta V_{\mathrm{sl},\ell} := \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{\mathbf{r}})(V_{\mathrm{ion},\ell}(r) - V_{\mathrm{ion},\ell_{\max}}(r))\langle Y_{\ell m}, \cdot \rangle$$

is however more expensive to compute. Let $(\widetilde{\psi}_{\mathbf{G}})$ be the Fourier coefficients of $\widetilde{\psi}$. Using the scattering expansion

$$e^{i\mathbf{G}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^{\ell} j_{\ell}(Gr) Y_{\ell,m}(\hat{\mathbf{G}}) Y_{\ell,m}(\hat{\mathbf{r}}),$$

where j_ℓ is the spherical Bessel function, the real space representation of $\delta V_{\mathrm{sl},\ell}\widetilde{\psi}$ is given by

$$(\delta V_{\mathrm{sl},\ell}\widetilde{\psi})(\mathbf{r}) = 4\pi i^{\ell} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{\mathbf{r}})(V_{\mathrm{ion},\ell}(r) - V_{\mathrm{ion},\ell_{\max}}(r)) \sum_{\mathbf{G}} \widetilde{\psi}_{\mathbf{G}} j_{\ell}(Gr) Y_{\ell,m}(\widehat{\mathbf{G}}).$$

Evaluating this expression in real space costs $\mathcal{O}(N_{\mathrm{pw}})$ operations, hence obtaining the reciprocal space representation of $\delta V_{\mathrm{sl},\ell}\widetilde{\psi}$ with a FFT costs $\mathcal{O}(N_{\mathrm{pw}}^2 \log(N_{\mathrm{pw}}))$ operations.

In [KB82], Kleinman and Bylander introduced a new way to write the semilocal part $\delta V_{\mathrm{sl},\ell}$ to reduce to $\mathcal{O}(N_{\mathrm{pw}})$ the cost of applying the semilocal part of the pseudopotential in reciprocal space. Let

$$\delta V_{\ell}(r) = V_{\mathrm{ion},\ell}(r) - V_{\mathrm{ion},\ell_{\max}}(r).$$

They defined the *truly non-local* potential $\delta V_{\mathrm{tnl},\ell}$ by (here again, the index ℓ on n_ℓ is dropped)

$$\delta V_{\mathrm{tnl},\ell} = \frac{1}{\langle \delta V_{\ell} \rangle} \sum_{m=-\ell}^{\ell} \delta V_{\ell}(r) \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}) \left\langle Y_{\ell m}(\hat{\mathbf{r}'}) \frac{\widetilde{R}_{n\ell}(r')}{r'} \delta V_{\ell}(r'), \cdot \right\rangle, \tag{1.2.39}$$

where

$$\langle \delta V_{\ell} \rangle = \int_0^{r_c} |\widetilde{R}_{n\ell}(r)|^2 \delta V_{\ell}(r)\, \mathrm{d}r.$$

It is easy to check that the truly non-local potential satisfies

$$\begin{aligned}\delta V_{\mathrm{tnl},\ell}\left(\frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})\right) &= \frac{1}{\langle \delta V_{\ell} \rangle} \sum_{m'=-\ell}^{\ell} \delta V_{\ell}(r) \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m'}(\hat{\mathbf{r}}) \left\langle Y_{\ell m'}(\hat{\mathbf{r}'}) \frac{\widetilde{R}_{n\ell}(r')}{r'} \delta V_{\ell}(r'), \frac{\widetilde{R}_{n\ell}(r')}{r'} Y_{\ell m}(\hat{\mathbf{r}'}) \right\rangle \\ &= \delta V_{\ell}(r) \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}).\end{aligned}$$

The condition (1.2.26) is therefore satisfied but with a nonlocal radial potential

$$\forall\, r \in (0, r_c),\ -\frac{1}{2}\widetilde{R}''_{n,\ell}(r) + \frac{\ell(\ell+1)}{2r^2}\widetilde{R}_{n,\ell}(r) + V_{\ell_{\max}}(r)\widetilde{R}_{n,\ell}(r) + \delta V_{\mathrm{tnl},\ell}\frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}) = \epsilon_{n\ell}\widetilde{R}_{n,\ell}(r).$$

The truly nonlocal form (1.2.39) is convenient for calculations in the reciprocal space. Indeed, denoting by $(T_{\mathbf{G}})$ the Fourier coefficients of $\mathbf{r} \mapsto \delta V_\ell(r)\frac{\widetilde{R}_{n\ell}(r)}{r}Y_{\ell m}(\hat{\mathbf{r}})$ and $(\widetilde{\psi}_{\mathbf{G}})$ the Fourier coefficients of the test function $\widetilde{\psi}$, the Fourier coefficient of $\delta V_{\mathrm{tnl},\ell}\widetilde{\psi}$ is simply

$$(\delta V_{\mathrm{tnl},\ell}\,\widetilde{\psi})_{\mathbf{G}} = \frac{T_{\mathbf{G}}}{\langle \delta V_\ell \rangle}\sum_{\mathbf{G}'} T_{\mathbf{G}'}\widetilde{\psi}_{\mathbf{G}'}.$$

First, the sum $\sum_{\mathbf{G}'} T_{\mathbf{G}'}\widetilde{\psi}_{\mathbf{G}'}$ is computed and this costs $\mathcal{O}(N_{\mathrm{pw}})$ operations. Then for each $\mathbf{G}$, the result of this sum is multiplied by $\frac{T_{\mathbf{G}}}{\langle \delta V_\ell \rangle}$. The computation hence scales as N_{pw} for a basis of N_{pw} plane-waves. Because of this special form, pseudopotentials given by (1.2.39) are called *fully separable*.

On the NC pseudopotential approximation

The great question with the pseudopotential approximation is the validity of the pseudopotentials generated above in a different molecular environment. To put it in other words, is it sufficient to reproduce the exact spectrum of atomic Hamiltonian to get accurate results in other calculations? This question is commonly referred to as the *transferability* of pseudopotentials. In practice, the answer to this question is positive in most of the situations encountered, however there are few theoretical justifications of the pseudopotential approach.

Formally the NC pseudopotential approach has been justified because the norm-conservation of the pseudo wave function preserves the scattering properties [SJH67, TH73]. Let $R(\cdot,\epsilon)$ be the solution of

$$\forall\, r \in (0, r_c),\ -\frac{1}{2}R(r,\epsilon)'' + \frac{\ell(\ell+1)}{2r^2}R(r,\epsilon) + V(r)R(r,\epsilon) = \epsilon R(r,\epsilon), \tag{1.2.40}$$

where $R(\cdot,\epsilon)$ is square integrable, normalized to 1 and satisfies $R(0,\epsilon) = 0$. Assuming the differentiability with respect to ϵ, we have

$$-|R(r_c,\epsilon)|^2\frac{\partial}{\partial\epsilon}\frac{\partial}{\partial r}\log R(r_c,\epsilon) = 2\int_0^{r_c}|R(r,\epsilon)|^2\,\mathrm{d}r. \tag{1.2.41}$$

The radial pseudo wave function $\widetilde{R}_{n\ell}$ and the radial atomic wave function $R_{n\ell}$ satisfy an equation of the type (1.2.40). Notice that (1.2.41) does not depend on the potential V. Since $\widetilde{R}_{n\ell}$ is chosen such that $\widetilde{R}_{n\ell}(r_c) = R_{n\ell}(r_c)$, $\widetilde{R}'_{n\ell}(r_c) = R'_{n\ell}(r_c)$ and $\int_0^{r_c}|R_{n\ell}|^2 = \int_0^{r_c}|\widetilde{R}_{n\ell}|^2$, at first order in ϵ, the radial wave function $R_{n\ell}$ and the radial pseudo wave function $\widetilde{R}_{n\ell}$ behave the same way.

Suppose that the pseudopotential computed from the pseudo wave function is used for the calculation of a molecular energy E close to ϵ. It seems reasonable to expect that the computation with the pseudopotential would yield results close to an all-electron computation for this targeted eigenvalue E.

Another criterion has later been found explaining the good results given by the most popular NC pseudopotentials (see [Tet93, FVZ+95]).

In practice, the transferability of the pseupotential is checked by computing the excited states of the atomic configuration with a pseudopotential and comparing them with an all-electron calculation

[FS99]. If the results match up to some previously fixed tolerance, the generated pseudopotential can be considered satisfactory.

A first limitation of the NC pseudopotential has been identified for fully separable pseudopotential. When performing these tests for atomic configurations, by the Sturm oscillation theorem, the lowest eigenvalue of the radial pseudized Hamiltonian should be nodeless and therefore match the all-electron eigenvalue $\epsilon_{n\ell}$. In [GKS90], the authors identified systems for which a non-physical eigenvalue appears in the spectrum of the pseudized Hamiltonian below the reference value $\epsilon_{n\ell}$. These are called *ghost states*. The violation of the Sturm oscillation theorem can be explained by the fact that the radial pseudized Hamiltonian is an *integro-differential* equation. The Sturm oscillation theorem does not hold for such equations. Later a more thoroughful analysis of separable potentials have been produced in [GSS91] (see also [Khe95]), giving guidelines on the design of separable pseudopotentials preventing the apparition of ghost states.

They introduced E_ℓ^{KB}, the Kleinman-Bylander energy

$$E_\ell^{KB} = \frac{\int_0^{r_c} |\widetilde{R}_{n\ell}(r)\delta V_{\mathrm{sl},\ell}(r)|^2 \,\mathrm{d}r}{\int_0^{r_c} |\widetilde{R}_{n\ell}(r)|^2 \delta V_{\mathrm{sl},\ell}(r) \,\mathrm{d}r}.$$

Using the definition of the truly non-local form (1.2.39), it is easy to check that we have

$$\delta V_{\mathrm{tnl},\ell}\left(\delta V_{\mathrm{sl},\ell}\widetilde{\phi}_{n\ell m}\right) = E_\ell^{KB}\delta V_{\mathrm{sl},\ell}(r)\widetilde{\phi}_{n\ell m}(\mathbf{r}),$$

where $\widetilde{\phi}_{n\ell m}(\mathbf{r}) = \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})$. Let ϕ_ℓ^{KB} and R_ℓ^{KB} be respectively the normalized eigenvector and its radial part

$$\phi_\ell^{KB}(\mathbf{r}) = \frac{\delta V_{\mathrm{sl},\ell}(r)\widetilde{\phi}_{n\ell m}(\mathbf{r})}{\|\delta V_{\mathrm{sl},\ell}\widetilde{\phi}_{n\ell m}\|}, \quad \phi_\ell^{KB}(\mathbf{r}) = \frac{R_\ell^{KB}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}),$$

then the truly non-local potential can be written

$$\langle \delta V_{\mathrm{tnl},\ell}(\mathbf{r},\cdot)\,,\cdot\rangle = E_\ell^{KB}\phi_\ell^{KB}(\mathbf{r})\left\langle \phi_\ell^{KB}\,,\cdot\right\rangle.$$

The parametric atomic radial pseudized operator is given by

$$\mathfrak{h}_\ell(\lambda) = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{2r^2} + V_{\ell_{\max}}(r) + \widetilde{\rho_v} \star \frac{1}{|\cdot|} + V_{\mathrm{xc}}[\widetilde{\rho}_v] + \lambda R_\ell^{KB}\int_0^{r_c} R_\ell^{KB}(r')\cdot \,\mathrm{d}r'.$$

Hence $\lambda R_\ell^{KB}\int_0^{r_c} R_\ell^{KB}(r')\cdot \,\mathrm{d}r'$ is a rank-one perturbation of $\mathfrak{h}_\ell(0)$. A rigorous analysis of finite rank pertubation can be found in [Ste69].

Let $\epsilon_1(\lambda) \le \epsilon_2(\lambda) \le \dots$ be the eigenvalues of $\mathfrak{h}_\ell(\lambda)$. For simplicity, we denote by $\epsilon_1 < \epsilon_2 < \dots$ the eigenvalues of $\mathfrak{h}_\ell(0)$. If $\lambda > 0$, the eigenvalues $(\epsilon_k(\lambda))_k$ of $\mathfrak{h}_\ell(\lambda)$ satisfy for $k \ge 1$, $\epsilon_k \le \epsilon_k(\lambda) < \epsilon_{k+1}$ [Ste69] (see Figure 1.2.2). If $\lambda < 0$, the inequalities are reversed: for $k \ge 1$, $\epsilon_k(\lambda) < \epsilon_k \le \epsilon_{k+1}(\lambda)$. For $\lambda = E_\ell^{KB}$, we know that by construction of the pseudopotential, the atomic reference energy $\epsilon_{n\ell}$ is an eigenvalue of $\mathfrak{h}_\ell(E_\ell^{KB})$. Hence it is the lowest eigenvalue of $\mathfrak{h}_\ell(E_\ell^{KB})$:

- if $E_\ell^{KB} < 0$ and $\epsilon_{n\ell} < \epsilon_1$;

- or if $E_\ell^{KB} > 0$ and $\epsilon_{n\ell} < \epsilon_2$.

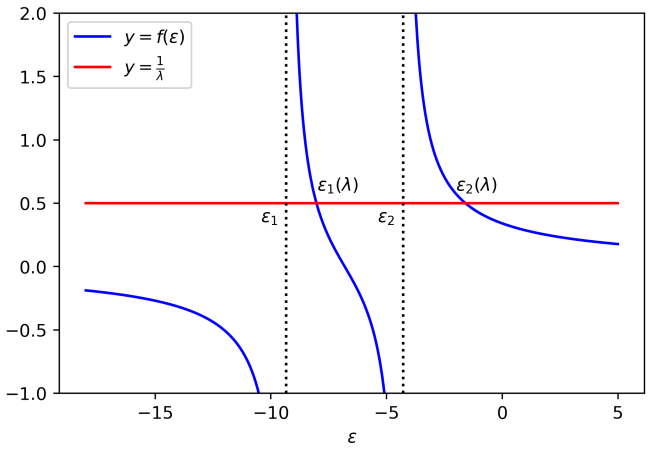


Figure 1.2.2 – The eigenvalues of the perturbed operator $\mathfrak{h}_\ell(\lambda)$ satisfy the equation $1 + \lambda\langle \mathcal{R}_\epsilon R_\ell^{KB}, R_\ell^{KB}\rangle = 0$ where $\epsilon \notin \sigma(\mathfrak{h}_\ell(0))$ and $\mathcal{R}_\epsilon$ is the resolvent of the operator $\mathfrak{h}_\ell(0)$ [Ste69]. In finite dimension, denoting (ψ_k, ϵ_k) the eigenpairs of a symmetric matrix A and vv^T the one-dimensional perturbation, with $v^T\psi_k \neq 0$, the equation becomes $\sum_{k=1}^n \frac{|\psi_k^T v|^2}{\epsilon - \epsilon_k} = \frac{1}{\lambda}$. Intersections of both curves give the eigenvalues $\epsilon_k(\lambda)$ of $A + \lambda vv^T$.

1.3 Vanderbilt ultrasoft pseudopotentials

The norm-conservation constraint (1.2.27) can be relaxed as shown by Vanderbilt [Van90], however in doing so a *generalized* eigenvalue problem is introduced. The presentation of the Vanderbilt pseudopotentials mostly follows [LPC+93] with a slight change of notation.

1.3.1 Pseudopotential generation

Like the previous pseudopotentials, the Vanderbilt pseudopotentials are generated from atomic Hamiltonians. For each angular momentum $\ell \in [\![0, \ell_{\max}]\!]$, let $\epsilon_{n\ell}$ be a valence eigenvalue of the atomic Kohn-Sham Hamiltonian. Contrary to NC pseudopotentials, several radial pseudo wave functions can be defined for the same angular momentum.

Let

$$K = \{(n, \ell, m) \mid \ell \in [\![0, \ell_{\max}]\!], |m| \leq \ell, n \text{ is a valence state for the angular momentum } \ell\}.$$

For $k, k' \in K$, we denote by $k = (n, \ell, m)$ and $k' = (n', \ell', m')$ the associated quantum numbers.

For $k \in K$, let $\widetilde{\phi}_k(\mathbf{r}) = \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}})$ be the pseudo wave function such that

1. $\forall\, r \geq r_c,\ \widetilde{R}_{n\ell}(r) = R_{n\ell}(r)$ where $R_{n\ell}$ is a radial eigenfunction of (1.2.3) associated to $\epsilon_{n\ell}$;
2. $\widetilde{R}_{n\ell}$ matches $R_{n\ell}$ and at least its first derivative at r_c.

Notice that contrary to the norm-conserving pseudopotential, no norm conservation constraint is imposed on the pseudo wave function $\widetilde{\phi}_k$. In practice, this allows one to choose smooth and slowly varying pseudo wave functions $\widetilde{\phi}_k$, which is why the Vanderbilt pseudopotentials are also called *ultrasoft*.

Let V_{loc} be a smooth potential such that $V_{\mathrm{loc}} = -\frac{Z}{r} + \rho \star \frac{1}{|\cdot|} + V_{\mathrm{xc}}[\rho]$ for $r \geq r_c$. We define the functions χ_k by

$$\chi_k = \left(\epsilon_{n\ell} + \frac{1}{2}\Delta - V_{\mathrm{loc}}\right)\widetilde{\phi}_k.$$

Since $V_{\mathrm{loc}} = -\frac{Z}{r} + \rho \star \frac{1}{|\cdot|} + V_{\mathrm{xc}}[\rho]$ and $\widetilde{\phi}_k(r) = \phi_k(r)$ for $r \geq r_c$, the functions χ_k are supported in $B(0, r_c)$. Let B the matrix of coefficients $B_{kk'} = \langle \phi_k | \chi_{k'} \rangle$, for $k, k' \in K$. We now form the quantities $V_{\mathrm{loc}}^{\mathrm{ion}}$, $D_{kk'}^{(0)}$, $Q_{kk'}$ and β_k needed to specify the pseudopotential. $Q_{kk'}$ and β_k are functions given by

$$\forall\, \mathbf{r} \in B(0, r_c),\ Q_{kk'}(\mathbf{r}) = \phi_k(\mathbf{r})\phi_{k'}(\mathbf{r}) - \widetilde{\phi}_k(\mathbf{r})\widetilde{\phi}_{k'}(\mathbf{r}),$$

and assuming that B is invertible

$$\forall\, \mathbf{r} \in B(0, r_c),\ \beta_k(\mathbf{r}) = \sum_{k' \in K} (B^{-1})_{k'k} \chi_{k'}(\mathbf{r}).$$

The functions $(\beta_k)_k$ are duals to the $(\phi_k)_k$: $\langle \beta_k | \phi_{k'} \rangle = \delta_{kk'}$. Let $q_{kk'} = \langle \phi_k | \phi_{k'} \rangle_{B(0,r_c)} - \langle \widetilde{\phi}_k | \widetilde{\phi}_{k'} \rangle_{B(0,r_c)}$. With all these definitions, we can check that the pseudo wave functions $\widetilde{\phi}_k$, $k \in K$ satisfy

$$\left(-\frac{1}{2}\Delta + V_{\mathrm{loc}} + \sum_{k,k' \in K} D_{kk'} \beta_k \langle \beta'_k | \cdot \rangle\right) \widetilde{\phi}_k = \epsilon_{n\ell} \left(\mathrm{Id} + \sum_{k,k' \in K} q_{kk'} \beta_k \langle \beta'_k | \cdot \rangle\right) \widetilde{\phi}_k,$$

where we have for $k, k' \in K$

$$D_{kk'} = B_{kk'} + \epsilon_{n'\ell'} q_{kk'}.$$

The function $V_{\mathrm{loc}}^{\mathrm{ion}}$ and the scalar $D_{kk'}^{(0)}$ are obtained by an unscreening procedure

$$V_{\mathrm{loc}}^{\mathrm{ion}} = V_{\mathrm{loc}} - \int_{\mathbb{R}^3} \frac{\widetilde{\rho}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}' - V_{\mathrm{xc}}[\widetilde{\rho}], \tag{1.3.1}$$

$$D_{kk'}^{(0)} = D_{kk'} - \int_{\mathbb{R}^3} V_{\mathrm{loc}}(\mathbf{r}) Q_{kk'}(\mathbf{r})\, \mathrm{d}\mathbf{r}, \tag{1.3.2}$$

where

$$\widetilde{\rho}(\mathbf{r}) = \sum_{k \in K} |\widetilde{\phi}_k(\mathbf{r})|^2 + \sum_{k,k',k'' \in K} Q_{kk'}(\mathbf{r}) \langle \phi_{k''} | \beta_k \rangle \langle \beta_{k'} | \phi_{k''} \rangle.$$

The formula for $D_{kk'}^{(0)}$ is different from [LPC+93], however it is easy to check in the atomic case that (1.3.2) is correct. The mistake is also confirmed in [KJ99] (Equation (34)).

1.3.2 Ultrasoft pseudopotential for a molecular system

For n_v valence electrons, the total energy of the molecular system is given by

$$E_0 = \inf \left\{ \sum_{i=1}^{n_v} \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \widetilde{\psi}_i|^2 + \langle \widetilde{\psi}_i | V_{NL} | \widetilde{\psi}_i \rangle + \sum_{I=1}^{N_{\text{at}}} \int_{\mathbb{R}^3} V_{\text{loc}}^{\text{ion},I} \widetilde{\rho} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\widetilde{\rho}(\mathbf{r}) \widetilde{\rho}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' + E_{\text{xc}}[\widetilde{\rho}], \right.$$
$$\left. \forall\, 1 \leq i \leq n_v,\ \widetilde{\psi}_i \in L^2(\mathbb{R}^3), \quad \forall\, 1 \leq i, j \leq n_v,\ \langle \widetilde{\psi}_i | S^{\text{US}} | \widetilde{\psi}_j \rangle = \delta_{ij} \right\}, \quad (1.3.3)$$

where the superscript I denotes the translation by $\mathbf{R}_I$ ($V_{\text{loc}}^{\text{ion},I}(\mathbf{r}) = V_{\text{loc}}^{\text{ion},I}(\mathbf{r} - \mathbf{R}_I)$, $\beta_k^I(\mathbf{r}) = \beta_k(\mathbf{r} - \mathbf{R}_I)$). $\widetilde{\rho}$ is the pseudo density given by

$$\widetilde{\rho}(\mathbf{r}) = \sum_{i=1}^{n_v} |\widetilde{\psi}_i(\mathbf{r})|^2 + \sum_{i=1}^{n_v} \sum_{I=1}^{N_{\text{at}}} \sum_{k,k' \in K} Q_{kk'}^I(\mathbf{r}) \langle \widetilde{\psi}_i | \beta_k^I \rangle \langle \beta_{k'}^I | \widetilde{\psi}_i \rangle, \quad (1.3.4)$$

V_{NL} is the nonlocal potential

$$V_{NL} = \sum_{I=1}^{N_{\text{at}}} \sum_{k,k' \in K} D_{kk'}^{(0)} \beta_k^I \langle \beta_{k'}^I | \cdot \rangle,$$

and S^{US} the overlap operator

$$S^{\text{US}} = \text{Id} + \sum_{I=1}^{N_{\text{at}}} \sum_{k,k' \in K} q_{kk'}^I \beta_k^I \langle \beta_{k'}^I | \cdot \rangle. \quad (1.3.5)$$

The Euler-Lagrange equations associated to the minimization problem (1.3.3) are given by

$$H^{\text{US}} \widetilde{\psi}_i = \lambda_i S^{\text{US}} \widetilde{\psi}_i, \quad \lambda_1 \leq \cdots \leq \lambda_{n_v}, \quad (1.3.6)$$

where

$$H^{\text{US}} = -\frac{1}{2}\Delta + V_{\text{eff}} + \sum_{I=1}^{N_{\text{at}}} \sum_{k,k' \in K} D_{kk'}^I \beta_k^I \langle \beta_{k'}^I | \cdot \rangle.$$

The potential V_{eff} is the effective potential

$$V_{\text{eff}} = \sum_{I=1}^{N_{\text{at}}} V_{\text{loc}}^{\text{ion},I} + \int_{\mathbb{R}^3} \frac{\widetilde{\rho}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' + V_{\text{xc}}[\widetilde{\rho}],$$

and for $k, k' \in K$,

$$D_{kk'}^I = D_{kk'}^{(0)} + \int_{\mathbb{R}^3} V_{\text{eff}}(\mathbf{r}) Q_{kk'}^I(\mathbf{r}) \, \mathrm{d}\mathbf{r}.$$

Vanderbilt pseudopotentials perform very well in practice yielding accurate results for small plane-wave energy cut-offs compared to norm-conserving pseudopotentials [FKBK00]. This good performance can be explained by the freedom in the choice of the cut-off radius r_c. For norm-conserving pseudopotentials, the cut-off radius is determined to guarantee the transferability of the

pseudopotential. In doing so, a low cut-off radius may have to be fixed. The corresponding pseudo wave function can be more peaked yielding a "harder" potential. For ultrasoft pseudopotentials, the cut-off radius can generally be set to half of the minimal interatomic distance, which is the largest cut-off radius available (otherwise, the balls where the pseudopotentials act would be overlapping). The corresponding pseudo wave functions are smooth and slowly varying, giving very soft pseudopotentials.

1.4 The PAW method

The PAW method [Blo94] introduced by Blöchl has become a popular method to compute accurately the electronic properties of crystals. It relies on an invertible transformation of the eigenvalue problem enabling one to incorporate pseudopotentials in a consistent way. In practice, infinite sums appearing in the PAW equations have to be truncated, introducing an error. However, contrary to NC pseudopotential theory, we have a systematic way to reduce this error by keeping more terms of the PAW equations. The exposition follows the original presentation by Blöchl in [Blo94].

1.4.1 General setting

The PAW method consists in replacing the original molecular eigenvalue problem $H\psi = E\psi$ where $H = -\frac{1}{2}\Delta + V$ is a Kohn-Sham Hamiltonian, by the generalized eigenvalue problem

$$(\mathrm{Id} + T^*)H(\mathrm{Id} + T)\widetilde{\psi} = E(\mathrm{Id} + T^*)(\mathrm{Id} + T)\widetilde{\psi}, \tag{1.4.1}$$

where $\mathrm{Id} + T$ is an invertible operator. It is clear that (1.4.1) is equivalent to $H\psi = E\psi$ where $\psi = (\mathrm{Id} + T)\widetilde{\psi}$. The transformation T is the sum of operators T_I acting locally around each nucleus. For each operator T_I, a cut-off radius r_c^I needs to be fixed such that the balls $B(\mathbf{R}_I, r_c^I)$ do not overlap.

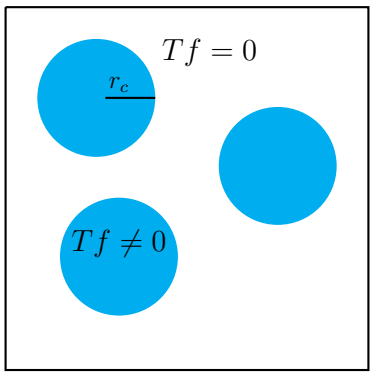


Figure 1.4.1 – Unit cell with PAW balls in blue

They are given by:

$$T_I = \sum_{k=1}^{\infty} (\phi_k^I - \widetilde{\phi}_k^I) \left\langle \widetilde{p}_k^I \, , \cdot \right\rangle , \tag{1.4.2}$$

where the functions ϕ_k^I, $\widetilde{\phi}_k^I$ and $\widetilde{p}_k^I$ are functions in $L^2(\mathbb{R}^3)$. The PAW functions $(\phi_k^I)_{k\in\mathbb{N}^*}$, $(\widetilde{\phi}_k^I)_{k\in\mathbb{N}^*}$ and $(\widetilde{p}_k^I)_{k\in\mathbb{N}^*}$ must satisfy the following essential properties:

1. $\mathrm{supp}\,(\phi_k^I - \widetilde{\phi}_k^I) \subset B(\mathbf{R}_I, r_c^I)$;
2. $\widetilde{\phi}_k^I$ restricted to $B(\mathbf{R}_I, r_c^I)$ is smooth and $(\widetilde{\phi}_k^I)_{k\in\mathbb{N}^*}$ form a Riesz basis of $H^1(B(\mathbf{R}_I, r_c^I))$;
3. $\widetilde{p}_k^I$ are supported in $B(\mathbf{R}_I, r_c^I)$ and $\forall\, i,j \in \mathbb{N}^*$, $\left\langle \widetilde{p}_i^I \, , \widetilde{\phi}_j^I \right\rangle = \delta_{ij}$ (that is $(\widetilde{p}_j^I)_{j\in\mathbb{N}^*}$ is dual to $(\widetilde{\phi}_j^I)_{j\in\mathbb{N}^*}$), hence for every $f \in H^1(B(\mathbf{R}_I, r_c^I))$, we have

$$f = \sum_{k=1}^{\infty} \left\langle \widetilde{p}_k^I \, , f \right\rangle \widetilde{\phi}_k^I \tag{1.4.3}$$

This way, the operators T_I satisfy

- for all $f \in L^2(\mathbb{R}^3)$, $\mathrm{supp}(T_I f) \subset \overline{B}(\mathbf{R}_I, r_c^I)$,
- if $\mathrm{supp}(f) \bigcap B(\mathbf{R}_I, r_c^I) = \emptyset$, then $T_I f = 0$.

The relation (1.4.3) enables one to write the expression of $(\mathrm{Id} + T^*)H(\mathrm{Id} + T)$ and $(\mathrm{Id} + T^*)(\mathrm{Id} + T)$ (see Appendix B) as

$$(\mathrm{Id} + T^*)H(\mathrm{Id} + T) = H + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\left\langle \phi_i^I \, , H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \, , H\widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \, , \cdot \right\rangle , \tag{1.4.4}$$

and

$$(\mathrm{Id} + T^*)(\mathrm{Id} + T) = \mathrm{Id} + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\left\langle \phi_i^I \, , \phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \, , \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \, , \cdot \right\rangle , \tag{1.4.5}$$

For the sake of clarity, we suppose that the cut-off radii r_c^I do not depend on the atomic site I and denote r_c the common cut-off radius.

Introduction of a pseudopotential

A further modification is possible. As the pseudo wave functions $\widetilde{\phi}_k^I$ are equal to ϕ_k^I outside $B(0, r_c)$, the integrals appearing in (1.4.4) can be truncated to the ball $B(\mathbf{R}_I, r_c)$. Doing so, another expression of $(\mathrm{Id} + T^*)H(\mathrm{Id} + T)$ can be obtained :

$$(\mathrm{Id} + T^*)H(\mathrm{Id} + T) = H + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\left\langle \phi_i^I \, , H\phi_j^I \right\rangle_{I,r_c} - \left\langle \widetilde{\phi}_i^I \, , H\widetilde{\phi}_j^I \right\rangle_{I,r_c} \right) \left\langle \widetilde{p}_j^I \, , \cdot \right\rangle ,$$

where

$$\left\langle f \, , Hg \right\rangle_{I,r_c} = \int_{B(\mathbf{R}_I, r_c)} \frac{1}{2} \nabla f \cdot \nabla g + V f g.$$

Using this expression of the operator $(\mathrm{Id}+T^*)H(\mathrm{Id}+T)$, it is possible to introduce a regular pseudopotential V^{PP} such that for each I, $V^{\mathrm{PP}}(\mathbf{r}) = V(\mathbf{r})$ for $\mathbf{r} \notin \bigcup_{I=1}^{M} B(\mathbf{R}_I, r_c)$.

The expression of $(\mathrm{Id}+T^*)H(\mathrm{Id}+T)$ becomes

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T) = H_{\mathrm{ps}} + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle_{I,r_c} - \left\langle \widetilde{\phi}_i^I \,, H_{\mathrm{ps}} \widetilde{\phi}_j^I \right\rangle_{I,r_c} \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{1.4.6}$$

with

$$H_{\mathrm{ps}} = -\frac{1}{2}\Delta + V^{\mathrm{PP}}.$$

1.4.2 The PAW method in practice

The infinite sums appearing in (1.4.5) and (1.4.6) have to be truncated to some level N_I which can depend on the atomic site:

$$H^{PAW} := H_{\mathrm{ps}} + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{N_I} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle_{I,r_c} - \left\langle \widetilde{\phi}_i^I \,, H_{\mathrm{ps}} \widetilde{\phi}_j^I \right\rangle_{I,r_c} \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{1.4.7}$$

and

$$S^{PAW} := \mathrm{Id} + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{N_I} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, \phi_j^I \right\rangle_{I,r_c} - \left\langle \widetilde{\phi}_i^I \,, \widetilde{\phi}_j^I \right\rangle_{I,r_c} \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle. \tag{1.4.8}$$

The PAW eigenvalue problem becomes

$$H^{PAW}\widetilde{\psi} = E^{PAW} S^{PAW} \widetilde{\psi}. \tag{1.4.9}$$

Since the Coulomb potentials have been replaced by regular pseudopotentials, the eigenfunctions of (1.4.9) are more regular than the eigenfunctions of the original eigenvalue problem. However, because the sums in (1.4.6) and (1.4.5) have been truncated, the sought eigenvalue is unlikely to be equal the original one. In practice, the PAW method has become one of the most efficient tools to compute energies of crystals and has been implemented in several popular electronic structure codes (AbInit [TJB+08], VASP [KF96, KJ99]).

1.4.3 Treatment of the nonlinearities

For linear Hamiltonians, application of the PAW method is quite straightforward:

1. PAW functions $(\phi_k^I)_{k\geq 1}$, $(\widetilde{\phi}_k^I)_{k\geq 1}$ and $(\widetilde{p}_k^I)_{k\geq 1}$ are constructed at each atomic site,
2. a smooth pseudopotential V^{PP} replaces the Coulomb interaction to get smooth eigenfunctions,
3. the generalized eigenvalue problem (1.4.9) is solved using a plane-wave basis.

For Kohn-Sham Hamiltonians, the PAW transformation is less clear since the Hartree and exchange-correlation potentials depend on the eigenfunctions of the Kohn-Sham equations. Hence,

the original electronic density ρ should be expressed in terms of the eigenfunctions of the PAW eigenvalue problem. Formally, since $(\mathrm{Id}+T)$ is invertible and $(\widetilde{\phi}_k^I)_{k\geq 1}$ and $(\widetilde{p}_k^I)_{k\geq 1}$ form a dual and complete basis of $L^2(B(\mathbf{R}_I, r_c))$, the electronic density ρ is given by:

$$\rho(\mathbf{r}) = \sum_{n=1}^{n_v} \left(|\widetilde{\psi}_n(\mathbf{r})|^2 + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \langle \widetilde{p}_i^I, \widetilde{\psi}_n \rangle \langle \widetilde{\psi}_n, \widetilde{p}_j^I \rangle \left(\phi_i^I(\mathbf{r})\phi_j^I(\mathbf{r}) - \widetilde{\phi}_i^I(\mathbf{r})\widetilde{\phi}_j^I(\mathbf{r}) \right) \right), \tag{1.4.10}$$

where $\widetilde{\psi}_n = (\mathrm{Id}+T)^{-1}\psi_n$ and ψ_n are the eigenfunctions associated to the lowest eigenvalue of the Hamiltonian H.

The expression of the electronic density can then be reinserted in the Hartree and exchange correlation potentials but the ensuing formulas are much more complicated.

Another way to treat the nonlinearity is to use the expression of the electronic density (1.4.10) directly in the energy functional and write the Euler-Lagrange equations associated to the new functional. The expression of the energy is however not very convenient when (1.4.10) is directly applied. Let

$$\rho_I(\mathbf{r}) = \sum_{n=1}^{n_v} \sum_{i,j=1}^{\infty} \langle \widetilde{p}_i^I, \widetilde{\psi}_n \rangle \langle \widetilde{\psi}_n, \widetilde{p}_j^I \rangle \phi_i^I(\mathbf{r})\phi_j^I(\mathbf{r}),$$

and

$$\widetilde{\rho}_I(\mathbf{r}) = \sum_{n=1}^{n_v} \sum_{i,j=1}^{\infty} \langle \widetilde{p}_i^I, \widetilde{\psi}_n \rangle \langle \widetilde{\psi}_n, \widetilde{p}_j^I \rangle \widetilde{\phi}_i^I(\mathbf{r})\widetilde{\phi}_j^I(\mathbf{r}).$$

The total electrostatic energy $E_S[\rho]$ is given by

$$\begin{aligned} E_S[\rho] :=& -\int_{\mathbb{R}^3} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ =& -\int_{\mathbb{R}^3} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} \left(\widetilde{\rho}(\mathbf{r}) + \sum_{I'=1}^{N_{\mathrm{at}}} (\rho_{I'} - \widetilde{\rho}_{I'})(\mathbf{r}) \right) \mathrm{d}\mathbf{r} \\ &+ \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\left(\widetilde{\rho}(\mathbf{r}) + \sum_{I=1}^{N_{\mathrm{at}}} (\rho_I(\mathbf{r}) - \widetilde{\rho}_I(\mathbf{r})) \right) \left(\widetilde{\rho}(\mathbf{r}') + \sum_{I=1}^{N_{\mathrm{at}}} (\rho_I(\mathbf{r}') - \widetilde{\rho}_I(\mathbf{r}')) \right)}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \end{aligned} \tag{1.4.11}$$

Because of the double sum on the atomic sites, the first term on the RHS of (1.4.11) scales as ${N_{\mathrm{at}}}^2$ thus badly with the size of the system. The second term is also problematic. By expanding this term, we have integrals involving the product of $\widetilde{\rho}$, which is represented with a plane-wave functions, and $\rho_I - \widetilde{\rho}_I$ which are represented on radial grids. Evaluating accurately and efficiently such terms is therefore not easy.

To solve this issue, which is already present in the initial derivation of the PAW equations,

Blöchl introduced compensation charges $\tilde{Z}_I$ supported in $B(\mathbf{R}_I, r_c)$ satisfying

$$\forall |m| \leq \ell, \int_{B(\mathbf{R}_I, r_c)} (\rho_I(\mathbf{r}) - \widetilde{\rho}_I(\mathbf{r}) - \tilde{Z}_I(\mathbf{r}))|\mathbf{r} - \mathbf{R}_I|^\ell Y_{\ell m}(\widehat{\mathbf{r} - \mathbf{R}_I})\, \mathrm{d}\mathbf{r} = -Z_I \delta_{0\ell}. \tag{1.4.12}$$

The exact definition of the compensation charge may differ in the different presentations of the PAW method, see [KJ99, Ros09].

The expression of the electrostatic energy can be rewritten:

$$\begin{aligned} E_S[\rho] = &\iint_{\mathbb{R}^3\times\mathbb{R}^3} \sum_{I=1}^{N_{\mathrm{at}}} \tilde{Z}_I(\mathbf{r})\widetilde{\rho}(\mathbf{r}')\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' + \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\widetilde{\rho}(\mathbf{r})\widetilde{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &+ \sum_{I=1}^{N_{\mathrm{at}}} \left(-\int_{\mathbb{R}^3} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\rho_I(\mathbf{r}) + \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_I(\mathbf{r})\rho_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \right. \\ &\left. - \iint_{\mathbb{R}^3\times\mathbb{R}^3} \tilde{Z}_I(\mathbf{r})\widetilde{\rho}_I(\mathbf{r}')\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' - \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\widetilde{\rho}_I(\mathbf{r})\widetilde{\rho}_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \right) \end{aligned} \tag{1.4.13}$$

The electrostatic energy in the PAW method is the sum of a new electrostatic functional with smoothed Coulomb potential and atom-centered corrections.

Note that this expression is valid only if the compensation charge property (1.4.12) holds for any angular momentum ℓ, m. In practice, the compensation charge is defined as a finite linear combination of smooth functions which satisfies (1.4.12) up to an angular momentum $\ell_{\max}$. This introduces a further approximation in the PAW treatment.

For the exchange-correlation energy, there are different ways to get an expression similar to (1.4.13), in the sense that the exchange-correlation energy is corrected by atom-centered terms:

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{xc}}[\widetilde{\rho}] + \sum_{I=1}^{N_{\mathrm{at}}} (E_{\mathrm{xc}}[\rho_I] - E_{\mathrm{xc}}[\widetilde{\rho}_I]).$$

The interested reader may refer to [HMD+97, KJ99, THM01] for more details.

1.4.4 Generation of the PAW functions

In practice, there are two main ways to generate the pseudo wave functions $\widetilde{\phi}_k$ and the projectors $\widetilde{p}_k$ introduced by Blöchl [Blo94] and Vanderbilt [LPC+93].

To generate the PAW functions, a range of angular momentum $\ell \in [\![0, \ell_{\max}]\!]$ is selected and for each angular momentum ℓ, n_ℓ PAW functions are defined. The total number of PAW functions is then equal to $N_I = \sum_{\ell=0}^{\ell_{\max}} (2\ell+1)n_\ell$. Generally, $\ell_{\max}$ is limited to the p or d orbitals (*i.e.* $\ell_{\max} \leq 1$ or 2) and one or two PAW functions for each orbital are sufficient.

Usually PAW functions are first defined in the ball $B(0, r_c)$ and translated to $\mathbf{R}_I$.

Vanderbilt scheme

Atomic wave function The functions ϕ_k are simply the atomic wave functions defined earlier *i.e.* solutions to the atomic eigenvalue problem

$$H_I\phi_k^I = \epsilon_k\phi_k^I, \quad \epsilon_1^I \leq \epsilon_2^I \leq \epsilon_3^I \leq \ldots, \quad \int_{\mathbb{R}^3} \phi_j^I\phi_k^I = \delta_{jk},$$

with

$$H_I = -\frac{1}{2}\Delta - \frac{Z_I}{|\mathbf{r}|} + W(|\mathbf{r}|).$$

The eigenfunctions ϕ_k can be decomposed into a spherical part $Y_{\ell m}$ and a radial part $R_{n\ell}$

$$\phi_k(\mathbf{r}) = \frac{R_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}),$$

where k stands for the multiple indices (n, ℓ, m).

Pseudo wave function The pseudo wave functions $\widetilde{\phi}_k$ are given by:

$$\forall \mathbf{r} \in \mathbb{R}^3, \ \widetilde{\phi}_k(\mathbf{r}) = \frac{\widetilde{R}_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}).$$

Various choices of $\widetilde{R}_{n\ell}$ are possible, for example, in [LPC+93], $\widetilde{R}_{n\ell}$ is a polynomial inside the augmentation region $\overline{B}(0, r_c)$:

$$\widetilde{R}_{n\ell}(r) = \begin{cases} r^{\ell+1} \sum_{k=0}^{p} c_{2k} r^{2k} & \text{for } 0 \leq r \leq r_c, \\ R_{n\ell}(r) & \text{for } r > r_c, \end{cases}$$

or in [KJ99], a sum of spherical Bessel functions j_ℓ :

$$\widetilde{R}_{n\ell}(r) = \begin{cases} r \sum_{k=1}^{p} \alpha_k j_\ell(q_k r) \ , & \text{for } 0 \leq r \leq r_c, \\ R_{n\ell}(r) & \text{for } r > r_c, \end{cases}$$

and the coefficients are chosen to match as many derivatives of $R_{n\ell}$ as possible at r_c.

Projector function First, define :

$$\chi_{n\ell}(r) = \frac{1}{2}\widetilde{R}''_{n\ell}(r) + \left(E_n - \frac{\ell(\ell+1)}{2r^2} - V_\ell^{\mathrm{PP}}(r)\right)\widetilde{R}_{n\ell}(r),$$

where $V_\ell^{\mathrm{PP}}(r)$ is usually the Troullier-Martins pseudopotential [TM91] although other choices are possible. By construction, $\mathrm{supp}(\chi_{n\ell}) \subset [0, r_c]$. Let B be the matrix

$$B_{n,n'} = \int_0^{r_c} \widetilde{R}_{n\ell}(r)\chi_{n'\ell}(r)\,\mathrm{d}r.$$

The radial parts of the projector functions are given by

$$p_{n\ell}(r) = \sum_{n'=1}^{N_I} \chi_{n'\ell}(r)\left(B^{-1}\right)_{n'n}.$$

This ensures that $\int_0^{r_c} p_{n\ell}(r)\widetilde{R}_{n'\ell'}(r)\,\mathrm{d}r = \delta_{nn'}\delta_{\ell\ell'}$. The projector functions are defined by

$$\widetilde{p}_{n\ell}(\mathbf{r}) = \frac{p_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}).$$

Blöchl scheme

The PAW functions are generated in two steps. For each angular momentum ℓ, we define auxiliary functions $\widetilde{R}^0_{n\ell}$ and $p^0_{n\ell}$:

Auxiliary functions Let $\chi(r)$ be the cut-off function

$$\chi(r) = \begin{cases} \frac{\sin(\pi r/r_c)}{(\pi r/r_c)} & \text{for } r \leq r_c, \\ 0 & \text{for } r > r_c, \end{cases}$$

and let $(C_{n\ell}, \widetilde{R}^0_{n\ell})_{n\in\mathbb{N}^*}$ be the unique solution to:

$$\begin{cases} -\frac{1}{2}(\widetilde{R}^0_{n\ell})''(r) + \frac{\ell(\ell+1)}{2r^2}\widetilde{R}^0_{n\ell} + (V_\ell^{\mathrm{PP}} - E_n)\widetilde{R}^0_{n\ell} = C_{n\ell}\chi(r)\widetilde{R}^0_{n\ell}, \quad 0 \leq r \leq r_c \\ \widetilde{R}^0_{n\ell}(0) = 0 \\ \widetilde{R}^0_{n\ell}(r_c) = R^0_{n\ell}(r_c), \quad (\widetilde{R}^0_{n\ell})'(r_c) = (R^0_{n\ell})'(r_c). \end{cases} \tag{1.4.14}$$

Let $p^0_{n\ell}$ be the auxiliary functions:

$$p^0_{n\ell}(r) = \frac{\chi(r)\widetilde{R}^0_{n\ell}(r)}{\left(\widetilde{R}^0_{n\ell}(r)|\chi(r)\widetilde{R}^0_{n\ell}(r)\right)},$$

where

$$(f|g) = \int_0^{r_c} f(r)g(r)\,\mathrm{d}r.$$

PAW functions The radial part of all the PAW functions are constructed with a Gram-Schmidt process. We describe it here assuming that only two quantum numbers $n_1 < n_2$ are needed for the computation. However, one should bear in mind that, on the one hand, usually, $n_2 = n_1 + 1$, and

on the other hand, although limiting the procedure to two quantum numbers is in general sufficient for practical purposes, it is straightforward to generalize the following orthogonalization procedure to an arbitrary number of quantum numbers.

1. *Basis:* the first set of functions $\widetilde{R}_{n_1\ell}$, $p_{n_1\ell}$ and $R_{n_1\ell}$, corresponding to the lowest principal quantum number n used, are defined by

$$\widetilde{R}_{n_1\ell} = \widetilde{R}^0_{n_1\ell}, \quad p_{n_1\ell} = p^0_{n_1\ell}, \quad R_{n_1\ell} = R^0_{n_1\ell}.$$

2. *Inductive step:* if there is a second radial basis function for $n_2 > n_1$,
   - first, the function $\widetilde{R}^0_{n_2\ell}$ is orthogonalized against $p_{n_1\ell}$:

$$\widetilde{R}_{n_2\ell}(r) = \mathcal{F}_{n_2\ell}\left(\widetilde{R}^0_{n_2\ell}(r) - \widetilde{R}_{n_1\ell}(r)\left(p_{n_1\ell}|\widetilde{R}^0_{n_2\ell}\right)\right), \tag{1.4.15}$$

     where the factor

$$\mathcal{F}_{n_2\ell} = \frac{1}{\left(1 - \left(\widetilde{R}^0_{n_2\ell}|p_{n_1\ell}\right)\left(\widetilde{R}^0_{n_1\ell}|p_{n_2\ell}\right)\right)^{1/2}}$$

     is a normalization constant;
   - similarly, the function $p^0_{n_2\ell}$ is orthogonalized against $\widetilde{R}_{n_1\ell}$ by noticing that $\left(\widetilde{R}^0_{n_2\ell}|p_{n_1\ell}\right) = \left(\widetilde{R}^0_{n_1\ell}|p^0_{n_2\ell}\right)$:

$$p_{n_2\ell}(r) = \mathcal{F}_{n_2\ell}\left(p^0_{n_2\ell} - p_{n_1\ell}\left(\widetilde{R}^0_{n_2\ell}|p_{n_1\ell}\right)\right);$$

   - finally, to ensure the continuity between the radial functions $R_{n_2\ell}$ and $\widetilde{R}_{n_2\ell}$, we apply to $R^0_{n_2\ell}$ the same linear combination in Equation (1.4.15)

$$R_{n_2\ell}(r) = \mathcal{F}_{n_2\ell}\left(R^0_{n_2\ell}(r) - R_{n_1\ell}(r)\left(p_{n_1\ell}|\widetilde{R}^0_{n_2\ell}\right)\right).$$

The PAW functions are given by

$$\phi_{n\ell m}(\mathbf{r}) = \frac{R_{n\ell}(r)}{r}\,Y_{\ell m}(\theta,\varphi), \quad \widetilde{\phi}_{n\ell m}(\mathbf{r}) = \frac{\widetilde{R}_{n\ell}(r)}{r}\,Y_{\ell m}(\theta,\varphi),$$
$$\widetilde{p}_{n\ell m}(\mathbf{r}) = \frac{p_{n\ell}(r)}{r}\,Y_{\ell m}(\theta,\varphi).$$

1.4.5 Relationship with the Vanderbilt ultrasoft pseudopotentials

The Vanderbilt ultrasoft pseudopotentials and the PAW method are closely related as first pointed out in [KJ99].

Indeed if in both methods, the same atomic wave functions (ϕ_i), pseudo wave functions ($\widetilde{\phi}_i$) are used and if the projector functions ($\widetilde{p}_k$) of the PAW method are generated using the Vanderbilt scheme, it is easy to see that the overlap operators S^{US} (1.3.5) and S^{PAW} (1.4.8) are equal and the expression of the electron densities (1.3.4) and (1.4.10) are the same.

For the ultrasoft and PAW Hamiltonians H^{US} and H^{PAW}, the comparison is harder to make because of the treatment of the exchange-correlation terms (see [KJ99]).

In practice, both methods yield similar results in most situations, however the PAW method seems superior in some specific settings, where the PAW predictions are closer to experiments [KJ99].

1.5 The APW method and its variants: a full-potential approach

Some methods have been developed aiming to solve directly the electronic eigenvalue problems of periodic Hamiltonians.

The augmented plane-wave (APW) method [Sla37] and its variants (linearized APW method [KA75], full-linearized APW method [WWF82]) are attempts in this direction. Instead of using plane-waves to solve the eigenvalue problem, a different basis set more adapted to the problem is used. The basis functions used in these methods are plane-waves that are modified in balls centered at each nucleus in order to capture the cusp behavior of the electronic wave function. A nonconforming method close to the APW method and the APW method applied to Kohn-Sham Hamiltonians have been analyzed in [CS15].

The VPAW method presented in Chapter 2 and analyzed in different settings in Chapters 3 and 5 relies on the same principles. It is thus interesting to compare both methods and present the results obtained in [CS15].

In this section, we consider a $\mathcal{R}$-periodic linear Hamiltonian

$$H = -\frac{1}{2}\Delta + V_{\mathrm{per}} + W_{\mathrm{per}}, \tag{1.5.1}$$

acting on $L^2_{\mathrm{per}}(\Gamma)$ with domain $H^2_{\mathrm{per}}(\Gamma)$ where $\Gamma = [-\frac{L}{2}, \frac{L}{2})^3$ is a unit cell repeated over a lattice $\mathcal{R} := \frac{L}{2}\mathbb{Z}\mathbf{e}_1 + \frac{L}{2}\mathbb{Z}\mathbf{e}_2 + \frac{L}{2}\mathbb{Z}\mathbf{e}_3$. W_{per} is a smooth $\mathcal{R}$-periodic function and V_{per} is given by

$$\begin{cases} -\Delta V_{\mathrm{per}} = 4\pi \left(\sum\limits_{\mathbf{T}\in\mathcal{R}} \sum\limits_{I=1}^{N_{\mathrm{at}}} Z_I \left(\delta_{\mathbf{R}_I}(\cdot + \mathbf{T}) - \frac{1}{|\Gamma|} \right) \right) \\ V_{\mathrm{per}} \text{ is } \mathcal{R}\text{-periodic.} \end{cases}$$

We denote by V the potential $V_{\mathrm{per}} + W_{\mathrm{per}}$ for the remainder of this section.

1.5.1 Basic theory

In this setting, the operator H is a self-adjoint operator, bounded below with a compact resolvent, hence, its spectrum is purely discrete. To take advantage of the periodicity, Fourier method is the method of choice. However, because of the lack of regularity of V_{per}, the plane-wave expansions of the eigenfunctions of H are slowly converging, which is why pseudopotential methods are used.

In the augmented plane-wave (APW) method, instead of modifying the Hamiltonian, a different basis set is used which is not sensitive to the cusps resulting from the Coulomb interaction with the nuclei. The new basis set is defined by partitioning the unit cell Γ into two types of regions (the so-called *muffin-tin division*):

i) balls $B(\mathbf{R}_I, r_c)$, $I = 1, \dots, M$;

ii) the remaining interstitial region $\mathcal{D}$.

The basis functions consist of augmentations of plane-waves:

$$\omega_{\mathbf{K}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{in } \mathcal{D} \\ \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} \alpha_{\ell m}^{\mathbf{K}} \chi_\ell(r_I) Y_{\ell m}(\widehat{\mathbf{r}_I}) & \text{in each } B(\mathbf{R}_I, r_c) \end{cases} \tag{1.5.2}$$

where $\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I$. The coefficients $(\alpha_{\ell m}^{\mathbf{K}})_{|m|\le\ell\le\ell_{\max}}$ are set to match the spherical harmonics expansion of $e^{i\mathbf{K}\cdot\mathbf{r}}$ at the boundaries of the balls $B(\mathbf{R}_I, r_c)$. More precisely, using the scattering expansion

$$e^{i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell j_\ell(Kr) Y_{\ell m}(\hat{\mathbf{K}}) Y_{\ell m}(\hat{\mathbf{r}}),$$

where j_ℓ is the spherical Bessel function of the first kind, the coefficients $\alpha_{\ell m}^{\mathbf{K}}$ are given by

$$\alpha_{\ell m}^{\mathbf{K}} = e^{i\mathbf{K}\cdot\mathbf{R}_I} \frac{4\pi i^\ell}{\chi_\ell(r_c)} j_\ell(Kr_c) Y_{\ell m}(\hat{\mathbf{K}}),$$

provided that $\chi_\ell(r_c) \neq 0$. The functions χ_ℓ will be made explicit in the description of the different types of APW methods.

The eigenvalue problem associated to the linear Hamiltonian H (1.5.1) is solved using the basis functions $\omega_{\mathbf{K}}$. These basis functions are however not continuous at the boundary of the balls $B(\mathbf{R}_I, r_c)$, hence they do not belong to $H^1(\Gamma)$: the APW method is a *nonconforming* method.

A mathematical analysis of this nonconforming method has been presented in [CS15]. The finite dimensional approximation space $V_{M,\ell_{\max},N}$ is given by the span of the functions of the form:

$$\omega_{\mathbf{K}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{in } \mathcal{D} \\ \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} \sum_{n=0}^{N} c_{n\ell m} \chi_n(r_I) Y_{\ell m}(\widehat{\mathbf{r}_I}) & \text{in each } B(\mathbf{R}_I, r_c) \end{cases},$$

where $|\mathbf{K}| \le M$, $(\chi_n)_{0\le n\le N}$ is a basis of the polynomials on $[0, r_c]$ of degree at most N and $c_{n\ell m}$ are any coefficients satisfying:

$$\sum_{n=0}^{N} c_{n\ell m} \chi_n(r_c) = 4\pi i^\ell j_\ell(Kr_c) Y_{\ell m}(\hat{\mathbf{K}}) e^{-i\mathbf{K}\cdot\mathbf{R}_I}.$$

They proved the following convergence theorem for this nonconforming method.

Theorem 1.5 (Theorem 3.4 in [CS15]). *Let $\eta = \min(M, \ell_{\max}, N)$ where $(M, \ell_{\max}, N)$ are the parameters of the nonconforming method. Let E_η be an eigenvalue computed using the variational space $V_{M,\ell_{\max},N}$ and E the corresponding exact eigenvalue of H (1.5.1). Then for η large enough and for any $s > 0$,*

$$|E_\eta - E| \leq \frac{C_s}{\eta^{s-\frac{3}{2}}},$$

where C_s depends on s.

The proof of Theorem 1.5 relies on the good behavior of the eigenfunctions of H in the interstitial region $\mathcal{D}$, where they are smooth, and a precise characterization of the singularities close to the nuclei given by the theory of weighted Sobolev space for Schrödinger type eigenvalue problem [HNS08, FSS08]. This characterization is also used in the analysis of the VPAW method for this type of eigenvalue problem (Chapter 5).

1.5.2 The APW method

For the classical APW method originally formulated by Slater [Sla37], the basis functions are of the form (1.5.2) where the functions χ_ℓ are nontrivial solutions of the radial Schrödinger equation

$$\forall\, r \in (0, r_c),\ -\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\chi_\ell}{\mathrm{d}r}\right) + \left(\frac{\ell(\ell+1)}{r^2} + \overline{V}(r) - \epsilon\right)\chi_\ell(r) = 0, \tag{1.5.3}$$

where $\overline{V}(r) = \frac{1}{4\pi}\int_{S(0,1)} V(\mathbf{r})\,\mathrm{d}\hat{\mathbf{r}}$ and V is the potential appearing in H (1.5.1).

The approximation space is $V^\epsilon_{M\ell_{\max}} = \mathrm{span}(\omega^\epsilon_{\mathbf{K}\ell_{\max}},\ |\mathbf{K}| \leq M)$ with

$$\omega^\epsilon_{\mathbf{K}\ell_{\max}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{in } \mathcal{D}, \\ \displaystyle\sum_{\ell=0}^{\ell_{\max}}\sum_{m=-\ell}^{\ell} \alpha^{\mathbf{K}}_{\ell m}\chi_\ell(r_I)Y_{\ell m}(\hat{\mathbf{r}}_I) & \text{in each } B(\mathbf{R}_I, r_c). \end{cases}$$

If the potential V is radial and if the parameter ϵ is equal to the exact eigenvalue, then χ_ℓ solves the eigenvalue problem inside the sphere. By the APW method, a nonlinear eigenvalue problem has to be solved: the eigenpair $(E_{M\ell_{\max}}, v_{M\ell_{\max}}) \in \mathbb{R} \times V^{E_{M\ell_{\max}}}_{M\ell_{\max}}$ is sought solving

$$\forall\, v \in V^{E_{M\ell_{\max}}}_{M\ell_{\max}},\ \langle v_{M\ell_{\max}}, Hv\rangle = E_{M\ell_{\max}}\langle v_{M\ell_{\max}}, v\rangle.$$

This method is thus computationally expensive and is restricted to simple systems with few eigenvalues.

The APW method has been analyzed in [CS15] under the assumption that the potential V is supposed radial in the augmentation balls $B(\mathbf{R}_I, r_c)$. The authors showed a convergence rate of the computed eigenvalue similar to the noncorforming method presented previously (Theorem 3.5 [CS15]).

A solution to the nonlinearity introduced by the APW method has been proposed in [KA75]. The authors suggested to add *energy derivatives* of the functions χ_ℓ. These energy derivatives are

defined by

$$\dot{\chi}_\ell(r,E) = \frac{\partial}{\partial\epsilon}\chi_\ell(r,\epsilon)|_{\epsilon=E},$$

where χ_ℓ is kept normalized in the ball. This leads to the LAPW (Linearized APW) method. The approximation space is $\widetilde{V}^E_{M\ell_{\max}} = \mathrm{span}(\widetilde{\omega}^\epsilon_{\mathbf{K},\ell_{\max}}, |\mathbf{K}| \leq M)$ with

$$\widetilde{\omega}^\epsilon_{\mathbf{K}\ell_{\max}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{in } \mathcal{D}, \\ \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} [\alpha^{\mathbf{K}}_{\ell m}\chi_\ell(r_I) + \beta^{\mathbf{K}}_{\ell m}\dot{\chi}_\ell(r_I)]Y_{\ell m}(\hat{\mathbf{r}_I}) & \text{in each } B(\mathbf{R}_I, r_c). \end{cases}$$

The coefficients $\alpha^{\mathbf{K}}_{\ell m}$ and $\beta^{\mathbf{K}}_{\ell m}$ are determined to match the coefficients of the scattering expansion of $e^{i\mathbf{K}\cdot\mathbf{r}}$ and its derivative at the sphere.

Heuristic arguments of the convergence properties of the LAPW have been given in [KA75, CS15]. Namely if the parameter ϵ appearing in (1.5.3) is chosen close to the exact eigenvalue E and under the assumption that the logarithmic derivatives of $\chi_\ell(\cdot,\epsilon)$ and $\chi_\ell(\cdot,E)$ match on the sphere *i.e.*

$$\frac{\chi'_\ell(r_c,\epsilon)}{\chi_\ell(r_c,\epsilon)} = \frac{\chi'_\ell(r_c,E)}{\chi_\ell(r_c,E)},$$

then the error on the eigenvalues computed with the LAPW method are controlled by:

$$\forall\, s > 1,\ |E_{\mathrm{LAPW}} - E| \leq C_s(M^{1-s} + {\ell_{\max}}^{1-s} + |E-\epsilon|^4).$$

The assumption on the logarithmic derivatives has not been proved, hence the convergence rate is only conjectured.

CHAPTER 2

THE VPAW METHOD AND ITS ANALYSIS

The PAW method presented in Section 1 introduces an approximation by truncating the PAW generalized eigenvalue problem. It is possible to avoid this by truncating the operator T_I acting locally around the nucleus I right at the beginning.

This new method, called *variational* PAW (VPAW) method [BCD17a], has been analyzed in a one-dimensional periodic Schrödinger operator with Dirac potentials [BCD17b]. It is shown that the VPAW method drastically improves the plane-wave convergence of the eigenvalues of this model. The VPAW method also helped to analyze the approximation induced by the PAW method [Dup17]. Finally, the plane-wave convergence of the VPAW method has also been analyzed when applied to periodic 3D Hamiltonians [Dup18].

In Section 2.1, the VPAW method is presented for eigenvalue problems arising from solid-state physics. In Section 2.2, the VPAW formalism is applied to the periodic one-dimensional Schrödinger operator with Dirac potentials. Estimates on the eigenvalues of the plane-wave discretization using the VPAW method are given. A summary of the analysis of the truncation error introduced by the PAW method is also exposed. Section 2.3 is devoted to the plane-wave discretization of eigenvalue problems of periodic 3D linear Hamiltonians with Coulomb potentials using the VPAW method.

2.1 The VPAW method

2.1.1 General setting

The crystal is modeled as an infinite periodic motif of N_{at} point charges at positions $\mathbf{R}_I$ in the unit cell

$$\Gamma = \left\{ \alpha_1 \mathbf{a}_1 + \alpha_2 \mathbf{a}_2 + \alpha_3 \mathbf{a}_3, (\alpha_1, \alpha_2, \alpha_3) \in [-1/2, 1/2)^3 \right\},$$

and repeated over the periodic lattice

$$\mathcal{R} = \mathbb{Z}\mathbf{a}_1 + \mathbb{Z}\mathbf{a}_2 + \mathbb{Z}\mathbf{a}_3,$$

where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are linearly independent vectors of $\mathbb{R}^3$.

In the linear model under consideration, the electronic properties of the crystal are encoded in the spectral properties of the periodic Hamiltonian H_{per} acting on $L^2(\mathbb{R}^3)$:

$$H_{\text{per}} = -\frac{1}{2}\Delta + V_{\text{per}} + W_{\text{per}},$$

where V_{per} is the $\mathcal{R}$-periodic potential defined (up to an irrelevant addition constant) by

$$\begin{cases} -\Delta V_{\text{per}} = 4\pi \left(\displaystyle\sum_{\mathbf{T}\in\mathcal{R}} \sum_{I=1}^{N_{\text{at}}} Z_I \left(\delta_{\mathbf{R}_I}(\cdot + \mathbf{T}) - \frac{1}{|\Gamma|} \right) \right) \\ V_{\text{per}} \text{ is } \mathcal{R}\text{-periodic.} \end{cases} \tag{2.1.1}$$

For simplicity, W_{per} is a regular enough $\mathcal{R}$-periodic potential. In practice, W_{per} is a nonlinear potential depending on the model chosen to describe the Hartree and exchange-correlation terms (typically a Kohn-Sham LDA potential).

The standard way to study the spectral properties of H_{per} is through Bloch theory ([RS78], Chapter XIII) which will be outlined in the next few lines. Let $\mathcal{R}^*$ be the dual lattice

$$\mathcal{R}^* = \mathbb{Z}\mathbf{a}_1^* + \mathbb{Z}\mathbf{a}_2^* + \mathbb{Z}\mathbf{a}_3^*,$$

where $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ satisfies $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$. The reciprocal unit cell is defined by

$$\Gamma^* = \left\{ \alpha_1\mathbf{a}_1^* + \alpha_2\mathbf{a}_2^* + \alpha_3\mathbf{a}_3^*, (\alpha_1, \alpha_2, \alpha_3) \in [-1/2, 1/2)^3 \right\}.$$

As H_{per} commutes with $\mathcal{R}$-translations, H_{per} admits a Bloch decomposition [RS78] in operators $H_{\mathbf{q}}$ acting on

$$L^2_{\text{per}}(\Gamma) = \{ f \in L^2_{\text{loc}}(\mathbb{R}^3) \mid f \text{ is } \mathcal{R}\text{-periodic} \},$$

with domain

$$H^2_{\text{per}}(\Gamma) = \{ f \in H^2_{\text{loc}}(\mathbb{R}^3) \mid f \text{ is } \mathcal{R}\text{-periodic} \}.$$

The operator $H_{\mathbf{q}}$ is given by:

$$H_{\mathbf{q}} = \frac{1}{2}|-i\nabla + \mathbf{q}|^2 + V_{\text{per}} + W_{\text{per}}, \quad \mathbf{q} \in \Gamma^*.$$

For each $\mathbf{q} \in \Gamma^*$, the operator $H_{\mathbf{q}}$ is self-adjoint, bounded below and with compact resolvent. It thus has a discrete spectrum. Denoting by $E_{1,\mathbf{q}} \leq E_{2,\mathbf{q}} \leq \ldots$, with $E_{n,\mathbf{q}} \underset{n\to+\infty}{\longrightarrow} +\infty$, its eigenvalues counted with multiplicities, there exists an orthonormal basis of $L^2_{\text{per}}(\Gamma)$ consisting of eigenfunctions $(\psi_{n,\mathbf{q}})_{n\in\mathbb{N}^*}$

$$H_{\mathbf{q}}\psi_{n,\mathbf{q}} = E_{n,\mathbf{q}}\psi_{n,\mathbf{q}}. \tag{2.1.2}$$

The spectrum of H_{per} is purely continuous and can be recovered from the discrete spectra of all the operators $H_{\mathbf{q}}$, $\mathbf{q} \in \Gamma^*$

$$\sigma(H_{\text{per}}) = \bigcup_{\mathbf{q}\in\Gamma^*} \sigma(H_{\mathbf{q}}).$$

The PAW and VPAW methods aim to ease the numerical approximation of the eigenvalue problem (2.1.2). For clarity, we will only present the case $\mathbf{q} = 0$ and denote H_0 by H as this special case encloses all the main difficulties encountered in numerically solving (2.1.2). Transposition to $\mathbf{q} \neq 0$ can be done without problem.

2.1.2 The VPAW method for solids

Following the idea of the PAW method, an invertible transformation $(\mathrm{Id} + T)$ is applied to the eigenvalue problem (2.1.2), where T is the sum of operators T_I, each T_I acting locally around nucleus I. For each operator T_I, two parameters N_I and r_c need to be fixed:

1. the number N_I of PAW functions used to build T_I,
2. a cut-off r_c radius which set the acting domain of T_I, more precisely:
   - for all $f \in L^2_{\mathrm{per}}(\Gamma)$, $\mathrm{supp}(T_I f) \subset \bigcup_{\mathbf{T}\in\mathcal{R}} \overline{B}(\mathbf{R}_I + \mathbf{T}, r_c)$,
   - if $\mathrm{supp}(f) \bigcap \bigcup_{\mathbf{T}\in\mathcal{R}} \overline{B}(\mathbf{R}_I + \mathbf{T}, r_c) = \emptyset$, then $T_I f = 0$.

The cut-off radius r_c must be chosen small enough to avoid pairwise overlaps of the balls $(B(\mathbf{R}_I + \mathbf{T}, r_c))_{1\leq I\leq N_{\mathrm{at}}, \mathbf{T}\in\mathcal{R}}$.

The operator T_I is given by:

$$T_I = \sum_{k=1}^{N_I} (\phi_k^I(\mathbf{r} - \mathbf{R}_I) - \widetilde{\phi}_k^I(\mathbf{r} - \mathbf{R}_I)) \left\langle \tilde{p}_k^I(\cdot - \mathbf{R}_I), \cdot \right\rangle, \tag{2.1.3}$$

where $\langle \cdot, \cdot \rangle$ is the usual L^2_{per}-scalar product and the functions ϕ_k^I, $\widetilde{\phi}_k^I$ and $\tilde{p}_k^I$ are functions in $L^2_{\mathrm{per}}(\Gamma)$. Compared to the PAW method, the sum appearing in (2.1.3) is finite.

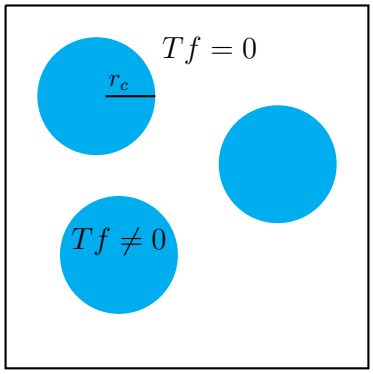


Figure 2.1.1 – Unit cell with PAW balls in blue

These functions, which will be referred to as the PAW functions in the sequel, are chosen as follows:

1. first, let $(\varphi_k^I)_{1\leq k\leq N_I} \in (L^2(\mathbb{R}^3))^{N_I}$ be eigenfunctions of an atomic *non-periodic* Hamiltonian

$$H_I \varphi_k^I = \epsilon_k \varphi_k^I, \quad \epsilon_1^I \leq \epsilon_2^I \leq \epsilon_3^I \leq \ldots, \quad \int_{\mathbb{R}^3} \varphi_k^I \varphi_{k'}^I = \delta_{kk'},$$

with H_I defined by

$$H_I = -\frac{1}{2}\Delta - \frac{Z_I}{|\mathbf{r}|} + W(|\mathbf{r}|), \tag{2.1.4}$$

where W is a regular enough bounded potential. The operator H_I is self-adjoint on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. Again, in practice, W is a nonlinear potential (assumed radial see the discussion Section 1.2.1) belonging to the same family of models as W_{per} in Equation (2.1.1). The PAW atomic wave functions $(\phi_k^I)_{1\leq k\leq N_I} \in (L^2_{\text{per}}(\Gamma))^{N_I}$ satisfy:

— for $1 \leq k \leq N_I$ and $\mathbf{r} \in B(0, r_c)$, $\phi_k^I(\mathbf{r}) = \varphi_k^I(\mathbf{r})$,

— ϕ_k^I is smoothly extended outside the ball, such that ϕ_k^I is $\mathcal{R}$-periodic.

The way ϕ_k^I is extended does not really matter since in the following, only the difference $\phi_k^I - \widetilde{\phi}_k^I$ -which vanishes outside the balls $\bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{T}, r_c)$- appears in the VPAW equations.

2. the pseudo wave functions $(\widetilde{\phi}_k^I)_{1\leq k\leq N_I}$, with $N_I \leq Z_I$, are determined by the next conditions:
   (a) inside the ball $B(0, r_c)$, $\widetilde{\phi}_k^I$ is smooth and matches ϕ_k^I and several of its derivatives on the sphere $\{|\mathbf{r}| = r_c\}$,
   (b) $\widetilde{\phi}_k^I$ is $\mathcal{R}$-periodic,
   (c) for $\mathbf{r} \in \mathbb{R}^3 \setminus \bigcup_{\mathbf{T}\in\mathcal{R}} \overline{B}(\mathbf{T}, r_c)$, $\widetilde{\phi}_k^I(\mathbf{r}) = \phi_k^I(\mathbf{r})$;
3. the projector functions $(\tilde{p}_k^I)_{1\leq k\leq N_I}$ are defined such that:
   (a) each projector function $\tilde{p}_k^I$ is supported in $\bigcup_{\mathbf{T}\in\mathcal{R}} \overline{B}(\mathbf{T}, r_c)$,
   (b) they form a dual family to the pseudo wave functions $(\widetilde{\phi}_k^I)_{1\leq k\leq N_I}$: $\left\langle \tilde{p}_k^I \,, \widetilde{\phi}_{k'}^I \right\rangle = \delta_{kk'}$.

By our choice of the pseudo wave functions $\widetilde{\phi}_k^I$ and the projectors $\tilde{p}_k^I$, T_I acts in $\bigcup_{\mathbf{T}\in\mathcal{R}} \overline{B}(\mathbf{R}_I + \mathbf{T}, r_c)$. Since the atomic Hamiltonian (2.1.4) is spherically symmetric, the PAW functions can be written as a product of radial function and a spherical harmonic. Examples of the radial parts is plotted in Figure 2.1.2.

The VPAW equations to solve are then:

$$\widetilde{H}\widetilde{\psi} = E\widetilde{S}\widetilde{\psi}, \tag{2.1.5}$$

where

$$\widetilde{H} = (\mathrm{Id} + T)^* H (\mathrm{Id} + T), \quad \widetilde{S} = (\mathrm{Id} + T)^* (\mathrm{Id} + T), \tag{2.1.6}$$

and

$$T = \sum_{I=1}^{N_{\text{at}}} T_I.$$

Thus if $(\mathrm{Id} + T)$ is invertible, it is easy to recover the eigenfunctions of H by the formula

$$\psi = (\mathrm{Id} + T)\widetilde{\psi}, \tag{2.1.7}$$

and the eigenvalues of H coincide with the generalized eigenvalues of (2.1.5).

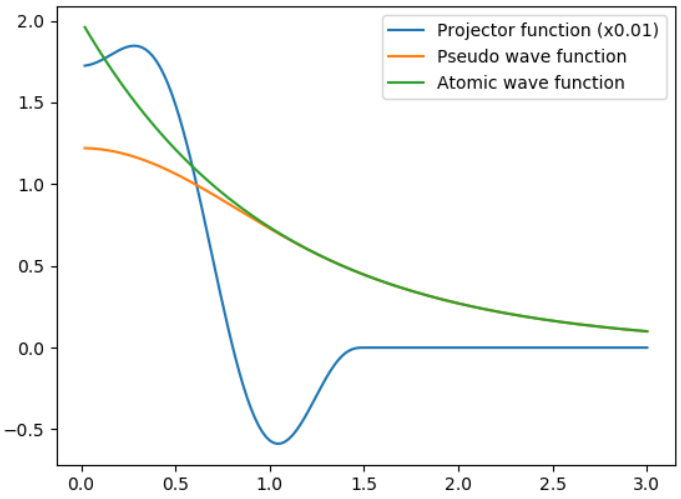


Figure 2.1.2 – Plot of the radial part of some PAW functions for $r_c = 1.5$.

By construction, the operator $(\mathrm{Id} + T_I)$ maps the pseudo wave functions $\tilde{\phi}$ to the atomic eigenfunctions ϕ:

$$(\mathrm{Id} + T_I)\tilde{\phi}_k^I(\cdot - \mathbf{R}_I) = \phi_k^I(\cdot - \mathbf{R}_I),$$

so if locally around each nucleus, the function ψ "behaves" like the atomic wave functions ϕ_k, we can expect that the cusp behavior of ψ is captured by the operator T, thus $\widetilde{\psi}$ is smoother than ψ and the plane-wave expansion of $\widetilde{\psi}$ converges faster than the expansion of ψ.

Remark 2.1. *The VPAW method, compared to the PAW method presented in Chapter 1, is* exact, *in the sense that no approximation is needed to get the VPAW equation* (2.1.5).

Since no pseudopotential is used to replace the Coulomb potentials, the discretized eigenfunction $\widetilde{\psi}$ may have cusps at the positions of the nuclei. However, the analysis of the VPAW method for a one-dimensional toy model and 3D linear Hamiltonian shows that the cusp is reduced significantly. Hence, the eigenvalues are accurately computed using small plane-wave cut-offs.

2.1.3 Computational complexity

A detailed analysis of the computational cost of the PAW method can be found in [LT15]: the cost scales like $\mathcal{O}(NM + M \log M)$ where $N = \sum_I N_I$ is the total number of projectors and M the number of plane-waves. Usually, N is chosen relatively small, but M may be large, so it is important to avoid a computational cost of order M^2.

In practice, we are interested in the cost of the computation of $\widetilde{H}\widetilde{\psi}$ and $\widetilde{S}\widetilde{\psi}$ where $\widetilde{\psi}$ is expanded in M plane-waves as the generalized eigenvalue problem is solved by a conjugate gradient algorithm. We will only focus on $\widetilde{H}\widetilde{\psi}$ since the analysis $\widetilde{S}\widetilde{\psi}$ is similar. Let us split $\widetilde{H}$ into four terms:

$$\widetilde{H}\widetilde{\psi} = H\widetilde{\psi} + PD_H P^T\widetilde{\psi} + H\left(\Phi - \widetilde{\Phi}\right)P^T\widetilde{\psi} + PH\left(\Phi - \widetilde{\Phi}\right)^T\widetilde{\psi},$$

where P is the $M \times N$ matrix of the projector functions, $H(\Phi - \widetilde{\Phi})$ the $M \times N$ matrix of the Fourier representation of the N functions $H(\phi_i - \widetilde{\phi}_i)$, and D_H is the $N \times N$ matrix $\left\langle \phi_i - \widetilde{\phi}_i \, , H(\phi_j - \widetilde{\phi}_j) \right\rangle$.

The computational cost can be estimated as follows (the cost at each step is given in brackets):

1. $H\widetilde{\psi}$ is assembled in two steps. First, $-\frac{1}{2}\Delta\widetilde{\psi}$ is computed in $\mathcal{O}(M)$ since the operator $\frac{1}{2}\Delta$ is diagonal in Fourier representation. For the potential V, apply an inverse FFT to $\widetilde{\psi}$ to have the real space representation of $\widetilde{\psi}$, multiply pointwise by V and apply a FFT to the whole result ($\mathcal{O}(M \log M)$);
2. for $PD_HP^T\widetilde{\psi}$, compute the N projections $P^T\widetilde{\psi}$ ($\mathcal{O}(MN)$), then successively apply the matrices D_H ($\mathcal{O}(N^2)$) and P ($\mathcal{O}(MN)$);
3. for $PH(\Phi-\widetilde{\Phi})^T\widetilde{\psi}$, similarly apply successively $H(\Phi-\widetilde{\Phi})^T$ to $\widetilde{\psi}$ ($\mathcal{O}(MN)$) and P to $H(\Phi-\widetilde{\Phi})^T\widetilde{\psi}$ ($\mathcal{O}(MN)$);
4. for $H(\Phi - \widetilde{\Phi})P^T\widetilde{\psi}$, we proceed as in step 3.

Thus, the total numerical cost is of order $\mathcal{O}(MN + M \log M)$ which is the same as for the PAW method.

The matrix $H(\Phi - \widetilde{\Phi})$ is approximated by a plane-wave expansion, which may be a poor approximation because of the singularities of Φ. However, it should be noticed that this is only an intermediary in the computation of $\tilde{\psi}$, which is well approximated by plane-waves. Hence it is not clear that a poor approximation of $H(\Phi - \widetilde{\Phi})$ should imply a poor approximation of $\tilde{\psi}$. Numerical tests seem to confirm this statement (see Sections 3.5 and 5.4).

2.2 Analysis in a one-dimensional setting

2.2.1 The one-dimensional model

The 1-D periodic Schrödinger operator selected to study the efficiency of the VPAW method is the following operator H acting on $L^2_{\text{per}}(0,1) := \{\phi \in L^2_{\text{loc}}(\mathbb{R}) \mid \phi \text{ 1-periodic}\}$ with form domain $H^1_{\text{per}}(0,1) := \{\phi \in L^2_{\text{per}}(\mathbb{R}) \mid \phi' \in L^2_{\text{loc}}(\mathbb{R})\}$:

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k - Z_a \sum_{k\in\mathbb{Z}} \delta_{k+a}, \tag{2.2.1}$$

where $0 < a < 1$, $Z_0, Z_a > 0$. A mathematical analysis of this model has been carried out in [CD17] where it is shown that the spectrum of H is purely discrete. The eigenfunctions of H have cusps at the location of the Dirac potentials that are reminiscent of the Kato cusp condition:

$$[\psi']_0 := \psi'(0_+) - \psi'(0_-) = -Z_0\psi(0).$$

There are two negative eigenvalues $E_0 = -\omega_0^2$ and $E_1 = -\omega_1^2$ which are given by the zeros of the function

$$f(\omega) = 2\omega^2(1 - \cosh(\omega)) + (Z_0 + Z_a)\omega \sinh(\omega) - Z_0Z_a \sinh(a\omega)\sinh((1-a)\omega).$$

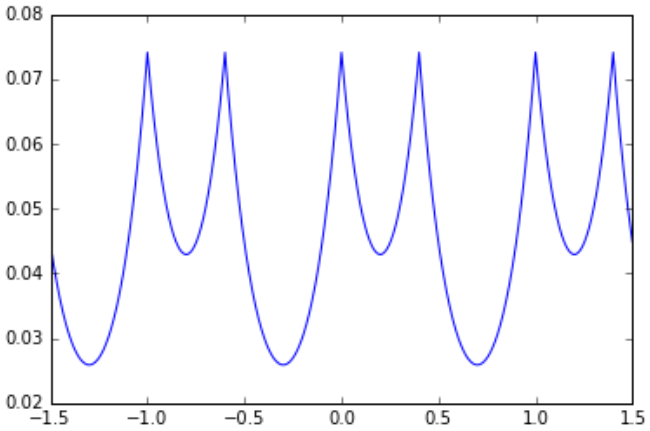


Figure 2.2.1 – Ground-state of the one-dimensional operator H defined in (2.2.1) for $Z_0 = Z_a = 10$

The corresponding eigenfunctions are

$$\psi_k(x) = \begin{cases} A_{1,k}\cosh(\omega_k x) + B_{1,k}\sinh(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cosh(\omega_k x) + B_{2,k}\sinh(\omega_k x)\ , & a \le x \le 1, \end{cases}$$

where the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a.

There is infinitely many positive eigenvalues $E_{k+2} = \omega_{k+2}^2$ which are given by the k-th zero of the function:

$$f(\omega) = 2\omega^2(1-\cos(\omega)) + (Z_0+Z_a)\omega\sin(\omega) + Z_0 Z_a \sin(a\omega)\sin((1-a)\omega),$$

and the corresponding eigenfunctions $H\psi_k = \omega_k^2\psi_k$ are

$$\psi_k(x) = \begin{cases} A_{1,k}\cos(\omega_k x) + B_{1,k}\sin(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cos(\omega_k x) + B_{2,k}\sin(\omega_k x)\ , & a \le x \le 1, \end{cases}$$

where again the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a.

2.2.2 Acceleration of convergence for the VPAW method

To transpose the VPAW method, an invertible operator $(\mathrm{Id}+T)$ is applied to the original eigenvalue problem

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T)\widetilde{\psi} = E(\mathrm{Id}+T^*)(\mathrm{Id}+T)\widetilde{\psi}, \tag{2.2.2}$$

where $T = T_0 + T_a$ and

$$T_0 = \sum_{i=1}^{N}(\phi_i - \tilde{\phi}_i)\left\langle \tilde{p}_i\,,\cdot\right\rangle, \qquad T_a = \sum_{i=1}^{N}(\phi_i^a - \tilde{\phi}_i^a)\left\langle \tilde{p}_i^a\,,\cdot\right\rangle,$$

where T_0 (respectively T_a) acts in $\bigcup_{k\in\mathbb{Z}}[-r_c+k, r_c+k]$ (resp. T_a acts in $\bigcup_{k\in\mathbb{Z}}[a-r_c+k, a+r_c+k]$)

For T_0, the PAW functions are defined by

1. the atomic wave functions $(\phi_k)_{1\le k\le N}$ are the even and nonsmooth solutions of the atomic operator
$$H_0 = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k$$
2. the pseudo wave functions $(\widetilde{\phi}_k)_{1\le k\le N}$ are the one-periodic functions satisfying
   — for $|x| \le r_c$, $\widetilde{\phi}_k$ is an even polynomial,
   — for $x \notin \bigcup_{k\in\mathbb{Z}}[-r_c+k, r_c+k]$, $\widetilde{\phi}_k(x) = \phi_k(x)$ and matches ϕ_k and its derivatives up to the $d-1$ order at r_c.
3. the projector functions are obtained by orthogonalizing the pseudo-wave functions $(\widetilde{\phi}_k)_{1\le k\le N}$ on the interval $[-r_c, r_c]$ against a nonnegative cut-off function ρ supported in $\bigcup_{k\in\mathbb{Z}}[-r_c+k, r_c+k]$.

The detailed definition of these functions can be found in Chapter 3. Examples of PAW functions are plotted in Figure 2.2.2. Notice that plots in Figure 2.1.2 and Figure 2.2.2 are very similar. In this regard, the analysis of the VPAW method in this one-dimensional setting as a preliminary step for a three-dimensional study seems relevant.

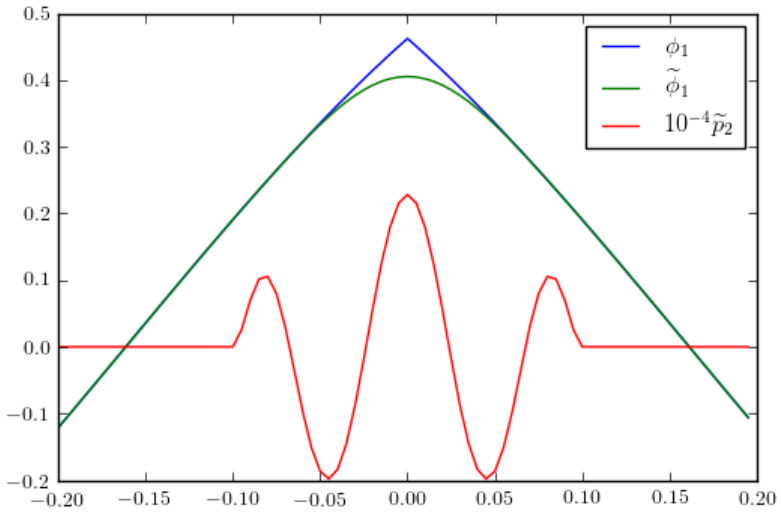


Figure 2.2.2 – Some PAW functions for the one-dimensional toy model ($Z_0 = 10$, $a = 0.4$, $r_c = 0.1$)

We are going to use the following assumptions.

Assumption 2.1. *1. The cut-off radius r_c is smaller than some $r_{\min} > 0$;*

2. The matrix $(\langle \widetilde{p}_k\,, \phi_\ell\rangle)_{1\le k,\ell\le N}$ is invertible for all $0 < r_c \le r_{\min}$.

Under Assumption 2.1, a simple argument proves that the VPAW method gives a well-posed problem, *i.e.* $(\mathrm{Id} + T)$ is invertible and the projector functions $(\widetilde{p}_k)_{1\le k\le N}$ are well-defined.

Cusp reduction and acceleration of convergence

The Fourier convergence of the eigenvalues is driven by the singularities of the pseudo-wave function $\widetilde{\psi}$, hence we need to study the cusp reduction of the pseudo-wave function $\widetilde{\psi}$.

From the invertibility of the operator $(\mathrm{Id}+T)$ and the duality of the families $(\widetilde{\phi}_j)_{1\leq j\leq N}$ and $(\widetilde{p}_k)_{1\leq k\leq N}$, we can show (see Lemma 3.11 in Chapter 3) that for any $(c_k)_{1\leq k\leq N}$, the cusp of the pseudo wave function $\widetilde{\psi}$ is given by

$$[\widetilde{\psi}']_0 = -Z_0\left(\psi(0) - \sum_{k=1}^{N} c_k\phi_k(0) - A^{-1}\langle\widetilde{p}, \psi - \sum_{k=1}^{N} c_k\phi_k\rangle\cdot\Phi(0)\right) \tag{2.2.3}$$

where $\widetilde{p} = (\widetilde{p}_1,\ldots,\widetilde{p}_N)^T$, $\Phi = (\phi_1,\ldots,\phi_N)^T$ and A the $N\times N$ matrix of coefficients $A_{jk} = \left\langle \widetilde{p}_j\,,\widetilde{\phi}_k\right\rangle$.

Since this holds for *any* set of coefficients $(c_k)_{1\leq k\leq N}$, the best approximation of ψ by a linear combination of ϕ_k on the interval $[-r_c,r_c]$ gives the order of the cusp reduction. As the atomic functions ϕ_k and the molecular wave function ψ behave similarly near a Dirac potential, the best approximation of ψ by ϕ_k should be very good. For this particular model, we are able to show there exists $(c_k)_{1\leq k\leq N}\in\mathbb{R}^N$ and a constant C independent of r_c such that the best approximation of the even part ψ_e of ψ satisfies

$$\left\|\psi_e - \sum_{k=1}^{N} c_k\phi_k\right\|_{L^\infty(-r_c,r_c)} \leq C{r_c}^{2N}. \tag{2.2.4}$$

The matrix A also depends on the cut-off radius r_c and becomes more and more ill-conditioned as r_c goes to 0. The previous estimate does not necessarily guarantee a cusp reduction of order ${r_c}^{2N}$. Using the behavior of the atomic wave function near a Dirac potential, we can show that there exists a constant C independent of r_c such that for any $f\in L^\infty(-r_c,r_c)$, $|A^{-1}\langle\widetilde{p},f\rangle\cdot\Phi(0)|\leq C\|f\|_{L^\infty(-r_c,r_c)}$ (see Lemmas 3.13 and 3.14). Hence, using (2.2.3) and (2.2.4), the cusp of the VPAW eigenfunction $\widetilde{\psi}$ is reduced by a factor ${r_c}^{2N}$, *i.e.* there exists a constant C independent of r_c such that

$$\left|[\widetilde{\psi}']_0\right| \leq C{r_c}^{2N}.$$

The cusp reduction comes at the expense of a d-th derivative blow-up where the pseudo atomic wave function $\widetilde{\phi}_i$ matches ϕ_i. This blow-up can be estimated and we can show that there exists a positive constant C independent of r_c such that

$$\left|[\widetilde{\psi}^{(d)}]_{r_c}\right| \leq \frac{C}{{r_c}^{d-1}}.$$

This estimate mostly stems from the fact that the pseudo wave functions $(\widetilde{\phi}_i)_{1\leq i\leq N}$ can be rewritten as even polynomials of the form $P(\frac{\cdot}{r_c})$, hence differentiating d times a factor $\frac{1}{{r_c}^d}$ comes. By a careful analysis, it is possible to save a factor r_c in full agreement with the numerical tests (see Chapter 3).

Using classical estimates on variational approximation of eigenvalue problems [Wei74], the following bounds are obtained on the convergence of the VPAW method.

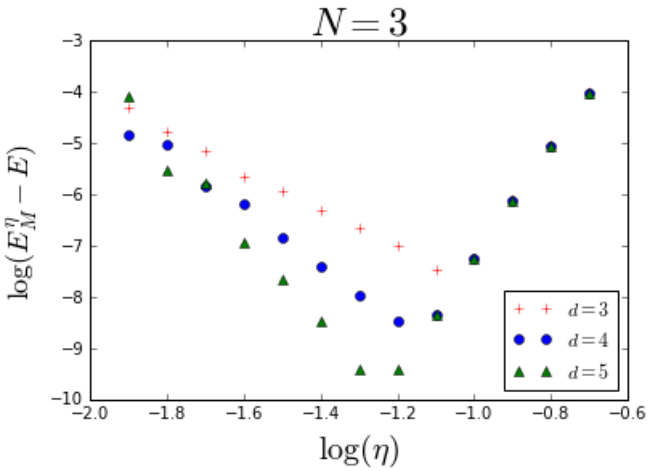


Figure 2.2.3 – VPAW error $E_M^\eta - E$

Theorem 2.2 (Estimates on the eigenvalues)**.** *Let $N \in \mathbb{N}^*$ be the number of PAW functions of smoothness $d \geq N$ used at each nucleus. Let $E_M^{r_c}$ be an eigenvalue of the variational approximation of (2.2.2) in a basis of M plane-waves and for a cut-off radius $0 < r_c \leq r_{\min}$ ($r_{\min}$ given by Assumption 2.1). Let E be the corresponding exact eigenvalue of (2.2.1). Under Assumption 2.1, there exists a constant $C > 0$ independent of r_c and M such that for all $0 < r_c \leq r_{\min}$ and $M \geq \frac{1}{r_c}$*

$$0 < E_M^{r_c} - E \leq C \left({r_c}^{4N} + \frac{1}{{r_c}^{2d-2}} \frac{1}{M^{2d-1}} \right). \tag{2.2.5}$$

Since the cusp is only reduced and not completely erased, for large M the VPAW method does not converge faster than the direct method applied to the original eigenvalue problem. However, in a pre-asymptotic regime, for small values of the cut-off radius r_c and/or large N, the prefactor ${r_c}^{4N}$ can be made small. For low values of the cut-off radius r_c, the prefactor ${r_c}^{2-2d}$ of the second term which become dominant in the eigenvalue error. Thus a natural strategy consists in balancing both errors.

Numerical tests show that the estimate (2.2.5) is optimal (see Section 3.5). Plots on the dependence on the cut-off radius (see Figure 2.2.3 and other examples in Section 3.5) suggest that a numerical study of the dependence on the other PAW parameters N, d of the prefactor in the estimate (2.2.5) is possible. Intercepts of the lines appearing in Figure 2.2.3 can be computed. It would be interesting to investigate the sensitivity of the prefactor with respect to the choice of these other PAW parameters.

2.2.3 Analysis of the PAW method

An analysis of the truncation error induced by the PAW method (*i.e.* before the plane-wave discretization) has been carried out for the lowest eigenvalue of the one-dimensional Schrödinger operator (2.2.1). This error is estimated for both PAW methods with and without pseudopotentials. Full proofs of the upcoming results are regrouped in Chapter 4.

PAW method without pseudopotentials

The eigenvalue problem for the PAW method without pseudopotential is

$$H^N f = E^{(r_c)} S^N f, \tag{2.2.6}$$

where the operators H^N and S^N are given by

$$H^N = H + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, H\widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{2.2.7}$$

and

$$S^N = \mathrm{Id} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, \phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle. \tag{2.2.8}$$

The PAW functions $(\phi_i)_{1\leq i\leq N}$, $(\widetilde{\phi}_i)_{1\leq i\leq N}$ and $(\widetilde{p}_i)_{1\leq i\leq N}$ are the same as for the VPAW method.

Theorem 2.3. *Let $N \in \mathbb{N}^*$ be the number of PAW functions used at each nucleus. Let $E^{(r_c)}$ be the lowest eigenvalue of the generalized eigenvalue problem (2.2.6). Let E_0 be the lowest eigenvalue of H (2.2.1). Under Assumption 2.1, there exists a positive constant C independent of r_c such that for all $0 < r_c \leq r_{\min}$*

$$-Cr_c \leq E^{(r_c)} - E_0 \leq C{r_c}^{2N}. \tag{2.2.9}$$

The bounds (2.2.9) on the PAW error are proved by noticing that the PAW eigenvalue problem (2.2.6) can be written as a perturbation of the VPAW eigenvalue problem (2.2.2), which has the same eigenvalues as the original problem. The good upper bound is a consequence of the good approximation (2.2.4) of the eigenfunction ψ of the one-dimensional Schrödinger operator H by N atomic wave functions $(\phi_k)_{1\leq k\leq N}$.

As N goes to ∞, the PAW and VPAW methods yield the same equations. Hence $E^{(r_c)}$ should converge to E_0, which is not obvious from (2.2.9). However the prefactor appearing in (2.2.9) depends on N and we expect this prefactor to go to 0 as N goes to ∞. The dependence on this parameter has however not been tracked in the proof of Theorem 2.3.

Since the Dirac potentials are not removed in the PAW eigenvalue problem (2.2.6), Fourier methods are expected to converge slowly, which makes this problem of little interest in practice.

PAW method with pseudopotentials

Introducing a smooth pseudopotential in the PAW eigenvalue problem is essential to solve the eigenvalue problem efficiently. In this one-dimensional setting, the Dirac potentials are replaced by a smooth 1-periodic potential $\chi_\epsilon = \sum_{k\in\mathbb{Z}} \frac{1}{\epsilon}\chi\left(\frac{\cdot - k}{\epsilon}\right)$ with $\epsilon \leq r_c$, such that

1. χ is a smooth nonnegative function with support $[-1,1]$ and $\int_{-1}^{1} \chi(x)\,\mathrm{d}x = 1$;
2. $\chi_\epsilon \underset{\epsilon\to 0}{\longrightarrow} \sum_{k\in\mathbb{Z}} \delta_k$ in $H^{-1}_{\mathrm{per}}(0,1)$.

The PAW eigenvalue problem becomes

$$H^{PAW} f = E^{PAW}_{(r_c)} S^{PAW} f, \tag{2.2.10}$$

where

$$H^{PAW} = H_{\text{ps}} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \, , H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \, , H_{\text{ps}} \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \, , \cdot \right\rangle , \tag{2.2.11}$$

with $H_{\text{ps}} = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \chi_\epsilon - Z_a \chi_\epsilon(\cdot - a)$ and

$$S^{PAW} = S^N = \mathrm{Id} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \, , \phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \, , \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \, , \cdot \right\rangle . \tag{2.2.12}$$

Using the same PAW functions as for the VPAW method, the following estimates can be proved on the lowest eigenvalue of (2.2.10).

Theorem 2.4. *Let $N \in \mathbb{N}^*$ be the number of PAW functions used at each nucleus. Let $E^{PAW}_{(r_c)}$ be the lowest eigenvalue of the generalized eigenvalue problem (2.2.10). Let E_0 be the lowest eigenvalue of H (2.2.1). Under Assumption 2.1, there exists a positive constant C independent of r_c such that for all $0 < r_c \leq r_{\min}$*

$$-C{r_c}^2 \leq E^{PAW}_{(r_c)} - E_0 \leq C{r_c}^2. \tag{2.2.13}$$

The PAW error estimates are again proved by considering the PAW method with pseudopotentials as a perturbation of the VPAW method. However, because of the introduction of pseudopotentials, the good upper bound in (2.2.9) of the PAW method without pseudopotentials is lost. This is due to the fact that the best approximation estimate (2.2.4) holds only for the *even* part of the molecular wave function ψ and that for a smooth odd function g, $\int_{-r_c}^{r_c} \chi_{r_c}(x)|g(x)|^2 \, \mathrm{d}x = \mathcal{O}({r_c}^2)$. By introducing odd PAW functions, the good upper bound of Theorem 2.3 can be recovered.

Theorem 2.5. *Let $N \in \mathbb{N}^*$ be the number of even and odd PAW functions used at each nucleus. Let $E^{PAW}_{(r_c)}$ be the lowest eigenvalue of the generalized eigenvalue problem (2.2.10). Let E_0 be the lowest eigenvalue of H (2.2.1). Under Assumption 2.1, there exists a positive constant C independent of r_c such that for all $0 < r_c \leq r_{\min}$*

$$-C{r_c} \leq E^{PAW}_{(r_c)} - E_0 \leq C{r_c}^{2N}.$$

Since the eigenfunctions of (2.2.10) are smooth, Fourier methods converge fast to the PAW eigenvalue. More precisely, the following bound can be proved.

Theorem 2.6. *Let $N \in \mathbb{N}^*$ be the number of PAW functions used at each nucleus. Let E^{PAW}_M be the lowest eigenvalue of the variational approximation of (2.2.10), with H^{PAW} given by (2.2.11) in a basis of M plane waves. Let E_0 be the lowest eigenvalue of H (2.2.1). There exists a positive constant C independent of r_c and M such that for all $0 < r_c < r_{\min}$ and for all $n \in \mathbb{N}^*$*

$$\left| E^{PAW}_M - E_0 \right| \leq C \left(r_c + \frac{{r_c}^2}{(r_c M)^n} \right).$$

To compute the lowest eigenvalue of the one-dimensional Schrödinger operator H (2.2.1) up to a tolerance ε, the cut-off radius should be set at $r_c = \frac{\varepsilon}{C}$ and the generalized eigenvalue problem (2.2.10) should be solved using $M = \lceil \frac{1}{r_c} \rceil$ plane-waves.

The prefactor appearing in Theorems 2.3 to 2.6 depends on the other PAW parameters N and d. It would be interesting to investigate numerically the sensitivity to these parameters.

2.3 Analysis of the VPAW method for 3D Hamiltonians

An analysis of the VPAW method for the plane-wave discretization of the 3D eigenvalue problem (2.1.2) has been achieved and can be found in Chapter 5. In the VPAW method, the eigenvalue problem $H\psi = E\psi$ is replaced by:

$$(\mathrm{Id} + T)^* H (\mathrm{Id} + T)\widetilde{\psi} = E(\mathrm{Id} + T)^*(\mathrm{Id} + T)\widetilde{\psi}. \tag{2.3.1}$$

The construction of the operator T has already been explained in Section 2.1.2. The atomic wave function $(\phi_k^I)_{1\leq k\leq N_I}$ are the eigenfunctions of the atomic Hamiltonian (2.1.4). When W is a smooth bounded function (this requirement can be weakened see Theorem XIII.8 in [RS78] or [Sol91]), the eigenfunctions $(\phi_k^I)_{1\leq k\leq N_I}$ can be written for some $\ell \in \mathbb{N}, |m| \leq \ell, n \in \mathbb{N}$:

$$\phi_k^I(\mathbf{r}) = r^\ell R_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}).$$

Since the definition of the pseudo-wave function $(\phi_k^I)_{1\leq k\leq N_I}$ depends on the form of the atomic wave functions, these can also be written in that form. This also applies to the projector functions $(\widetilde{p}_k)_{1\leq k\leq N_I}$. Hence the PAW functions can be written

$$\phi_k^I(\mathbf{r}) = r^\ell R_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}), \quad \widetilde{\phi}_k^I(\mathbf{r}) = r^\ell \widetilde{R}_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}),$$
$$p_k^I(\mathbf{r}) = r^\ell p_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}).$$

The PAW functions are chosen from a range $(0, \ldots, \ell_{\max})$ of angular momentum and for each angular momentum ℓ, n_ℓ PAW functions are defined. The total number of PAW functions is then $N_I = \sum_{\ell=0}^{\ell_{\max}} (2\ell+1) n_\ell$.

Because the PAW functions have some radial symmetry, conditions for the well-posedness of the VPAW method are very similar to the one-dimensional case.

Assumption 2.2. *1. (Existence of the projector functions $(\widetilde{p}_k)_{1\leq k\leq N_I}$) For all $0 < r_c < r_{\min}$ and each $0 \leq \ell \leq \ell_{\max}$, $(\mathcal{R}^{(k)}(r_c))_{0\leq k\leq n_\ell - 1}$ is a linearly independent family, where $\mathcal{R}$ is the vector of the functions $(R_{1\ell}, \ldots, R_{n_\ell \ell})$.*

2. (Invertibility of $\mathrm{Id}+T$) For all $0 < r_c < r_{\min}$ and any $0 \leq \ell \leq \ell_{\max}$, the matrix $(\langle p_{n\ell}\,, R_{n'\ell}\rangle)_{1\leq n,n'\leq n_\ell}$ is invertible.

The plane-wave convergence rate of the computed eigenvalues depends on the singularities of the associated eigenfunction. The proper way to characterize their singularities is through weighted Sobolev spaces [ES12].

2.3.1 Weighted Sobolev space

We denote by $\mathcal{S}$ the set of the position of the nuclei

$$\mathcal{S} = \{\mathbf{R}_I + \mathbf{T},\ I = 1, \dots, N_{\text{at}},\ \mathbf{T} \in \mathcal{R}\}.$$

Let χ be a $\mathcal{R}$-periodic continuous function such that $\chi(\mathbf{R}_I + \mathbf{r}) = r$ for small r, $\chi \in C^\infty_{\text{loc}}(\mathbb{R}^3 \setminus \mathcal{S})$.

Definition 2.7 ([ES12])**.** *Let $k \in \mathbb{N}$ and $\gamma \in \mathbb{R}$. We define the k-th weighted Sobolev space with index γ by:*

$$\mathcal{K}^{k,\gamma}(\Gamma) = \left\{u \in L^2_{\text{per}}(\Gamma) : \chi^{|\alpha|-\gamma}\partial^\alpha u \in L^2_{\text{per}}(\Gamma)\ \forall\ |\alpha| \le k\right\}. \tag{2.3.2}$$

Consider a subspace of functions with the asymptotic expansions

$$u(\mathbf{R}_I + \mathbf{r}) \sim \sum_{j\in\mathbb{N}} c_j(\hat{\mathbf{r}})r^j \text{ as } r \to 0, \quad I \in [\![1, N_{\text{at}}]\!] \tag{2.3.3}$$

where c_j belongs to the finite dimensional subspace $M_j = \text{span}\{Y_{\ell m}, 0 \le \ell \le j, |m| \le \ell\}$.

Definition 2.8. *For $k \in \mathbb{N}$, $\gamma \in \mathbb{R}$, we define the weighted Sobolev spaces with asymptotic type (2.3.3):*

$$\mathscr{K}^{k,\gamma}(\Gamma) = \left\{ u \in \mathcal{K}^{k,\gamma}(\Gamma) \,\middle|\, \eta_N \in \mathcal{K}^{k,\gamma+N+1}(\Gamma) \text{ where } \eta_N \text{ is the } \Gamma\text{-periodic function defined in } \Gamma \text{ by} \right.$$
$$\left. \forall N \in \mathbb{N},\ \forall \mathbf{r} \in \Gamma,\ \eta_N(\mathbf{r}) = u(\mathbf{r}) - \sum_{I=1}^{N_{\text{at}}} \omega(|r - \mathbf{R}_I|) \sum_{j=0}^{N} c_j(\widehat{\mathbf{r} - \mathbf{R}_I})|\mathbf{r} - \mathbf{R}_I|^j \right\}, \tag{2.3.4}$$

where ω is a smooth positive cutoff function, i.e. *$\omega = 1$ near 0 and $\omega = 0$ outside some neighbourhood of 0.*

The expansion (2.3.3) can be viewed as a "regularity expansion". Let us suppose that the functions c_j in the singular expansion are constant. Then all the even terms appearing in (2.3.4) are smooth since for any $k \in \mathbb{N}$, $r \mapsto r^{2k}$ is smooth. For the odd terms in the expansion, the function $r \mapsto r$ is continuous but not differentiable at the origin, the function $r \mapsto r^3$ is C^2 but not C^3 and so on. Since the decay of the Fourier coefficients depends on the regularity of the function, this expansion enables one to characterize precisely this decay.

Definition 2.9. *A function u is asymptotically well-behaved if $u \in \mathscr{K}^{\infty,\gamma}(\Gamma)$ for $\gamma < 3/2$.*

Remark 2.10. *It is easy to see that if u is asymptotically well-behaved then by the definition of the weighted Sobolev space with asymptotic type (2.3.3), the remainder $\eta(\mathbf{r}) = u(\mathbf{r}) - \omega(r)\sum_{j=0}^{N} c_j(\hat{\mathbf{r}})r^j$ is in the classical Sobolev space $H^{5/2+N-\varepsilon}_{\text{per}}(\Gamma)$.*

The following result, stated in [HNS08, CS15] (see also [FSS08] for similar results for Hartree-Fock models), gives the regularity of the eigenfunction of (2.1.2) in terms of the previously defined weighted Sobolev space.

Theorem 2.11. *Let ψ be an eigenfunction of $H\psi = E\psi$ where H is defined in (2.1.2). Then ψ is asymptotically well-behaved.*

Theorem 2.11 enables to characterize precisely the singularity of the Hamiltonian wave function and generalizes the Kato cusp condition for eigenfunctions of 3D-Hamiltonians (see Theorem 5.5 in Chapter 5).

2.3.2 Acceleration of convergence

From Definition 2.8 and the asymptotic expansion of the molecular wave function ψ, it is possible to identify the origin of the slow decay of the Fourier coefficients of ψ, which is the cusps at each nucleus. Similarly to the study in the one-dimensional model, we can show that the cusp of the pseudo wave function $\widetilde{\psi}$ is significantly reduced. More precisely, if n_0 PAW functions associated to the angular momentum $\ell = m = 0$ are used, then there is a constant C independent of r_c such that for any $0 < r_c \leq r_{\min}$ and for all $\varepsilon > 0$:

$$\left| \frac{\partial}{\partial r}\bigg|_{r=0} \int_{S(0,1)} \widetilde{\psi}(\mathbf{r})\, \mathrm{d}\hat{\mathbf{r}} \right| \leq C {r_c}^{\min(2n_0,5)-\varepsilon}.$$

The reduction factor is less impressive than in the one-dimensional case because the structure of the singularity is not as simple.

The blow-up of the d-th derivative is controlled similarly. It is possible to show that there exists a constant C independent of r_c such that for any $0 < r_c \leq r_{\min}$ and for all $\varepsilon > 0$:

$$\left| \left[\int_{S(0,1)} \widetilde{\psi}^{(d)}(\mathbf{r})\, \mathrm{d}\hat{\mathbf{r}} \right]_{r_c} \right| \leq \frac{C}{{r_c}^{d-1}}.$$

From both estimates, the following plane-wave convergence for the computation of the eigenvalues with the VPAW method can be proved.

Theorem 2.12. *Let E_M be an eigenvalue of the variational approximation of (2.1.6) in a plane-wave basis with wavenumber $|\mathbf{K}| \leq M$, with n_0 PAW functions associated to the angular momentum $\ell = 0, m = 0$ with smoothness $d \geq n_0$ and cut-off radius r_c. Let E be the corresponding exact eigenvalue. Under Assumption 2.2, there exists a constant $C > 0$ independent of r_c and M such that for all $\varepsilon > 0$, and for all $\frac{1}{M} < r_c < r_{\min}$*

$$0 < E_M - E \leq C \left(\frac{{r_c}^{2\min(2n_0,5)-2\varepsilon}}{M^3} + \frac{{r_c}^{\min(2n_0,5)-\varepsilon}}{M^{4-\varepsilon}} + \frac{1}{{r_c}^{2d-2}} \frac{1}{M^{2d-1}} + o\left(\frac{1}{M^{5-\varepsilon}} \right) \right). \tag{2.3.5}$$

The VPAW method does not erase the cusps appearing in the molecular wave function ψ, hence in the asymptotic regime, the plane-wave convergence rate is the same as the brute force discretization of the original eigenvalue problem. The prefactor ${r_c}^{2\min(2n_0,5)-2\varepsilon}$ can be made small by taking r_c small, however, if it is too small, the second prefactor $\frac{1}{{r_c}^{2d-2}}$ can become dominant in the eigenvalue error. Balancing both error terms gives an optimal cut-off radius equal to $r_{\text{opt}} = \frac{1}{M^{\frac{2d-4}{4n_0+2d-2}}}$. For $n_0 = 2$ and $d = 6$ (which are typical for PAW simulations) and $r_c = r_{\text{opt}}$,

both error terms behave like $\frac{1}{M^{41/9}}$. This is much better than the convergence of the brute force discretization which is of order $\frac{1}{M^3}$.

As for the one-dimensional toy model in Section 2.2.2, the prefactor in (2.3.5) depends on the other VPAW parameters n_0 and d.

It is interesting to compare the VPAW method convergence with other full-potential approaches like the APW method.

In [CS15], a nonforming method for the resolution of the eigenvalue problem (2.1.2) close to the APW method is analyzed. The basis functions for this method are given by

$$\omega_{\mathbf{K}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{in } \Gamma \setminus \bigcup_{I=1,\dots,N_{\text{at}}} B(\mathbf{R}_I, r_c) \\ \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} \sum_{n=0}^{N} c_{n\ell m} \chi_n(|\mathbf{r}-\mathbf{R}_I|) Y_{\ell m}(\widehat{\mathbf{r}-\mathbf{R}_I}) & \text{in each } B(\mathbf{R}_I, r_c), \end{cases}$$

with $|\mathbf{K}| \leq M$, $(\chi_n)_{0\leq n\leq N}$ a basis of the polynomials of degree at most N.

The authors showed [CS15] that the error on the computed eigenvalues is bounded by

$$\forall s > \frac{3}{2},\ |E_\eta^{\text{APW}} - E| \leq \frac{C_s}{\eta^{s-\frac{3}{2}}},$$

where $\eta = \min(M, \ell_{\max}, N)$.

Although this bound holds for any $s > \frac{3}{2}$, the prefactor depends on s and this dependency is not explicit in the paper. Moreover, in most situations, η is equal to the maximal angular momentum $\ell_{\max}$. Hence, increasing this parameter is more and more costly since it introduces $(2\ell+1)(N+1)$ terms in the nonconforming method basis function. The convergence of the VPAW method is already very good for $n_0 \leq 2$ PAW functions for $\ell = 0$.

CHAPTER 3

THE VPAW METHOD IN A ONE-DIMENSIONAL MODEL

Introduction

In this chapter, mostly based on [BCD17b], we apply the VPAW formalism to the double Dirac potential with periodic boundary conditions in one dimension. The eigenfunctions of this model have a derivative jump at the positions of the Dirac potentials which is similar to the electronic wave function cusp. Furthermore, the eigenvalues and eigenfunctions being known analytically, it is possible to confront our theoretical results to very accurate numerical tests.

In Section 3.1, we carefully present the VPAW method in our framework. In Section 3.2, Fourier decay estimates of the pseudo wave functions are given as well as estimates on the computed eigenvalues. Proofs of these results are gathered in Section 3.3. In Section 3.4, we discuss the effect of the addition of a smooth potential to the double Dirac model. Numerical simulations which confirm the obtained theoretical results are provided in Section 3.5.

Notation

From now on, $\langle \cdot\,, \cdot \rangle$ denotes the usual inner product in $L^2_{\mathrm{per}}(0,1)$.

Let f be a piecewise continuous function. We denote by:

$$[f]_x := f(x_+) - f(x_-),$$

where $f(x_+)$ and $f(x_-)$ are respectively the right-sided and left-sided limits of f at x.

Let f be a continuous function. We denote by

$$\underbrace{\int \cdots \int}_{2j+2} f(x) = \int_0^x \int_0^{t_1} \cdots \int_0^{t_{2j+1}} f(t_{2j+2})\, \mathrm{d}t_{2j+2} \ldots \mathrm{d}t_1$$

the $(2j+2)$-primitive function of f vanishing at 0 as well as its first $(2j+1)$-st derivatives.

For a and b in $\mathbb{R}^N$, $a \cdot b$ is the Euclidean inner product. e_k is the k-th canonical vector of $\mathbb{R}^d$ or $\mathbb{R}^N$. I_N is the identity matrix of size N.

3.1 The VPAW method for a one-dimensional model

3.1.1 The double Dirac potential

We are interested in the lowest eigenvalues of the 1-D periodic Schrödinger operator H on $L^2_{\text{per}}(0,1) := \{\phi \in L^2_{\text{loc}}(\mathbb{R}) \mid \phi \text{ 1-periodic}\}$ with form domain $H^1_{\text{per}}(0,1) := \{\phi \in L^2_{\text{loc}}(\mathbb{R}) \mid \phi' \in L^2_{\text{loc}}(\mathbb{R})\}$:

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k - Z_a \sum_{k\in\mathbb{Z}} \delta_{k+a}, \tag{3.1.1}$$

where $0 < a < 1$, $Z_0, Z_a > 0$.

A mathematical analysis of this model has been carried out in [CD17]. There are two negative eigenvalues $E_0 = -\omega_0^2$ and $E_1 = -\omega_1^2$ which are given by the zeros of the function

$$f(\omega) = 2\omega^2(1-\cosh(\omega)) + (Z_0+Z_a)\omega\sinh(\omega) - Z_0Z_a\sinh(a\omega)\sinh((1-a)\omega).$$

The corresponding eigenfunctions are

$$\psi_k(x) = \begin{cases} A_{1,k}\cosh(\omega_k x) + B_{1,k}\sinh(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cosh(\omega_k x) + B_{2,k}\sinh(\omega_k x)\ , & a \le x \le 1, \end{cases}$$

where the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a.

There is an infinity of positive eigenvalues $E_{k+2} = \omega_{k+2}^2$ which are given by the k-th zero of the function :

$$f(\omega) = 2\omega^2(1-\cos(\omega)) + (Z_0+Z_a)\omega\sin(\omega) + Z_0Z_a\sin(a\omega)\sin((1-a)\omega),$$

and the corresponding eigenfunctions $H\psi_k = \omega_k^2\psi_k$ are

$$\psi_k(x) = \begin{cases} A_{1,k}\cos(\omega_k x) + B_{1,k}\sin(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cos(\omega_k x) + B_{2,k}\sin(\omega_k x)\ , & a \le x \le 1, \end{cases}$$

where again the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a.

3.1.2 The VPAW method

The principle of the VPAW method consists in replacing the original eigenvalue problem

$$H\psi = E\psi,$$

by the generalized eigenvalue problem:

$$(\mathrm{Id}+T)^* H(\mathrm{Id}+T)\tilde{\psi} = E(\mathrm{Id}+T)^*(\mathrm{Id}+T)\tilde{\psi}, \tag{3.1.2}$$

where $\mathrm{Id}+T$ is an invertible bounded linear operator on $L^2_{\mathrm{per}}(0,1)$. Thus both problems have the same eigenvalues and it is straightforward to recover the eigenfunctions of the former from the generalized eigenfunctions of the latter:

$$\psi = (\mathrm{Id}+T)\tilde{\psi}. \tag{3.1.3}$$

T is the sum of two operators acting near the atomic sites

$$T = T_0 + T_a.$$

To define T_0, we fix an integer N and a radius $0 < \eta < \min(\frac{a}{2}, \frac{1-a}{2})$ so that T_0 and T_a act on two disjoint regions $\bigcup_{k\in\mathbb{Z}}[-\eta+k, \eta+k]$ and $\bigcup_{k\in\mathbb{Z}}[a-\eta+k, a+\eta+k]$ respectively.

Atomic wave function ϕ_k Let H_0 be the operator defined by :

$$H_0 = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k.$$

By parity, the eigenfunctions of this operator are even or odd. The odd eigenfunctions are in fact $x \mapsto \sin(2\pi k x)$ and the even ones are the 1-periodic functions such that

$$\begin{cases} \phi_0(x) := \cosh(\omega_0(x-\frac{1}{2})), \text{for } x \in [0,1], \\ \phi_k(x) := \cos(\omega_k(x-\frac{1}{2})), \text{for } x \in [0,1], k \in \mathbb{N}^*. \end{cases}$$

To construct T_0, we will only select the non-smooth thus even eigenfunctions $(\phi_k)_{1\le k\le N}$ and denote by $(\epsilon_k)_{1\le k\le N}$ the corresponding eigenvalue:

$$H_0\phi_k = \epsilon_k\phi_k.$$

Pseudo wave function $\tilde{\phi}_i$ The pseudo wave functions $(\tilde{\phi}_i)_{1\le i\le N} \in \left(H^1_{\mathrm{per}}(0,1)\right)^N$ are defined as follows:

1. for $|x| \notin \bigcup_{k\in\mathbb{Z}}[-\eta+k, \eta+k]$, $\tilde{\phi}_i(x) = \phi_i(x)$.
2. for $|x| \in \bigcup_{k\in\mathbb{Z}}[-\eta+k, \eta+k]$, $\tilde{\phi}_i$ is an even polynomial of degree at most $2d-2$, $d \ge N$.
3. $\tilde{\phi}_i$ is C^{d-1} at η *i.e.* $\tilde{\phi}_i^{(k)}(\eta) = \phi_i^{(k)}(\eta)$ for $0 \le k \le d-1$.

Projector functions $\tilde{p}_i$ Let ρ be a positive, continuous function with support $[-1,1]$ and $\rho_\eta(t) = \sum_{k\in\mathbb{Z}} \rho(\frac{t-k}{\eta})$. The projector functions $(\tilde{p}_i)_{1\le i\le N}$ are obtained by an orthonormalization

procedure from the functions $p_i(t) = \rho_\eta(t)\tilde{\phi}_i(t)$ in order to satisfy the duality condition :

$$\left\langle \tilde{p}_i \, , \tilde{\phi}_j \right\rangle = \delta_{ij}.$$

More precisely, we compute the matrix $B_{ij} := \left\langle p_i \, , \tilde{\phi}_j \right\rangle$ and invert it to obtain the projector functions

$$\tilde{p}_k = \sum_{j=1}^{N} (B^{-1})_{kj} p_j.$$

The matrix B is the Gram matrix of the functions $\tilde{\phi}_j$ for the weight ρ_η. The orthogonalization is possible only if the family $(\tilde{\phi}_i)_{1\leq i\leq N}$ is independent - thus necessarily $d \geq N$.

T_0 and T_a are given by :

$$T_0 = \sum_{i=1}^{N} (\phi_i - \tilde{\phi}_i) \left\langle \tilde{p}_i \, , \cdot \right\rangle , \qquad T_a = \sum_{i=1}^{N} (\phi_i^a - \tilde{\phi}_i^a) \left\langle \tilde{p}_i^a \, , \cdot \right\rangle \ , \tag{3.1.4}$$

where ϕ_i^a are singular eigenfunctions of the operator $H_a = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_a \sum_{k\in\mathbb{Z}} \delta_{a+k}$ and $\tilde{\phi}_i^a$, $\tilde{p}_i^a$ are defined as before.

In the VPAW method, the generalized eigenvalue problem (3.1.2) is solved by expanding $\tilde{\psi}$ in plane-waves.

Remark 3.1. *Here we have followed the Vanderbilt scheme to generate the pseudo wave functions and the projector functions with the difference that the orthogonalized functions p are taken from the Blöchl construction (see Section 1.4.4).*

3.1.3 Well-posedness of the VPAW method

To be well-posed the VPAW method requires

1. the family of pseudo wave functions $(\tilde{\phi}_i)_{1\leq i\leq N}$ to be independent on $[-\eta, \eta]$, so that the projector functions $(\tilde{p}_k)_{1\leq k\leq N}$ are well defined,
2. $(\mathrm{Id} + T)$ to be invertible.

The conditions on the VPAW functions and parameters are given by the following propositions. Proofs can be found in Section 3.3.

Proposition 3.2 (Linear independence of the pseudo wave functions)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. There exists $\eta_0 > 0$ such that for all $0 < \eta \leq \eta_0$, the family $(\tilde{\phi}_i|_{[-\eta,\eta]})_{1\leq i\leq N}$ is linearly independent.*

Proposition 3.3 (Invertibility of $\mathrm{Id} + T$)**.** *The operator $\mathrm{Id} + T$ is invertible in $L^2_{\mathrm{per}}(0,1)$ if and only if the matrix $(\langle \tilde{p}_k \, , \phi_\ell \rangle)_{1\leq k,\ell\leq N}$ is invertible.*

From now on, we will establish our results under the following

Assumption : the matrix $(\langle \tilde{p}_k \, , \phi_\ell \rangle)_{1\leq k,\ell\leq N}$ is invertible for all $0 < \eta \leq \eta_0$.

3.2 Main results

We know from (3.1.3) that

$$\tilde{\psi} = \psi - \sum_{i=1}^{N} (\phi_i - \tilde{\phi}_i) \left\langle \tilde{p}_i \, , \tilde{\psi} \right\rangle - \sum_{i=1}^{N} (\phi_i^a - \tilde{\phi}_i^a) \left\langle \tilde{p}_i^a \, , \tilde{\psi} \right\rangle .$$

In addition, $\tilde{\psi}$ is a piecewise smooth function with first derivative jumps (due to ψ and the atomic wave function ϕ_k) at points of $\mathbb{Z}$, $\mathbb{Z}+a$ and d-th derivative jumps (due to the pseudo wave functions $\tilde{\phi}_k$) at points of $\mathbb{Z} \pm \eta$ and $\mathbb{Z}+a \pm \eta$. These singularities drive the decays of the Fourier coefficients. Thus to study the Fourier convergence rate, it suffices to study the dependency of the different singularities with respect to N -the number of PAW functions used-, d -the smoothness of the pseudo wave functions $\tilde{\phi}_k$- and η -the cut-off radius.

Proposition 3.4 (Derivative jumps at 0)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. Then, there exists a positive constant C independent of η such that for $0 \leq j \leq N-1$*

$$\forall\, 0 < \eta \leq \eta_0, \ \left| \left[\tilde{\psi}^{(2j+1)} \right]_0 \right| \leq C \eta^{2N-2j} \ , \tag{3.2.1}$$

and for $j \geq N$

$$\forall\, 0 < \eta \leq \eta_0, \ \left| \left[\tilde{\psi}^{(2j+1)} \right]_0 \right| \leq C. \tag{3.2.2}$$

The proof of Proposition 3.4 relies on the particular structure induced by the equations satisfied by ψ and ϕ_i. Locally around a Dirac potential, their singularities have the same behavior. More precisely, if we consider the even part ψ_e of ψ, the best approximation of ψ_e by N eigenfunctions ϕ_i is of order $2N$. It is then possible to rewrite the singularity at 0 of $\tilde{\psi}$ to make use of this approximation.

Proposition 3.5 (d-th derivative jump at η)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. There exists a constant C independent of η such that for $d \leq k \leq 2d-2$*

$$\forall\, 0 < \eta \leq \eta_0, \ \left| \left[\tilde{\psi}^{(k)} \right]_\eta \right| \leq \frac{C}{\eta^{k-1}}.$$

The derivative jump of $\tilde{\psi}$ at η is due to the lack of regularity of the pseudo wave functions $\tilde{\phi}_j$ at η. The latter can be written as rescaled polynomials $P_{2d-2}(\frac{x}{\eta})$ where P_{2d-2} is of degree at most $2d-2$. If we suppose that the coefficients of P_{2d-2} are uniformly bounded in η and if the dependence on η of the projector functions $\tilde{p}_k$ is neglected, by deriving k times the polynomials $P_{2d-2}(\frac{x}{\eta})$, $k \geq d$, we can see why the derivative jump of $\tilde{\psi}$ at η is expected to grow as η^{-k}. Tracking all the dependencies on η, we can in fact show that a factor η can be gained, which is in full agreement with Figure 3.5.2.

Using Proposition 3.8 and classical estimates on eigenvalue approximations [Wei74], we have the following theorems.

Theorem 3.6 (Estimates on the Fourier coefficients)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let $\widehat{\tilde{\psi}}_m$ be the m-th Fourier coefficient of $\tilde{\psi}$. There exists a constant $C > 0$ independent of η and m such that for all*

$0 < \eta \leq \eta_0$ *and* $m \geq \frac{1}{\eta}$

$$\left|\widehat{\tilde{\psi}}_m\right| \leq C\left(\frac{\eta^{2N}}{m^2} + \frac{1}{\eta^{d-1}m^{d+1}}\right).$$

Theorem 3.7 (Estimates on the eigenvalues)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let E_M^η be an eigenvalue of the variational approximation of (3.1.2) in a basis of M plane-waves and for a cut-off radius $0 < \eta \leq \eta_0$, and let E be the corresponding exact eigenvalue. There exists a constant $C > 0$ independent of η and M such that for all $0 < \eta \leq \eta_0$ and $M \geq \frac{1}{\eta}$*

$$0 < E_M^\eta - E \leq C\left(\frac{\eta^{4N}}{M} + \frac{1}{\eta^{2d-2}}\frac{1}{M^{2d-1}}\right). \tag{3.2.3}$$

The first term has the same asymptotic decay in M as the brute force discretization of the problem with the original Dirac potential. However the prefactor η^{4N} can be made small by using a small cut-off radius η and/or a large N. Doing so, we introduce another error term which decays as M^{1-2d}, with a prefactor of order η^{2-2d}. A natural strategy would thus be to balance these two error terms. This allows one to choose the numerical parameters in a consistent way. The numerical tests in Section 3.5 suggest that the estimate (3.2.3) is optimal.

3.3 Proofs

This section is organized as follows. First, we prove that the VPAW method is well defined. The remainder of the section is then devoted to the proofs of Theorems 3.6 and 3.7. After estimating the decay of the Fourier coefficients of the pseudo wave function $\tilde{\psi}$, we will precisely characterize the singularities of the functions ψ and ϕ_k in order to estimate the derivative jumps of $\tilde{\psi}$.

3.3.1 Well-posedness of the VPAW method

Proof of Proposition 3.2. To prove the linear independence of the pseudo wave functions is equivalent to show that the matrix $(\phi_{j+1}^{(k)}(\eta))_{0\leq j\leq N-1, 0\leq k\leq d-1}$ is full rank. In fact, we will show that the submatrix $(\phi_{j+1}^{(k)}(\eta))_{0\leq j,k\leq N-1}$ is invertible. Using the expression of ϕ_{j+1}, we have for $0 \leq j, k \leq N-1$,

$$\phi_{j+1}^k(\eta) = \begin{cases} (-1)^{k/2}\omega_{j+1}^k \cos(\omega_{j+1}(\eta - \frac{1}{2})) & \text{if } k \text{ is even,} \\ (-1)^{(k+1)/2}\omega_{j+1}^k \sin(\omega_{j+1}(\eta - \frac{1}{2})) & \text{if } k \text{ is odd} \end{cases}$$

Let $A(\eta)$ the matrix defined by

$$A(\eta) := \begin{pmatrix} \cos(\omega_{j+1}(\eta - \frac{1}{2})) & -\omega_{j+1}\sin(\omega_{j+1}(\eta - \frac{1}{2})) & -\omega_{j+1}^2\cos(\omega_{j+1}(\eta - \frac{1}{2})) & \cdots \end{pmatrix}.$$

The function $\eta \mapsto \det A(\eta)$ is complex analytic, thus if it is not identically equal to 0, there exists an interval $(0, \eta_0)$ with $\eta_0 > 0$ such that the matrix $A(\eta)$ is invertible. It suffices to show that there exists $\eta \in \mathbb{C}$ such that $A(\eta)$ is invertible. Let $\eta = -ix + \frac{1}{2}$, $x > 0$. Then for x large, we have

$\cos(\omega_{j+1}x) \sim \frac{1}{2}e^{\omega_{j+1}x}$ and $\sin(\omega_{j+1}x) \sim \frac{1}{2}e^{\omega_{j+1}x}$, thus

$$A(-ix+\tfrac{1}{2}) = \frac{1}{2}\begin{pmatrix} e^{\omega_{j+1}x} & -\omega_{j+1}e^{\omega_{j+1}x} & -\omega_{j+1}^2 e^{\omega_{j+1}x}\dots \end{pmatrix} + \varepsilon(x),$$

where

$$\|\varepsilon(x)\| \ll \left\| \begin{pmatrix} e^{\omega_{j+1}x} & -\omega_{j+1}e^{\omega_{j+1}x} & -\omega_{j+1}^2 e^{\omega_{j+1}x}\dots \end{pmatrix} \right\|.$$

We have

$$\begin{pmatrix} e^{\omega_{j+1}x} & -\omega_{j+1}e^{\omega_{j+1}x} & -\omega_{j+1}^2 e^{\omega_{j+1}x}\dots \end{pmatrix} = \begin{pmatrix} e^{\omega_1 x} & & 0 \\ & \ddots & \\ 0 & & e^{\omega_N x} \end{pmatrix} \begin{pmatrix} 1 & \omega_1 & & \omega_1^{N-1} \\ \vdots & \vdots & \dots & \vdots \\ 1 & \omega_N & & \omega_N^{N-1} \end{pmatrix}$$

which is invertible because the phases $(\omega_j)_{1\le j\le N}$ are pairwise distinct. Hence $A(-ix+\frac{1}{2})$ is invertible for x large enough. □

Proof of Proposition 3.3. As T is a finite rank and thus compact operator, proving the statement is equivalent to show that $\mathrm{Ker}(\mathrm{Id}+T) = \{0\}$. First, suppose that the matrix $(\langle \tilde{p}_k\,,\phi_i\rangle)_{k,i}$ is invertible and let $f \in \mathrm{Ker}(\mathrm{Id}+T)$. We have

$$\sum_{i=1}^{N} \langle \tilde{p}_i\,, f\rangle\,(\phi_i - \tilde{\phi}_i) + f = 0 \tag{3.3.1}$$

Since $\phi_i - \tilde{\phi}_i$ is supported in $[-\eta,\eta]$ we also have $\mathrm{supp}(f) \subset [-\eta,\eta]$.

By multiplying each side of Equation (3.3.1) by $\tilde{p}_k$, $1 \le k \le N$ and integrating on $[-\frac{1}{2},\frac{1}{2}]$, we obtain:

$$0 = \sum_{i=1}^{N} \langle \tilde{p}_i\,, f\rangle \left\langle \tilde{p}_k\,, \phi_i - \tilde{\phi}_i \right\rangle + \langle \tilde{p}_k\,, f\rangle = \sum_{i=1}^{N} \langle \tilde{p}_i\,, f\rangle\,(\langle \tilde{p}_k\,,\phi_i\rangle - \underbrace{\left\langle \tilde{p}_k\,, \tilde{\phi}_i \right\rangle}_{=\delta_{ki}}) + \langle \tilde{p}_k\,, f\rangle \ ,$$

so that

$$\forall 1 \le k \le N,\ 0 = \sum_{i=1}^{N} \langle \tilde{p}_i\,, f\rangle\,\langle \tilde{p}_k\,,\phi_i\rangle\,.$$

Since we assumed that the matrix $(\langle \tilde{p}_k\,,\phi_i\rangle)_{k,i}$ is invertible,

$$\forall\, 1 \le i \le N,\ \langle \tilde{p}_i\,, f\rangle = 0\ .$$

Going back to (3.3.1), this implies $f = 0$ and $\mathrm{Id}+T$ is invertible.

Now we suppose that the matrix $(\langle \tilde{p}_k \, , \phi_i \rangle)_{k,i}$ is not invertible. Thus there is $(\alpha_i)_{1 \leq i \leq N}$ such that

$$\forall 1 \leq i \leq N, \ \sum_{j=1}^{N} \alpha_j \langle \tilde{p}_i \, , \phi_j \rangle = 0.$$

Let $f(x) = \sum_{j=1}^{N} \alpha_j (\phi_j - \tilde{\phi}_j)$. Then

$$\begin{aligned}
(\mathrm{Id} + T) f &= \sum_{j=1}^{N} \alpha_j (\phi_j - \tilde{\phi}_j) + \sum_{i=1}^{N} \sum_{j=1}^{N} \alpha_j \left\langle \tilde{p}_i \, , \phi_j - \tilde{\phi}_j \right\rangle (\phi_j - \tilde{\phi}_j) \\
&= \sum_{i=1}^{N} \sum_{j=1}^{N} \alpha_j \langle \tilde{p}_i \, , \phi_j \rangle (\phi_j - \tilde{\phi}_j) \\
&= 0
\end{aligned}$$

Thus $\mathrm{Ker}(I + T) \neq \{0\}$ and $(I + T)$ is not invertible. □

3.3.2 Structure and approximation lemmas

A key intermediate result in our study is the estimation of the decay of the Fourier coefficients of $\tilde{\psi}$ as a function of its derivative jumps.

Proposition 3.8. *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let $\widehat{\tilde{\psi}}_m$ be the m-th Fourier coefficient of $\tilde{\psi}$. Then*

$$\begin{aligned}
\widehat{\tilde{\psi}}_m = &\sum_{j=0}^{\lfloor \frac{d}{2} \rfloor - 1} \frac{1}{(2i\pi m)^{2+2j}} \left[\tilde{\psi}^{(2j+1)} \right]_0 + \sum_{k=d}^{2d-2} \frac{e^{\mp 2i\pi m\eta}}{(2i\pi m)^{k+1}} \left[\tilde{\psi}^{(k)} \right]_{\pm\eta} \\
&+ e^{-2i\pi ma} \left(\sum_{j=0}^{\lfloor \frac{d}{2} \rfloor - 1} \frac{1}{(2i\pi m)^{2+2j}} \left[\tilde{\psi}^{(2j+1)} \right]_a + \sum_{k=d}^{2d-2} \frac{e^{\mp 2i\pi m\eta}}{(2i\pi m)^{k+1}} \left[\tilde{\psi}^{(k)} \right]_{a\pm\eta} \right) \\
&+ \frac{1}{(2i\pi m)^{2d-1}} \int_0^1 \tilde{\psi}^{(2d-1)}(x) e^{-2i\pi mx} \, \mathrm{d}x.
\end{aligned}$$

Proof. This result follows from the definition of the Fourier coefficients and integration by parts. □

In view of the Proposition 3.8, the decay of the Fourier coefficients can be inferred from the derivative jumps of $\tilde{\psi}$ according to the VPAW parameters. The singularities of $\tilde{\psi}$ at integer values are caused by the singularity of the functions ψ and ϕ_k. Thus, to get an accurate characterization of the singularities of $\tilde{\psi}$, we need to precisely know how the functions ψ and ϕ_k behave in a neighborhood of their singularities.

Lemma 3.9 (Structure lemma)**.** *Let ψ be an eigenfunction (3.1.1) associated to the eigenvalue E.*

Then in a neighborhood of 0*, we have the following expansion :*

$$\psi(x) = \psi(0)\left(\sum_{j=0}^{k}\frac{(-E)^j}{(2j)!}x^{2j} - \frac{Z_0}{2}\sum_{j=0}^{k}\frac{(-E)^j}{(2j+1)!}|x|^{2j+1}\right) + \frac{\psi'(0_+)+\psi'(0_-)}{2}\sum_{j=0}^{k}\frac{(-E)^j}{(2j+1)!}x^{2j+1} + \psi_{2k+2}(x), \quad (3.3.2)$$

where ψ_{2k+2} *is a* C^{2k+2} *function satisfying in a neighbourhood of* 0*,*

$$\begin{cases}\psi_{2k+2}^{(2k+2)} = (-E)^{k+1}\psi,\\ |\psi_{2k+2}(x)| \le C\frac{|-E|^{k+1}}{(2k+2)!}|x|^{2k+2}.\end{cases}$$

Proof. This lemma is proved by induction.

Initialization For $k = 0$, let

$$\theta_2(x) = \psi(x) + Z_0\frac{|x|}{2}\psi(0).$$

We differentiate θ_2 twice:

$$\theta_2''(x) = \psi''(x) - [\psi']_0\delta_0 = -E\psi(x), \quad \text{on } (-\tfrac{1}{2},\tfrac{1}{2}). \quad (3.3.3)$$

The function ψ being continuous, θ_2 is C^2 in a neighborhood of 0. Moreover,

$$\theta_2(0) = \psi(0),$$

and

$$\theta_2'(x) = \psi'(x) - \frac{\operatorname{sign}(x)}{2}[\psi']_0.$$

When x tends to 0_+ or 0_-, we obtain the same expression:

$$\theta_2'(0) = \frac{\psi'(0_+)+\psi'(0_-)}{2}.$$

Setting

$$\psi_2(x) = \theta_2(x) - \psi(0) - \frac{\psi'(0_+)+\psi'(0_-)}{2}x,$$

the statement is true for $k = 0$.

Inductive step Suppose the statement is true for $k-1$. Then, we have in a neighbourhood of 0,

$$\psi_{2k}^{(2k)}(x) = (-E)^k\psi(x).$$

Let

$$\theta_{2k+2}(x) = \psi_{2k}(x) - (-E)^k\frac{|x|}{2}[\psi']_0\frac{x^{2k}}{(2k+1)!}.$$

Then

$$\theta_{2k+2}^{(2k)}(x) = (-E)^k \left(\psi(x) - \frac{|x|}{2}[\psi']_0 \right),$$

so that in view of (3.3.3),

$$\theta_{2k+2}^{(2k+2)}(x) = (-E)^k \left(\psi''(x) - [\psi']_0 \delta_0 \right) = (-E)^{k+1}\psi(x),$$

in the neighbourhood of 0.

So θ_{2k+2} is a C^{2k+2} function in a neighbourhood of 0 and we have:

$$\psi(x) = \psi(0) \left(\sum_{j=0}^{k-1} \frac{(-E)^j}{(2j)!} x^{2j} - Z_0 \sum_{j=0}^{k} \frac{(-E)^j}{(2j+1)!} \frac{|x|^{2j+1}}{2} \right) + \sum_{j=0}^{k-1} \frac{(-E)^j}{(2j+1)!} \frac{\psi'(0_+) + \psi'(0_-)}{2} x^{2j+1} + \theta_{2k+2}(x).$$

Il suffices to evaluate $\theta_{2k+2}^{(2k)}(0)$ and $\theta_{2k+2}^{(2k+1)}(0)$ to conclude the proof. We have

$$\theta_{2k+2}^{(2k)}(0) = (-E)^k \psi(0) \ ,$$

and

$$\theta_{2k+2}^{(2k+1)}(x) = (-E)^k \left(\psi'(x) - \frac{\mathrm{sign}(x)}{2}[\psi']_0 \right) \ ,$$

so if x tends to 0, we have :

$$\theta_{2k+2}^{(2k+1)}(0) = \frac{\psi'(0_+) + \psi'(0_-)}{2}(-E)^k.$$

Define

$$\psi_{2k+2}(x) = \theta_{2k+2}(x) - \psi(0)\frac{x^{2k}}{(2k)!} - \frac{\psi'(0_+) + \psi'(0_-)}{2}\frac{x^{2k+1}}{(2k+1)!} \ ,$$

and the induction is proved. □

Let ψ_e be the even part of ψ. We have in a neighbourhood of 0

$$\psi_e(x) = \psi(0) \sum_{k=0}^{N-1} \left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!} \right) (-E)^k + \frac{1}{2}(\psi_{2N}(x) + \psi_{2N}(-x)). \tag{3.3.4}$$

Lemma 3.10 (Approximation)**.** *There exist constants $(c_j)_{1\le j\le N} \in \mathbb{R}^N$ satisfying*

$$\psi_e(x) = \sum_{j=1}^{N} c_j \phi_j(x) + \mathcal{O}\left(x^{2N}\right), \qquad \text{as } x \to 0.$$

Proof. By Lemma 3.9 applied to ϕ_j, we have

$$\phi_j(x) = \phi_j(0)\left(\sum_{k=0}^{N-1}\frac{(-\epsilon_j)^k}{(2k)!}x^{2k} - \frac{Z_0}{2}\sum_{k=0}^{N-1}\frac{(-\epsilon_j)^k}{(2k+1)!}|x|^{2k+1}\right) + \phi_{j,2N}(x)\ ,$$

where

$$\phi_{j,2N}(x) = \mathcal{O}(x^{2N}).$$

So

$$\begin{aligned}\psi_e(x) - \sum_{j=1}^{N} c_j\phi_j(x) = &\sum_{k=0}^{N-1}\left(\psi(0)(-E)^k - \sum_{j=1}^{N}(-\epsilon_j)^k c_j\phi_j(0)\right)\frac{x^{2k}}{(2k)!}\\ &- \frac{Z_0}{2}\sum_{k=0}^{N-1}\left(\psi(0)(-E)^k - \sum_{j=1}^{N}(-\epsilon_j)^k c_j\phi_j(0)\right)\frac{|x|^{2k+1}}{(2k+1)!} + \psi_{2N}(x) - \sum_{j=1}^{N} c_j\phi_{j,2N}(x).\end{aligned}$$

To prove the lemma, it remains to show that there exist coefficients (c_j) such that :

$$\forall\, 0 \le k \le N-1,\ \sum_{j=1}^{N}(-\epsilon_j)^k c_j\phi_j(0) = \psi(0)(-E)^k\ .$$

We have chosen the functions ϕ_j so that $\phi_j(0) \neq 0$. By defining $\alpha_j = c_j\phi_j(0)$, we recognize a Vandermonde linear system. The eigenvalues ϵ_j are all different so the system is invertible and the lemma is proved. □

3.3.3 Derivative jumps at 0

Recall $p_i(t) = \rho_\eta(t)\tilde{\phi}_i(t)$. We will introduce some notation used in the next proofs:

$$\begin{aligned}p(t) &:= (p_1(t), \dots, p_N(t))^T \in \mathbb{R}^N,\\ \left\langle \tilde{p}\,, \tilde{\psi}\right\rangle &:= \left(\left\langle \tilde{p}_1\,, \tilde{\psi}\right\rangle, \dots, \left\langle \tilde{p}_N\,, \tilde{\psi}\right\rangle\right)^T \in \mathbb{R}^N,\\ \langle \tilde{p}\,, \psi\rangle &:= (\langle \tilde{p}_1\,, \psi\rangle, \dots, \langle \tilde{p}_N\,, \psi\rangle)^T \in \mathbb{R}^N,\\ \Phi(t) &:= (\phi_1(t), \dots, \phi_N(t))^T \in \mathbb{R}^N,\\ \widetilde{\Phi}(t) &:= (\tilde{\phi}_1(t), \dots, \tilde{\phi}_N(t))^T \in \mathbb{R}^N,\\ B &:= (\langle p_i, \tilde{\phi}_j\rangle)_{1\le i,j\le N} \in \mathbb{R}^{N\times N},\\ \widetilde{A} &:= (\langle \tilde{p}_i, \phi_j\rangle)_{1\le i,j\le N} \in \mathbb{R}^{N\times N},\\ A &:= (\langle p_i, \phi_j\rangle)_{1\le i,j\le N} = B\widetilde{A} \in \mathbb{R}^{N\times N}.\end{aligned}$$

Lemma 3.11. *Let $(c_k)_{1\leq k\leq N}$ be any vector of $\mathbb{R}^N$ and $j\in\mathbb{N}$. Then,*

$$[\tilde{\psi}^{(2j+1)}]_0 = -Z_0\left((-E)^j\psi(0) - \sum_{k=1}^{N} c_k(-\epsilon_k)^j\phi_k(0) - \left\langle A^{-1}p\,,\psi - \sum_{k=1}^{N} c_k\phi_k\right\rangle\cdot\mathcal{E}^j\Phi(0)\right).$$

where $\mathcal{E}$ is the diagonal matrix

$$\mathcal{E} = \begin{pmatrix} -\epsilon_1 & 0 & \dots & 0 \\ 0 & -\epsilon_2 & \dots & \vdots \\ \vdots & \vdots & \ddots & 0 \\ 0 & \dots & 0 & -\epsilon_N \end{pmatrix}.$$

Proof. We first prove the statement for $j=0$. In a neighbourhood of 0, we have:

$$\tilde{\psi} = \psi - \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle(\phi_i-\tilde{\phi}_i). \tag{3.3.5}$$

Using the equations satisfied by ψ and ϕ_i gives for the first derivative jump at 0 of $\tilde{\psi}$:

$$\begin{aligned}[\tilde{\psi}']_0 &= [\psi']_0 - \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle[\phi_i']_0 \\ &= -Z_0\left(\psi(0) - \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle\phi_i(0)\right).\end{aligned} \tag{3.3.6}$$

Multiplying equation (3.3.5) by $\tilde{p}_k$ and integrating on $[-1/2,1/2]$,

$$\langle\tilde{p}_k\,,\psi\rangle - \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle\langle\tilde{p}_k\,,\phi_i\rangle = \left\langle\tilde{p}_k\,,\tilde{\psi}\right\rangle - \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle\underbrace{\left\langle\tilde{p}_k\,,\tilde{\phi}_i\right\rangle}_{=\delta_{ki}} = 0\ ,$$

$$\langle\tilde{p}_k\,,\psi\rangle = \sum_{i=1}^{N}\left\langle\tilde{p}_i\,,\tilde{\psi}\right\rangle\langle\tilde{p}_k\,,\phi_i\rangle\ .$$

Therefore

$$\widetilde{A}\left\langle\tilde{p}\,,\tilde{\psi}\right\rangle = \langle\tilde{p}\,,\psi\rangle \tag{3.3.7}$$

Likewise

$$B\,\langle\tilde{p}\,,\psi\rangle = \langle p\,,\psi\rangle\,,$$

since for $1 \leq i \leq N$:

$$\begin{aligned}\sum_{j=1}^{N} B_{ij} \left\langle \tilde{p}_j \, , \psi \right\rangle &= \sum_{j=1}^{N} \left\langle p_i \, , \tilde{\phi}_j \right\rangle \left\langle \tilde{p}_j \, , \psi \right\rangle \\ &= \left\langle p_i \, , \psi \right\rangle\end{aligned}$$

According to Proposition 3.3, the matrix $\widetilde{A}$ is invertible and so is B since $B = A\widetilde{A}$, with A invertible by assumption. We therefore have

$$\begin{aligned}\sum_{i=1}^{N} \left\langle \tilde{p}_i \, , \tilde{\psi} \right\rangle \phi_i(0) &= \left\langle \tilde{p} \, , \tilde{\psi} \right\rangle \cdot \Phi(0) \\ &= \widetilde{A}^{-1} \left\langle \tilde{p} \, , \psi \right\rangle \cdot \Phi(0) \\ &= (B\widetilde{A})^{-1} \left\langle p \, , \psi \right\rangle \cdot \Phi(0) \\ &= \left\langle A^{-1} p \, , \psi \right\rangle \cdot \Phi(0).\end{aligned}$$

We thus obtain the more compact form:

$$[\tilde{\psi}']_0 = -Z_0 \left(\psi(0) - \left\langle A^{-1} p \, , \psi \right\rangle \cdot \Phi(0) \right).$$

To complete the proof the lemma, it suffices to show that

$$\left\langle A^{-1} p \, , \phi_{i+1} \right\rangle = e_i,$$

where e_i is the i-th vector of the canonical basis of $\mathbb{R}^N$. This is straightforward since $\langle p \, , \phi_{i+1} \rangle$ is simply the i-th column of the matrix A.

For $j \geq 1$, we proceed in the same way using

$$\begin{cases} [\psi^{(2j+1)}]_0 = -Z_0 (-E)^j \psi(0), \\ [\phi_k^{(2j+1)}]_0 = -Z_0 (-\epsilon_k)^j \phi_k(0). \end{cases}$$

□

Remark 3.12. *Notice that we showed*

$$\left\langle \tilde{p} \, , \tilde{\psi} \right\rangle = \left\langle A^{-1} p \, , \psi \right\rangle. \tag{3.3.8}$$

This equality will be used later in the estimation of the d-th derivative jump.

To prove Lemma 3.4, it remains to study the behavior of $A^{-T} \mathcal{E}^j \Phi(0)$ as η goes to 0. By assumption, A is invertible for all $\eta > 0$ but when $\eta = 0$, A is a rank 1 matrix. Actually, in the special case of the 1D Schrödinger operator with Dirac potentials, we have a precise characterization of the behavior of $A^{-T} \mathcal{E}^j \Phi(0)$ as η goes to 0.

Lemma 3.13. *Let f be a function in $L^2_{\text{per}}(0,1)$ and $Q(t) = (Q_0(t), \ldots, Q_{d-1}(t))^T$ be a vector of even polynomials which forms a basis of the space of even polynomials of degree at most $2d-2$. Let*

G_η be the $d \times N$ matrix and C_η the $N \times d$ matrix defined by:

$$G_\eta = \int_{-1}^{1} \rho(t) Q(t) \Phi(\eta t)^T \, \mathrm{d}t,$$
$$\widetilde{\Phi}(t) = C_\eta Q(t/\eta), \ \forall t \in (-\eta, \eta).$$

Then we have

$$\left\langle A^{-1} p \, , f \right\rangle = \int_{-1}^{1} \rho(t) (C_\eta G_\eta)^{-1} C_\eta Q(t) f(\eta t) \, \mathrm{d}t. \tag{3.3.9}$$

Proof. We have

$$\begin{aligned} A_{ij} &= \langle p_{i+1} \, , \phi_{j+1} \rangle \\ &= \int_{-\eta}^{\eta} \rho(t/\eta) \tilde{\phi}_{i+1}(t) \phi_{j+1}(t) \, \mathrm{d}t \\ &= \eta \int_{-1}^{1} \rho(t) \tilde{\phi}_{i+1}(\eta t) \phi_{j+1}(\eta t) \, \mathrm{d}t. \end{aligned}$$

Therefore,

$$\begin{aligned} A &= \eta \int_{-1}^{1} \rho(t) \widetilde{\Phi}(\eta t) \Phi(\eta t)^T \, \mathrm{d}t \\ &= \eta \, C_\eta \int_{-1}^{1} \rho(t) Q(t) \Phi(\eta t)^T \, \mathrm{d}t \\ &= \eta \, C_\eta G_\eta. \end{aligned}$$

Since $(\tilde{\phi}_i)_{1 \le i \le N}$ is free, the matrix C_η is invertible :

$$A^{-1} p = \frac{1}{\eta} \rho(t/\eta) (C_\eta G_\eta)^{-1} C_\eta Q(t/\eta).$$

Thus

$$\begin{aligned} \left\langle A^{-1} p \, , f \right\rangle &= \frac{1}{\eta} \int_{-\eta}^{\eta} \rho(t/\eta) (C_\eta G_\eta)^{-1} C_\eta Q(t/\eta) f(t) \, \mathrm{d}t \\ &= \int_{-1}^{1} \rho(t) (C_\eta G_\eta)^{-1} C_\eta Q(t) f(\eta t) \, \mathrm{d}t. \end{aligned}$$

□

Before moving to the next lemma, we introduce the following notation. Let Q_k be the even polynomials of degrees at most $2d-2$ defined by

$$\int_{-1}^{1} \rho(t) Q_k(t) t^{2j} \, \mathrm{d}t = \delta_{kj}, \ 0 \le k, j \le d-1 \ ,$$

and let P_k, $0 \leq k \leq d-1$ and P be defined by

$$\begin{aligned} P_k(t) &= \frac{1}{2^k k!}(t^2-1)^k \ , \\ P(t) &= (P_0(t), \dots, P_{d-1}(t))^T. \end{aligned}$$

It is easy to see that P_k satisfies

$$\begin{cases} P_k^{(j)}(1) = 0, \ 0 \leq j \leq k-1 \ , \\ P_k^{(k)}(1) = 1. \end{cases}$$

Let Π be the transition matrix from Q to P :

$$\Pi Q = P.$$

Finally we denote by C_η the matrix of the expansion of $\widetilde{\Phi}$ in the basis Q and $C_\eta^{(P)}$ the matrix of the expansion of $\widetilde{\Phi}$ in the basis P :

$$\begin{cases} \widetilde{\Phi}(t) = C_\eta Q(t/\eta) \ , \\ \widetilde{\Phi}(t) = C_\eta^{(P)} P(t/\eta). \end{cases}$$

It is easy to see that

$$C_\eta = C_\eta^{(P)} \Pi.$$

Lemma 3.14. *For $0 \leq j \leq N-1$, we have*

$$\frac{\eta^{2j}}{(2j)!}(\mathcal{E}^j \Phi(0))^T (C_\eta G_\eta)^{-1} C_\eta \underset{\eta \to 0}{\longrightarrow} e_j^T \begin{pmatrix} I_N & M_\pi \end{pmatrix}, \tag{3.3.10}$$

where M_π is a $(d-N) \times N$ matrix.

Furthermore

$$\|(C_\eta G_\eta)^{-1} C_\eta\| = \mathcal{O}\left(\frac{1}{\eta^{2N-2}}\right).$$

Remark 3.15. *The main idea of the proof is to use the particular structures of the matrices C_η and G_η. We denote by C_1, C_2, G_1 and G_2 the matrices defined by*

$$\begin{cases} C_\eta = \left(C_1 \,\middle|\, C_2\right), \\ G_\eta = \begin{pmatrix} G_1 \\ \hline G_2 \end{pmatrix}. \end{cases}$$

Suppose that C_1 is invertible and such that $\|C_1^{-1} C_2\| = \mathcal{O}(1)$ as $\eta \to 0$, and there exists an invertible matrix H_1 such that

$$\begin{cases} G_1 H_1 = I_N + \mathcal{O}(\eta) \ , \\ G_2 H_1 = \mathcal{O}(\eta) \ , \\ e_0^T H_1^{-1} = \Phi(0)^T. \end{cases}$$

Then it is easy to see that

$$\Phi(0)^T(C_\eta G_\eta)^{-1}C_\eta = e_0^T\left(I_N \;\middle|\; C_1^{-1}C_2\right) + \mathcal{O}(\eta).$$

Using Lemma 3.9 applied to Φ, it is easy to unveil the dependence in η of the matrix G_η but we have no hint on the structure of C_η. Likewise, $C_\eta^{(P)}$ is easy to study but the matrix $\int_{-1}^1 \rho(t)P(t)\Phi(\eta t)^T\,\mathrm{d}t$ is not. So we have to work with both bases P and Q, exhibit the structures of the matrices $C_\eta^{(P)}$ and G_η and recombine everything with the transition matrix Π.

Before proving Lemma 3.14, we state some properties of the matrix $C_\eta^{(P)}$ and its submatrices C_1, C_2.

Lemma 3.16. *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let $C_1 \in \mathbb{R}^{N\times N}$ and $C_2 \in \mathbb{R}^{N\times(d-N)}$ be the matrices such that:*

$$C_\eta^{(P)} = \left(C_1 \,\middle|\, C_2\right). \tag{3.3.11}$$

Let $(g_k)_{0\leq k\leq N-1}$ be the dual family of the vectors $(\eta^k\Phi^{(k)}(\eta))_{0\leq k\leq N-1}$ and K_1 be the matrix

$$K_1 = \begin{pmatrix} g_0^T \\ \vdots \\ g_{N-1}^T \end{pmatrix} \in \mathbb{R}^{N\times N}.$$

Then, there exists an upper triangular matrix $\mathcal{P}$ independent of η of the form

$$\mathcal{P} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & \ddots & * & * \\ \vdots & 0 & \ddots & * \\ 0 & \dots & 0 & 1 \end{pmatrix} \in \mathbb{R}^{N\times N}$$

such that

$$\begin{cases} C_1^{-1} = \mathcal{P}K_1, \\ C_1^{-1}C_2 = M + \mathcal{O}(\eta), \end{cases}$$

where $M \in \mathbb{R}^{N\times(d-N)}$ is a matrix independent of η.

Remark 3.17. *The particular form of the matrix $\mathcal{P}$ will be used in the estimation of the d-th derivative jump of $\tilde{\psi}$ at η (Lemma 3.5) and of $Tf(x)$ (Lemmas 3.20 and 3.21).*

Proof. Let $(c_k)_{0\leq k\leq d-1}$ be the columns of $C_\eta^{(P)}$. By the continuity conditions at η and our choice of the polynomials P_k, we have

$$\forall 0 \leq j \leq d-1,\; c_j = \eta^j\Phi^{(j)}(\eta) - \sum_{k=0}^{j-1} P_k^{(j)}(1)c_k. \tag{3.3.12}$$

Thus c_j is a linear combination of the vectors $\eta^k\Phi^{(k)}(\eta)$ for $k \leq j$ whose coefficients are *independent* of η. Moreover as $P_0 = 1$, we have $P_0^{(j)} = 0$ for $j \geq 1$. So in fact, for $j \geq 1$, c_j is spanned by the

vectors $\eta^k \Phi^{(k)}(\eta)$ for $1 \leq k \leq j$. Then, by definition of K_1 and the vectors g_k,

$$K_1 C_1 = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & \ddots & * & * \\ \vdots & 0 & \ddots & * \\ 0 & \dots & 0 & 1 \end{pmatrix}. \tag{3.3.13}$$

Note that this matrix is independent of η. Let us denote it by $\mathcal{P}^{-1}$. Then the inverse of C_1 is $\mathcal{P}K_1$ and $\mathcal{P}$ has the same structure as $\mathcal{P}^{-1}$. Recall that for $k \geq N$, c_k is a linear combination of the vectors $\eta^j \Phi^{(j)}(\eta)$ for $j \leq k$. As g_j is the dual family of the vectors $(\eta^l \Phi^{(l)}(\eta))_{0 \leq l \leq N-1}$ and $\|g_j\| = \mathcal{O}(\eta^{1-N})$, we have

$$C_1^{-1} C_2 = M + \mathcal{O}(\eta), \tag{3.3.14}$$

where M is a $N \times (d-N)$ matrix independent of η. □

Proof of Lemma 3.14. Let $G_1 \in \mathbb{R}^{N \times N}$ and $G_2 \in \mathbb{R}^{(d-N) \times N}$ be the unique matrices such that

$$G_\eta = \left(\frac{G_1}{G_2} \right) \in \mathbb{R}^{d \times N}.$$

By definition

$$G_\eta = \int_{-1}^{1} \rho(t) Q(t) \Phi(\eta t)^T \, \mathrm{d}t.$$

By Lemma 3.9 applied to each ϕ_j,

$$\Phi(\eta t) = \sum_{k=0}^{N-1} \left(t^{2j} - \eta \frac{Z_0}{2} \frac{|t|^{2j+1}}{2j+1} \right) \frac{\eta^{2j}}{(2j)!} \mathcal{E}^j \Phi(0) + \mathcal{O}(\eta^{2N}).$$

Let $a_j \in \mathbb{R}^d, a_j^N \in \mathbb{R}^N, a_j^{d-N} \in \mathbb{R}^{d-N}$ be defined by

$$a_j := -\int_{-1}^{1} \rho(t) \frac{Z_0}{2} \frac{|t|^{2j+1}}{2j+1} Q(t) \, \mathrm{d}t =: \begin{pmatrix} a_j^N \\ a_j^{d-N} \end{pmatrix}.$$

Then by definition of the polynomials Q we have

$$\begin{cases} G_1 = \sum_{j=0}^{N-1} (e_j + \eta a_j^N) \frac{\eta^{2j}}{(2j)!} (\mathcal{E}^j \Phi(0))^T + \mathcal{O}(\eta^{2N}), \\ G_2 = \sum_{j=0}^{N-1} \eta a_j^{d-N} \frac{\eta^{2j}}{(2j)!} (\mathcal{E}^j \Phi(0))^T + \mathcal{O}(\eta^{2N}). \end{cases}$$

Let $(f_0, \dots, f_{N-1})$ be the dual basis of $\left(\mathcal{E}^j \Phi(0) \frac{\eta^{2j}}{(2j)!} \right)_{0 \leq j \leq N-1}$ in $\mathbb{R}^N$ and H_1 be the matrix

$$H_1 := \begin{pmatrix} f_0 & \cdots & f_{N-1} \end{pmatrix} \in \mathbb{R}^{N \times N}.$$

It is straightforward to see that $\|H_1\| = \mathcal{O}(\eta^{2-2N})$ and

$$\begin{cases} G_1 H_1 = I_N + \mathcal{O}(\eta) \ , \\ G_2 H_1 = \mathcal{O}(\eta). \end{cases}$$

The matrix H_1 is invertible and its inverse is

$$H_1^{-1} = \sum_{j=0}^{N-1} e_j \frac{\eta^{2j}}{(2j)!} (\mathcal{E}^j \Phi(0))^T.$$

Let us now prove (3.3.10) for $j = 0$. We have

$$\begin{aligned} \Phi(0)^T (C_\eta G_\eta)^{-1} C_\eta &= e_0^T H_1^{-1} \left(C_\eta^{(P)} \Pi G_\eta\right)^{-1} C_\eta^{(P)} \Pi \\ &= e_0^T \left(C_1^{-1} C_\eta^{(P)} \Pi G_\eta H_1\right)^{-1} \Pi \Big(I_N \ \Big| \ C_1^{-1} C_2 \Big) \\ &= e_0^T \left(\Big(I_N \ \Big| \ M + \mathcal{O}(\eta) \Big) \Pi \Big(I_N \ \Big| \ \mathcal{O}(\eta) \Big)^T \right)^{-1} \Big(I_N \ \Big| \ M + \mathcal{O}(\eta) \Big) \Pi. \end{aligned}$$

Decomposing Π into four blocks

$$\Pi = \begin{pmatrix} \Pi_1 & \Pi_2 \\ \Pi_3 & \Pi_4 \end{pmatrix}, \text{ with } \Pi_1 \in \mathbb{R}^{N \times N},$$

we obtain

$$\begin{aligned} \Phi(0)^T (C_\eta G_\eta)^{-1} C_\eta &= e_0^T \left(\Pi_1 + M\Pi_3 + \mathcal{O}(\eta)\right)^{-1} \Big(\Pi_1 + M\Pi_3 + \mathcal{O}(\eta) \ \Big| \ \Pi_2 + M\Pi_4 + \mathcal{O}(\eta) \Big) \\ &= e_0^T \Big(I_N \ \Big| \ M_\pi \Big) + \mathcal{O}(\eta). \end{aligned}$$

For $1 \leq j \leq N-1$ we proceed in the same way, using $e_j^T H_1^{-1} = \frac{\eta^{2j}}{(2j)!} (\mathcal{E}^j \Phi(0))^T$. □

Proof of Proposition 3.4. Let $0 \leq j \leq N-1$ and let $(c_k)_{1 \leq k \leq N}$ be as in Lemma 3.10. Then by Lemma 3.11 we have :

$$\begin{aligned} [\tilde{\psi}^{(2j+1)}]_0 &= \underbrace{(-E)^j \psi(0) - \sum_{k=1}^N c_k (-\epsilon_k)^j \phi_k(0)}_{=0} + \left\langle A^{-1} p \, , \psi - \sum_{k=1}^N c_k \phi_k \right\rangle \cdot \mathcal{E}^j \Phi(0) \\ &= \left\langle A^{-1} p \, , \psi - \sum_{k=1}^N c_k \phi_k \right\rangle \cdot \mathcal{E}^j \Phi(0) \\ &= \left\langle A^{-1} p \, , \psi_e - \sum_{k=1}^N c_k \phi_k \right\rangle \cdot \mathcal{E}^j \Phi(0) \ , \end{aligned}$$

as p is even.

Combining Lemmas 3.13 and 3.14, we get

$$(\mathcal{E}^j\Phi(0))^T A^{-1}p = \rho(t/\eta)(\mathcal{E}^j\Phi(0))^T(C_\eta G_\eta)^{-1}C_\eta Q(t/\eta) = \rho(t/\eta)x_\eta^T Q(t/\eta)\ ,$$

where $\|x_\eta\| = \mathcal{O}(\eta^{-2j})$.

Using again Lemma 3.10, we obtain

$$\begin{aligned}\left|\left\langle A^{-1}p\,,\psi - \sum_{k=1}^N c_k\phi_k\right\rangle \cdot \mathcal{E}^j\Phi(0)\right| &\le C\|x_\eta\|\left\|\rho(t)\sum_{\ell=0}^{N-1}|Q_\ell(t)|\right\|_{L^1[-1,1]}\left\|\psi - \sum_{k=1}^N c_k\phi_k\right\|_{L^\infty[-\eta,\eta]}\\ &\le C\eta^{2N-2j}.\end{aligned}$$

We therefore obtain

$$|[\tilde{\psi}^{(2j+1)}]_0| \le C\eta^{2N-2j}.$$

For $j \ge N$, we then have

$$(-E)^j\psi(0) - \sum_{k=1}^N c_k(-\epsilon_k)^j\phi_k(0) \ne 0,$$

and by Lemmas 3.10 and 3.14,

$$\left|\left\langle A^{-1}p\,,\psi - \sum_{j=1}^N c_j\phi_j\right\rangle \cdot \mathcal{E}^j\Phi(0)\right| \le C\underbrace{\|(C_\eta G_\eta)^{-1}C_\eta\|}_{=\mathcal{O}(\eta^{2-2N})}\underbrace{\left\|\psi - \sum_{k=1}^N c_k\phi_k\right\|_{L^\infty[-\eta,\eta]}}_{=\mathcal{O}(\eta^{2N})} \le C\eta^2.$$

We therefore have

$$[\tilde{\psi}^{(2j+1)}]_0 = \underbrace{(-E)^j\psi(0) - \sum_{k=1}^N c_k(-\epsilon_k)^j\phi_k(0)}_{\ne 0} + \underbrace{\left\langle A^{-1}p\,,\psi - \sum_{k=1}^N c_k\phi_k\right\rangle \cdot \mathcal{E}^j\Phi(0)}_{=\mathcal{O}(\eta^2)}.$$

Thus,

$$|[\tilde{\psi}^{(2j+1)}]_0| \le C,$$

which completes the proof. □

3.3.4 d-th derivative jump

We use the notation introduced in the previous section.

Proof of Proposition 3.5. We give the proof only for $k = d$ as the proof for $d+1 \le k \le 2d-2$ is

very similar. By definition of $\tilde{\psi}$ and $\widetilde{\Phi}$,

$$\begin{aligned}
[\tilde{\psi}^{(d)}]_\eta &= \left\langle \tilde{p}\,, \tilde{\psi} \right\rangle \cdot [\widetilde{\Phi}^{(d)}]_\eta \\
&= \frac{1}{\eta^d} \left\langle \tilde{p}\,, \tilde{\psi} \right\rangle \cdot (C_\eta^{(P)} P^{(d)}(1) - \eta^d \Phi^{(d)}(\eta)) \\
&= \frac{1}{\eta^d} \left\langle A^{-1} p\,, \psi \right\rangle \cdot (C_\eta^{(P)} P^{(d)}(1) - \eta^d \Phi^{(d)}(\eta)) \qquad \text{(by Equation (3.3.8))}, \\
&= \frac{1}{\eta^d} \int_{-1}^{1} \rho(t)\psi(\eta t) Q(t)\,\mathrm{d}t \cdot C_\eta^T (G_\eta^T C_\eta^T)^{-1} (C_\eta^{(P)} P^{(d)}(1) - \eta^d \Phi^{(d)}(\eta)) \text{ (by Lemma 3.13)}.
\end{aligned}$$

We know from (3.3.12) that the columns of $C_\eta^{(P)}$ are linear combinations of $\eta^k \Phi^{(k)}(\eta)$. Let us apply Lemma 3.9 to Φ. As the remainder is C^{2d-2}, for $k \leq d-1$, we can differentiate k times and we have for k even :

$$\eta^k \Phi^{(k)}(\eta) = \sum_{j=\frac{k}{2}}^{N-1} \left(\frac{\eta^{2j}}{(2j-k)!} - \frac{Z_0}{2} \frac{\eta^{2j+1}}{(2j+1-k)!} \right) \mathcal{E}^j \Phi(0) + \mathcal{O}(\eta^{2N}),$$

and for k odd, we have

$$\eta^k \Phi^{(k)}(\eta) = -\frac{Z_0}{2} \eta^k D^{\frac{k-1}{2}} \Phi(0) + \sum_{j=\frac{k+1}{2}}^{N-1} \left(\frac{\eta^{2j}}{(2j-k)!} - \frac{Z_0}{2} \frac{\eta^{2j+1}}{(2j+1-k)!} \right) \mathcal{E}^j \Phi(0) + \mathcal{O}(\eta^{2N}).$$

But by Lemma 3.14, for $0 \leq k \leq 2N-2$, k even, we have :

$$\begin{aligned}
C_\eta^T (G_\eta^T C_\eta^T)^{-1} \eta^k \Phi^{(k)}(\eta) &= \sum_{j=\frac{k}{2}}^{N-1} \left(\frac{\eta^{2j}}{(2j-k)!} - \frac{Z_0}{2} \frac{\eta^{2j+1}}{(2j+1-k)!} \right) C_\eta^T (G_\eta^T C_\eta^T)^{-1} \mathcal{E}^j \Phi(0) + \mathcal{O}(\eta^2) \\
&= \sum_{j=\frac{k}{2}}^{N-1} \frac{(2j)!}{(2j-k)!} \begin{pmatrix} I_N \\ M_\pi^T \end{pmatrix} e_j + \mathcal{O}(\eta). \qquad (3.3.15)
\end{aligned}$$

Similarly for $0 \leq k \leq 2N-1$, k odd :

$$\begin{aligned}
C_\eta^T (G_\eta^T C_\eta^T)^{-1} \eta^k \Phi^{(k)}(\eta) &= -\frac{Z_0}{2} C_\eta^T (G_\eta^T C_\eta^T)^{-1} \eta^k D^{\frac{k-1}{2}} \Phi(0) \\
&\quad + \sum_{j=\frac{k+1}{2}}^{N-1} \left(\frac{\eta^{2j}}{(2j-k)!} - \frac{Z_0}{2} \frac{\eta^{2j+1}}{(2j+1-k)!} \right) C_\eta^T (G_\eta^T C_\eta^T)^{-1} \mathcal{E}^j \Phi(0) + \mathcal{O}(\eta^2) \\
&= \sum_{j=\frac{k+1}{2}}^{N-1} \frac{(2j)!}{(2j-k)!} \begin{pmatrix} I_N \\ M_\pi^T \end{pmatrix} e_j + \mathcal{O}(\eta)\ , \qquad (3.3.16)
\end{aligned}$$

and for $k \geq 2N$, using $\|C_\eta^T (G_\eta^T C_\eta^T)^{-1}\| = \mathcal{O}(\eta^{2-2N})$ we have

$$C_\eta^T (G_\eta^T C_\eta^T)^{-1} \eta^k \Phi^{(k)}(\eta) = \mathcal{O}(\eta).$$

We have proved that $[\tilde{\psi}^{(d)}]_\eta = \mathcal{O}(\eta^{-d})$ but it is possible to have a slightly better estimate.

Observing that ψ is in fact a Lipschitz function and not only a continuous function, we have for $|t| \leq 1$:

$$\psi(\eta t) = \psi(0) + \mathcal{O}(\eta).$$

By definition of the polynomials Q_k, we have

$$\begin{aligned}\int_{-1}^{1} \rho(t) Q(t) \psi(\eta t)\, \mathrm{d}t &= \psi(0) \int_{-1}^{1} \rho(t) Q(t)\, \mathrm{d}t + \mathcal{O}(\eta) \\ &= \psi(0) e_0 + \mathcal{O}(\eta).\end{aligned}$$

To complete the proof of the proposition, it remains to show

$$e_0 \cdot C_\eta^T (G_\eta^T C_\eta^T)^{-1} (C_\eta^{(P)} P^{(d)}(1) - \eta^d \Phi^{(d)}(\eta)) = \mathcal{O}(\eta).$$

As we have for $j \geq 1$

$$e_0^T \begin{pmatrix} I_N \\ M_\pi^T \end{pmatrix} e_j = 0,$$

then for $d \geq 2$, equations (3.3.15) and (3.3.16) lead to

$$e_0 \cdot C_\eta^T (G_\eta^T C_\eta^T)^{-1} \eta^d \Phi^{(d)}(\eta) = \mathcal{O}(\eta).$$

Recall that the columns of $C_\eta^{(P)}$ satisfy the relation

$$\forall 0 \leq j \leq d-1,\ c_j = \eta^j \Phi^{(j)}(\eta) - \sum_{k=0}^{j-1} P_k^{(j)}(1) c_k.$$

But $P_0^{(j)}(1) = 0$ for $j \geq 1$ so in fact, for all $k \geq 1$, c_k is a linear combination of the vectors $\eta^j \Phi^{(j)}(\eta)$ for $1 \leq j \leq k$. Moreover by definition, we have

$$P^{(d)}(1) = (\underbrace{0, \ldots, 0}_{\lfloor \frac{d}{2} \rfloor}, *, \ldots, *)^T,$$

so $C_\eta^{(P)} P^{(d)}(1)$ is a linear combination of the last $\lceil \frac{d}{2} \rceil$ columns of $C_\eta^{(P)}$. Thus $C_\eta^{(P)} P^{(d)}(1)$ is a linear combination of the vectors $\eta^j \Phi^{(j)}(\eta)$ for $1 \leq j \leq d-1$ and therefore in view of (3.3.15) and (3.3.16), we have

$$e_0^T C_\eta^T (G_\eta^T C_\eta^T)^{-1} C_\eta^{(P)} P^{(d)}(1) = \mathcal{O}(\eta).$$

□

Proof of Theorem 3.6. First, we need to bound the remainder $\int_0^1 \tilde{\psi}^{(2d-1)}(x) e^{-2i\pi m x}\, \mathrm{d}x$ with respect

to η. $\widetilde{\Phi}$ is a vector of polynomials of degree at most $2d-2$, thus $\widetilde{\Phi}^{(2d-1)} = 0$. Thus

$$\left|\int_0^1 \tilde{\psi}^{(2d-1)}(x)e^{-2i\pi mx}\,\mathrm{d}x\right| \leq \int_0^1 |\psi^{(2d-1)}(x)|\,\mathrm{d}x + \int_{-\eta}^{\eta} |\left\langle \tilde{p}\,,\tilde{\psi}\right\rangle \cdot \Phi^{(2d-1)}(x)|\,\mathrm{d}x + \int_{a-\eta}^{a+\eta} \left|\left\langle \tilde{p}^a\,,\tilde{\psi}\right\rangle \cdot \Phi^{(2d-1)}(x-a)\right|\,\mathrm{d}x.$$

We have $\left\langle \tilde{p}\,,\tilde{\psi}\right\rangle = \langle A^{-1}p\,,\psi\rangle$ by (3.3.8) and by Lemmas 3.13 and 3.14,

$$\left|\langle A^{-1}p\,,\psi\rangle\right| \leq \frac{C}{\eta^{2N-2}},$$

where C is a positive constant independent of η. Thus

$$\int_{-\eta}^{\eta} |\left\langle \tilde{p}\,,\tilde{\psi}\right\rangle \cdot \Phi^{(2d-1)}(x)|\,\mathrm{d}x \leq \frac{C}{\eta^{2N-3}}.$$

Then by Proposition 3.8, using the estimates (3.2.1) and (3.2.2) on the derivative jumps

$$\begin{aligned}
|\widehat{\tilde{\psi}}_m| &\leq C\left(\sum_{j=0}^{\lfloor\frac{d}{2}\rfloor-1} \frac{1}{(2\pi m)^{2+2j}}\left|\left[\tilde{\psi}^{(2j+1)}\right]_0\right| + \sum_{k=d}^{2d-2}\frac{1}{(2\pi m)^{k+1}}\left|\left[\tilde{\psi}^{(k)}\right]_{\pm\eta}\right|\right.\\
&+ \sum_{j=0}^{\lfloor\frac{d}{2}\rfloor-1} \frac{1}{(2\pi m)^{2+2j}}\left|\left[\tilde{\psi}^{(2j+1)}\right]_0\right| + \sum_{k=d}^{2d-2}\frac{1}{(2\pi m)^{k+1}}\left|\left[\tilde{\psi}^{(k)}\right]_{a\pm\eta}\right|\\
&\left.+ \frac{1}{(2\pi m)^{2d-1}}\left|\int_0^1 \tilde{\psi}^{(2d-1)}(x)e^{-2i\pi mx}\,\mathrm{d}x\right|\right)\\
&\leq C\left(\sum_{j=0}^{\lfloor\frac{d}{2}\rfloor-1}\frac{\eta^{2N-2j}}{m^{2+2j}} + \sum_{k=d}^{2d-2}\frac{1}{\eta^{k-1}m^{k+1}} + \frac{1}{\eta^{2N-3}m^{2d-1}}\right).
\end{aligned}$$

Since $N \leq d$ and $m \geq \frac{1}{\eta}$, we have the result. □

3.3.5 Error bound on the eigenvalues

To derive the estimate on the eigenvalues, we would like to use the following classical result ([Wei74], p. 68).

Proposition 3.18. *Let H be a self-adjoint coercive H^1-bounded operator, $E_1 \leq \cdots \leq E_n$ be the lowest eigenvalues of H and $\psi_1, \ldots, \psi_n$ be L^2-normalized associated eigenfunctions. Let $E_1^{(M)} \leq \cdots \leq E_n^{(M)}$ be the lowest eigenvalues of the Rayleigh quotient of H restricted to the subspace V_M of dimension M.*

Let $w_k \in V_M$ for $1 \leq k \leq n$ be such that

$$\sum_{k=1}^{n} \|w_k - \psi_k\|_{H^1}^2 < 1.$$

Then there exists a positive constant C which depends on the H^1 norm of H and the coercivity constant such that for all $1 \leq k \leq n$

$$\left|E_k^{(M)} - E_k\right| \leq C \sum_{k=1}^{n} \|w_k - \psi_k\|_{H^1}^2.$$

We would like to apply this result to $\psi_M = (\mathrm{Id} + T)\tilde{\psi}_M$ where $\tilde{\psi}_M$ is the truncation of $\tilde{\psi}$ to the first M plane-waves but we need to bound the H^1 norm of T with respect to η. Coercivity for our one-dimensional model has been proved in [CD17]. To find this bound, we will need to rewrite Tf in a convenient way.

Lemma 3.19. *For $f \in H^1_{\mathrm{per}}(0,1)$, we have for $|x| \leq \eta$:*

$$\begin{aligned} Tf(x) &= \langle \tilde{p}\,, f\rangle \cdot \left(\Phi(x) - \widetilde{\Phi}(x)\right) \\ &= \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t \cdot \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi(x) - P(x/\eta)\right), \end{aligned}$$

where $G(P)$ is the following Gram matrix :

$$G(P) = \int_{-1}^{1} \rho(t) P(t) P(t)^T\,\mathrm{d}t,$$

and $C_1 \in \mathbb{R}^{N\times N}$ is the square matrix defined in Lemma 3.16.

Proof. For $|x| \leq \eta$, we have :

$$\begin{aligned} (Tf)(x) &= \langle \tilde{p}\,, f\rangle \cdot (\Phi(x) - \widetilde{\Phi}(x)) \\ &= \left\langle B^{-1} p\,, f\right\rangle \cdot (\Phi(x) - \widetilde{\Phi}(x)). \end{aligned}$$

Recall that

$$\begin{aligned} B &= \left\langle p\,, \widetilde{\Phi}^T \right\rangle \\ &= \left\langle \rho(t/\eta)\widetilde{\Phi}\,, \widetilde{\Phi}^T \right\rangle \\ &= \eta \int_{-1}^{1} \rho(t) C_\eta^{(P)} P(t) P(t)^T \left(C_\eta^{(P)}\right)^T \mathrm{d}t \\ &= \eta C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T. \end{aligned}$$

Thus,

$$\begin{aligned}\left\langle B^{-1}p\,,f\right\rangle\cdot\widetilde{\Phi}(x) &= \left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}\int_{-1}^{1}\rho(t)f(\eta t)P(t)\,\mathrm{d}t\cdot C_\eta^{(P)}P(x/\eta)\\ &= \left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}\int_{-1}^{1}\rho(t)f(\eta t)P(t)\,\mathrm{d}t\cdot P(x/\eta).\end{aligned}$$

Using the identity

$$C_\eta^{(P)}\begin{pmatrix}C_1^{-1}\\0\end{pmatrix} = \begin{pmatrix}C_1 \mid C_2\end{pmatrix}\begin{pmatrix}C_1^{-1}\\0\end{pmatrix} = I_N,$$

we can formally rewrite $\left\langle B^{-1}p\,,f\right\rangle$ as

$$\left\langle B^{-1}p\,,f\right\rangle\cdot\Phi(x) = \left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}\int_{-1}^{1}\rho(t)f(\eta t)P(t)\,\mathrm{d}t\cdot\begin{pmatrix}C_1^{-1}\\0\end{pmatrix}\Phi(x), \tag{3.3.17}$$

and the result follows. □

Lemma 3.20. *There exists a positive constant C independent of η such that for all $f\in H^1_{\mathrm{per}}(0,1)$ and for all $x\in\mathbb{R}$, we have*

$$\forall\, 0<\eta\le\eta_0,\ \left|\langle\tilde{p}\,,f\rangle\cdot\left(\Phi(x)-\widetilde{\Phi}(x)\right)\right|\le C\eta\|f\|_{H^1_{\mathrm{per}}}.$$

Proof. In this proof, C denotes a generic constant that does not depend on η or f. Let $f\in H^1_{\mathrm{per}}(0,1)$. On $|x|\ge\eta$, we have by definition of $\widetilde{\Phi}$

$$\langle\tilde{p}\,,f\rangle\cdot\left(\Phi(x)-\widetilde{\Phi}(x)\right)=0.$$

We deduce from Lemma 3.19 that for $|x|\le\eta$ we have

$$\begin{aligned}\langle\tilde{p}\,,f\rangle\cdot\left(\Phi(x)-\widetilde{\Phi}(x)\right) = \left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}\int_{-1}^{1}\rho(t)f(\eta t)P(t)\,\mathrm{d}t\\ \cdot\left(\begin{pmatrix}C_1^{-1}\\0\end{pmatrix}\Phi(x)-P(x/\eta)\right).\end{aligned}$$

The proof of the lemma consists of four steps. We will successively show that

1. $\begin{pmatrix}C_1^{-1}\\0\end{pmatrix}\Phi(x)-P(x/\eta)=\begin{pmatrix}0*\end{pmatrix}+\mathcal{O}(\eta)$, where $\begin{pmatrix}0*\end{pmatrix}$ is uniformly bounded in η and x;
2. $\int_{-1}^{1}\rho(t)f(\eta t)P(t)\,\mathrm{d}t = f(0)G(P)e_0+\mathcal{O}(\eta)\|f\|_{H^1_{\mathrm{per}}}$;
3. the norm of $\left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}$ is uniformly bounded in η;
4. for $j\ge 1$, $e_j^T\left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}G(P)e_0$ is of order $\mathcal{O}(\eta)$.

Indeed, assuming these statements hold, we can infer from statement 2 that

$$\begin{aligned}
&\left|\langle \tilde{p}\,, f\rangle \cdot \left(\Phi(x) - \widetilde{\Phi}(x)\right)\right| \\
&\qquad \leq |f(0)| \left| \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} G(P) e_0 \cdot \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi(x) - P(x/\eta)\right)\right| \\
&\qquad\quad + \mathcal{O}(\eta)\|f\|_{H^1_{\mathrm{per}}} \left| \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi(x) - P(x/\eta)\right)\right|.
\end{aligned}$$

We treat both terms separately. For the second term, by statements 1 and 3, we have

$$\left| \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi(x) - P(x/\eta)\right)\right| \leq C.$$

For the first one, by statement 1, we only have to check that for $j \geq 1$, we have

$$\left| \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} G(P) e_0 \cdot e_j \right| \leq C\eta,$$

which is exactly statement 4. The lemma is then proved using the Sobolev embedding $\|f\|_{L^\infty_{\mathrm{per}}} \leq C\|f\|_{H^1_{\mathrm{per}}}$.

Step 1 Writing down the Taylor expansion of Φ at η, we obtain

$$\begin{aligned}
\Phi(x) &= \sum_{k=0}^{N-1} \frac{(x-\eta)^k}{k!} \Phi^{(k)}(\eta) + \mathcal{O}((x-\eta)^N) \\
&= \sum_{k=0}^{N-1} \frac{1}{k!} \left(\frac{x}{\eta} - 1\right)^k \eta^k \Phi^{(k)}(\eta) + \mathcal{O}((x-\eta)^N).
\end{aligned}$$

By Lemma 3.16, we have

$$C_1^{-1} \eta^k \Phi^{(k)}(\eta) = \mathcal{P} K_1 \eta^k \Phi^{(k)}(\eta) = \mathcal{P} e_k,$$

and for $k \neq 0$, $\mathcal{P} e_k \cdot e_0 = 0$. We also know that $\|C_1^{-1}\| = \mathcal{O}(\eta^{1-N})$, so that

$$C_1^{-1} \Phi(x) = \begin{pmatrix} 1 \\ * \end{pmatrix} + \mathcal{O}(\eta).$$

By definition $P_0 = 1$, and therefore

$$\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi(x) - P(x/\eta) = \begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(\eta).$$

Step 2 Since $f \in H^1_{\text{per}}(0,1)$, by the Sobolev embedding theorem, f is continuous and $f(0)$ exists. Thus we can write

$$\begin{aligned}\int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t &= f(0)\int_{-1}^{1}\rho(t)P(t)\,\mathrm{d}t + \int_{-1}^{1}\rho(t)(f(\eta t)-f(0))P(t)\,\mathrm{d}t \\ &= f(0)G(P)e_0 + \int_{-1}^{1}\rho(t)(f(\eta t)-f(0))P(t)\,\mathrm{d}t,\end{aligned}$$

since $P_0 = 1$. Using

$$f(\eta t) = f(0) + \int_0^{\eta t} f'(x)\,\mathrm{d}x,$$

and Cauchy-Schwarz inequality, we obtain

$$\begin{aligned}\left|\int_{-1}^{1}\rho(t)(f(\eta t)-f(0))P(t)\,\mathrm{d}t\right| &\le \left(\int_{-1}^{1}\rho(t)^2P^2(t)\,\mathrm{d}t\int_{-1}^{1}\left(\int_0^{\eta t} f'(x)\,\mathrm{d}x\right)^2\mathrm{d}t\right)^{1/2} \\ &\le C\left(\int_{-1}^{1}\left(\int_0^{\eta t} f'(x)^2\,\mathrm{d}x\right)\eta^2 t^2\,\mathrm{d}t\right)^{1/2} \\ &\le C\eta\|f\|_{H^1_{\text{per}}}.\end{aligned}$$

Step 3 We want to bound the norm of the matrix

$$\left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}.$$

Since $G(P)$ is the Gram matrix of the polynomials P_k for the weight ρ, $G(P)$ is a symmetric positive definite matrix and thus admits a square root. It is easy to check that

$$G(P)^{1/2}\left(C_\eta^{(P)}\right)^T\left(C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T\right)^{-1}C_\eta^{(P)}G(P)^{1/2}$$

is an orthogonal projector. Its norm is therefore uniformly bounded in η.

Step 4 Let $G_1 \in \mathbb{R}^{N\times N}$, $G_2 \in \mathbb{R}^{N\times(d-N)}$ and $G_3 \in \mathbb{R}^{(d-N)\times(d-N)}$ be the matrices respectively defined by

$$G(P) = \begin{pmatrix} G_1 & G_2 \\ G_2^T & G_3 \end{pmatrix}.$$

Let M_η be the matrix

$$C_1^{-1}C_2 = M_\eta.$$

Recall that by Lemma 3.16, $\|M_\eta\| \le C$. With this notation, we have

$$C_\eta^{(P)}G(P)\left(C_\eta^{(P)}\right)^T = C_1\left(G_1 + M_\eta G_2^T + G_2M_\eta^T + M_\eta G_3 M_\eta^T\right)C_1^T,$$

and therefore,

$$\left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} G(P) e_0 \\ = \begin{pmatrix} I_N \\ M_\eta^T \end{pmatrix} \left(G_1 + M_\eta G_2^T + G_2 M_\eta^T + M_\eta G_3 M_\eta^T\right)^{-1} \left(G_1 + M_\eta G_2^T\right) e_0. \quad (3.3.18)$$

We will now show that $M_\eta^T e_0 = \mathcal{O}(\eta)$. By definition,

$$e_0^T M_\eta = e_0^T C_1^{-1} C_2 = e_0^T \mathcal{P} K_1 C_2.$$

By Lemma 3.16, $e_0^T \mathcal{P} = e_0$ and by definition of K_1, $e_0^T K_1 = g_0^T$ where g_0 is the vector satisfying $g_0^T \eta^k \Phi^{(k)}(\eta) = \delta_{0k}$ for $k \leq N-1$. Again by Lemma 3.16, the columns of $C_\eta^{(P)}$ satisfy :

$$\forall 0 \leq j \leq d-1,\ c_j = \eta^j \Phi^{(j)}(\eta) - \sum_{k=0}^{j-1} P_k^{(j)}(1) c_k,$$

with $P_0^{(j)}(1) = 0$ for $j \geq 1$. Consequently c_j is a linear combination of the vectors $\eta^k \Phi^{(k)}(\eta)$ for $1 \leq k \leq j$. Since $\|g_0\| = \mathcal{O}(\eta^{1-N})$, we get $g_0^T C_2 = \mathcal{O}(\eta)$. Coming back to Equation (3.3.18), we have

$$\left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} e_0 = \begin{pmatrix} I_N \\ M_\eta^T \end{pmatrix} e_0 + \mathcal{O}(\eta).$$

Consequently,

$$e_j^T \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)} e_0 = e_j^T \begin{pmatrix} I_N \\ M_\eta^T \end{pmatrix} e_0 + \mathcal{O}(\eta) \\ = \begin{cases} \mathcal{O}(\eta), & 0 \leq j \leq N-1, \\ e_{j-N}^T M_\eta^T e_0 = \mathcal{O}(\eta), & N \leq j \leq d-1. \end{cases}$$

□

We can establish a similar result for $\langle \tilde{p}\,, f \rangle \cdot \left(\Phi'(x) - \widetilde{\Phi}'(x)\right)$.

Lemma 3.21. *There exists a positive constant C independent of η such that for all $f \in H^1_{\mathrm{per}}(0,1)$ and for all $x \in \mathbb{R}$, we have*

$$\forall\, 0 < \eta \leq \eta_0,\ \left|\langle \tilde{p}\,, f \rangle \cdot \left(\Phi'(x) - \widetilde{\Phi}'(x)\right)\right| \leq C \|f\|_{H^1_{\mathrm{per}}},$$

Proof. It is a transposition of the proof of the previous lemma. The first step is simply replaced by

1. $\begin{pmatrix} C_1^{-1} \\ \hline 0 \end{pmatrix} \Phi'(x) - \frac{1}{\eta} P'(x/\eta) = \frac{1}{\eta} \begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(1)$, where $\begin{pmatrix} 0 \\ * \end{pmatrix}$ is uniformly bounded in η and x.

To prove the latter statement, we observe that $P_0' = 0$ and by a Taylor expansion of Φ', we obtain

$$\Phi'(x) = \frac{1}{\eta}\sum_{k=1}^{N-1} \frac{1}{(k-1)!}\left(\frac{x}{\eta} - 1\right)^{k-1} \eta^k \Phi^{(k)}(\eta) + \mathcal{O}(\eta^{N-1}),$$

hence

$$C_1^{-1}\Phi'(x) = \frac{1}{\eta}\begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(1).$$

□

Lemma 3.22. *There exists a positive constant C independent of η such that for all $f \in H^1_{\mathrm{per}}(0,1)$, we have*

$$\forall\, 0 < \eta \leq \eta_0,\ \|Tf\|_{H^1_{\mathrm{per}}} \leq C\eta^{\frac{1}{2}}\|f\|_{H^1_{\mathrm{per}}}$$

Proof. This is a straightforward consequence of Lemmas 3.20 and 3.21. □

Proof of Theorem 3.7. Applying Proposition 3.18 to $\psi_M = (\mathrm{Id} + T)\Pi_M\tilde{\psi}$, where Π_M is the truncation to the first M plane-waves, we have

$$\begin{aligned} |E_M^\eta - E| &\leq C\|(\mathrm{Id} + T)(\Pi_M\tilde{\psi} - \tilde{\psi})\|^2_{H^1_{\mathrm{per}}} \\ &\leq C(\|\Pi_M\tilde{\psi} - \tilde{\psi}\|^2_{H^1_{\mathrm{per}}} + \|T(\Pi_M\tilde{\psi} - \tilde{\psi})\|^2_{H^1_{\mathrm{per}}}). \end{aligned}$$

By Lemma 3.22,

$$\|T(\Pi_M\tilde{\psi} - \tilde{\psi})\|^2_{H^1_{\mathrm{per}}} \leq C\|\Pi_M\tilde{\psi} - \tilde{\psi}\|^2_{H^1_{\mathrm{per}}}\ ,$$

and we deduce from Theorem 3.6 that

$$\begin{aligned} |E_M^\eta - E| &\leq C\|\Pi_M\tilde{\psi} - \tilde{\psi}\|^2_{H^1_{\mathrm{per}}} \\ &\leq C\sum_{j=M+1}^{\infty}(1+j^2)|\widehat{\tilde{\psi}}_j|^2 \\ &\leq C\sum_{j=M+1}^{\infty}\left(\frac{\eta^{4N}}{j^2} + \frac{1}{\eta^{2d-2}j^{2d}}\right) \\ &\leq C\left(\frac{\eta^{4N}}{M} + \frac{1}{\eta^{2d-2}M^{2d-1}}\right). \end{aligned}$$

□

3.4 Perturbation by a continuous potential

In standard electronic structure calculations, the Hartree and exchange-correlation terms are modelled by a potential that is smoother than the Coulomb potential. To reproduce this setting in

our one-dimensional toy model, a smoother potential W is added to the Hamiltonian (3.1.1). In the following, we examine how the VPAW method accelerates the computation of eigenvalues.

Consider the Hamiltonian

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k - Z_a \sum_{k\in\mathbb{Z}} \delta_{a+k} + W \ , \tag{3.4.1}$$

where W is 1-periodic, continuous, $0 < a < 1$, $Z_0, Z_a > 0$.

With the VPAW method, the generalized eigenvalue problem

$$(\mathrm{Id} + T^*)H(\mathrm{Id} + T)\tilde{\psi} = E(\mathrm{Id} + T^*)(\mathrm{Id} + T)\tilde{\psi}, \tag{3.4.2}$$

is solved by expanding $\tilde{\psi}$ in plane-waves. Like in Section 3.1.2, $T = T_0 + T_a$, where T_0 and T_a act on two disjoint regions $\bigcup_{k\in\mathbb{Z}} [-\eta + k, \eta + k]$ and $\bigcup_{k\in\mathbb{Z}} [a - \eta + k, a + \eta + k]$ respectively. The atomic wave functions $(\phi_k)_{0\le k\le N-1}$ are the non-smooth solutions of the atomic Hamiltonian

$$H_0 = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k + V \ ,$$

where V can be different from W. The eigenvalues associated to $(\phi_k)_{0\le k\le N-1}$ are denoted by ϵ_k. To define the pseudo wave functions $(\tilde{\phi}_k)_{0\le k\le N-1}$ and the projectors $(\tilde{p}_k)_{0\le k\le N-1}$, we proceed as in Section 3.1.2.

It follows from the study of the double Dirac delta potential Hamiltonian that the key lemma of the analysis is the structure Lemma 3.9, which describes the behavior of eigenfunctions near the singularities. It is possible to establish a similar result for the eigenfunctions of the Hamiltonian (3.4.1).

Lemma 3.23. *Let ψ be an eigenfunction of the Hamiltonian H given by (3.4.1) for the eigenvalue E. Then in a neighborhood of 0, we have the following expansion :*

$$\psi(x) = \psi(0)\left(\sum_{j=0}^{k} \frac{(-E)^j}{(2j)!}x^{2j} - \frac{Z_0}{2}\frac{(-E)^j}{(2j+1)!}|x|^{2j+1}\right) + \frac{\psi'(0_+) + \psi'(0_-)}{2}\sum_{j=0}^{k}\frac{(-E)^j}{(2j+1)!}x^{2j+1} + \sum_{j=0}^{k}\underbrace{\int\cdots\int}_{2j+2} W\psi(x) + \psi_{2k+2}(x),$$

where ψ_{2k+2} is a C^{2k+2} function satisfying in a neighbourhood of 0

$$\begin{cases} \psi_{2k+2}^{(2k+2)} = (-E)^{k+1}\psi, \\ \psi_{2k+2}(x) = \mathcal{O}(x^{2k+2}). \end{cases}$$

Proof. This lemma can be proved by induction. For $k = 0$, we set

$$\theta_2(x) = \psi(x) + \frac{Z_0}{2}|x|\psi(0) - \int_0^x \int_0^t W(s)\psi(s)\mathrm{d}s\mathrm{d}t$$

and then proceed as in the proof of Lemma 3.9. □

We will now make some assumptions on the potentials V and W:

1. V and W are smooth and 1-periodic;
2. V is even. This property would indeed be satisfied by potentials that does not break the crystal symmetry;

Lemma 3.24. *For $N \geq 2$:*

$$\iint V\Phi(x) = \sum_{k=1}^{N-1} (V\Phi)_k \left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!} \right) + \mathcal{O}\left(x^{2N}\right),$$

where $(V\Phi)_k$ is in $\mathrm{span}(\mathcal{E}^j\Phi(0),\ j \leq N-2)$.

Proof. This lemma is proved by induction.

Initialization Applying Lemma 3.23 with $Z_a = 0$ and $W = V$ to each function ϕ_k, we obtain expansions of the atomic PAW functions ϕ_k in the vicinity of 0:

$$\Phi(x) = \Phi(0)\left(1 - \frac{Z_0}{2}|x|\right) + \mathcal{O}(x^2).$$

Deriving twice $\iint V\Phi$ gives

$$\begin{aligned}\left(\iint V\Phi(x)\right)'' &= V(x)\Phi(x) \\ &= V(0)\Phi(0)\left(1 - \frac{Z_0}{2}|x|\right) + \mathcal{O}(x^2).\end{aligned}$$

Therefore

$$\iint V\Phi(x) = V(0)\Phi(0)\left(\frac{x^2}{2} - \frac{Z_0}{2}\frac{|x|^3}{6}\right) + \mathcal{O}(x^4).$$

Inductive step Let us derive twice $\iint V\Phi$:

$$\begin{aligned}\left(\iint V\Phi(x)\right)'' &= V(x)\Phi(x)\\ &= \left(\sum_{k=0}^{2N-2} V^{(2k)}(0)\frac{x^{2k}}{(2k)!}\right)\left(\sum_{k=0}^{N-1}\left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!}\right) D^k\Phi(0)\right.\\ &\left. + \sum_{j=0}^{N-2}\underbrace{\int\cdots\int}_{(2j+2)} V\Phi(x)\right) + \mathcal{O}(x^{2N}). \end{aligned} \tag{3.4.3}$$

By the induction hypothesis,

$$\underbrace{\int\cdots\int}_{(2j+2)} V\Phi(x) = \sum_{k=j+1}^{N-1}(V\Phi)_{k-j}\left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!}\right) + \mathcal{O}(x^{2N}).$$

Thus,

$$\begin{aligned}\sum_{j=0}^{N-1}\underbrace{\int\cdots\int}_{(2j+2)} V\Phi(x) &= \sum_{j=0}^{N-2}\sum_{k=j+1}^{N-1}(V\Phi)_{k-j}\left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!}\right)\\ &= \sum_{k=1}^{N-1}\sum_{j=0}^{k-1}(V\Phi)_{k-j}\left(\frac{x^{2k}}{(2k)!} - \frac{Z_0}{2}\frac{|x|^{2k+1}}{(2k+1)!}\right).\end{aligned}$$

Going back to (3.4.3), expanding the equation and using the last equation, we obtain the result. □

Lemma 3.25. *In a neighbourhood of* 0*, the vector* Φ *has the following expansion :*

$$\Phi(x) = \sum_{j=0}^{k}\left(\frac{x^{2j}}{(2j)!} - \frac{Z_0}{2}\frac{|x|^{2j+1}}{(2j+1)!}\right)X_j + \Phi_{2k+2}(x)\ ,$$

where the function Φ_{2k+2} *is* C^{2k+2} *at 0 and* X_j *are vectors satisfying*

$$\begin{cases} X_j \in \operatorname{span}(\mathcal{E}^\ell\Phi(0),\ \ell \le j),\\ X_j - \mathcal{E}^j\Phi(0) \in \operatorname{span}(\mathcal{E}^\ell\Phi(0),\ \ell \le j-1),\end{cases} \tag{3.4.4}$$

where $\mathcal{E}$ *is the diagonal matrix with entries* $-\epsilon_0,\dots,-\epsilon_{N-1}$.

Proof. We apply Lemmas 3.23 and 3.24 and notice that the vectors $(V\Phi)_k$ are spanned by $(\mathcal{E}^j\Phi(0),\ j \le k-1)$. □

Lemma 3.26. *The even part of ψ satisfies*

$$\psi_e(x) = \sum_{j=0}^{1} \left(\frac{(-E)^j}{(2j)!} x^{2j} - \frac{Z_0}{2} \frac{(-E)^j}{(2j+1)!} |x|^{2j+1} \right) + W(0)\psi(0) \left(\frac{x^2}{2} - \frac{Z_0}{2} \frac{|x|^3}{3!} \right) + \left(W'(0)\psi_s'(0) - \frac{E}{2} W(0)\psi(0) \right) \frac{x^4}{4!} - \frac{Z_0}{2} \left(\frac{W''(0)}{2} \psi(0) - EW(0)\psi(0) \right) \frac{|x|^5}{5!} + W(0)\psi(0) \left(\frac{x^4}{4!} - \frac{Z_0}{2} \frac{x^5}{5!} \right) + \mathcal{O}\left(x^6\right),$$

where

$$\psi_s'(0) = \frac{\psi'(0_+) + \psi'(0_-)}{2}.$$

Proof. The proof follows from Lemma 3.23 and a careful estimation of the terms $\iint W\psi$ and $\iiiint W\psi$. □

Since W is not even, ψ does not have the same structure as for the double delta potential. More precisely, we can show that because of the term $\iint W\psi$ the singularity of the fifth order term cannot be removed by the VPAW approach.

Lemma 3.27. *For $N = 2$ there exist coefficients c_0 and c_1 such that:*

$$\psi_e(x) - c_0\phi_0(x) - c_1\phi_1(x) = \mathcal{O}\left(x^4\right).$$

For $N \geq 3$, there exists a family of coefficients $(c_k)_{0 \leq k \leq N-1}$ such that:

$$\psi_e(x) - \sum_{k=0}^{N-1} c_k \phi_k(x) = \mathcal{O}\left(x^5\right).$$

Following the same steps as in Section 3.3, we can establish the following theorems.

Theorem 3.28 (Estimates on the Fourier coefficients)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let $\widehat{\tilde{\psi}}_m$ be the m-th Fourier coefficient of $\tilde{\psi}$. Then, there exists a positive constant C such that for all $0 < \eta \leq \eta_0$ and $m \geq \frac{1}{\eta}$*

$$\left| \widehat{\tilde{\psi}}_m \right| \leq C \left(\frac{\eta^{2N \wedge 5}}{m^2} + \frac{1}{\eta^{d-1} m^{d+1}} \right),$$

where $a \wedge b = \min(a, b)$.

Theorem 3.29 (Estimates on the eigenvalues)**.** *Let $N \in \mathbb{N}^*$ and $d \geq N$. Let E_M^η be an eigenvalue of the variational approximation of (3.4.2) in a basis of M plane-waves and for a cut-off radius $0 < \eta \leq \eta_0$, and let E be the corresponding exact eigenvalue. There exists a constant $C > 0$ independent of η and M such that for all $0 < \eta \leq \eta_0$ and $M \geq \frac{1}{\eta}$*

$$|E_M^\eta - E| \leq C \left(\frac{\eta^{4N \wedge 10}}{M} + \frac{1}{\eta^{2d-2}} \frac{1}{M^{2d-1}} \right). \tag{3.4.5}$$

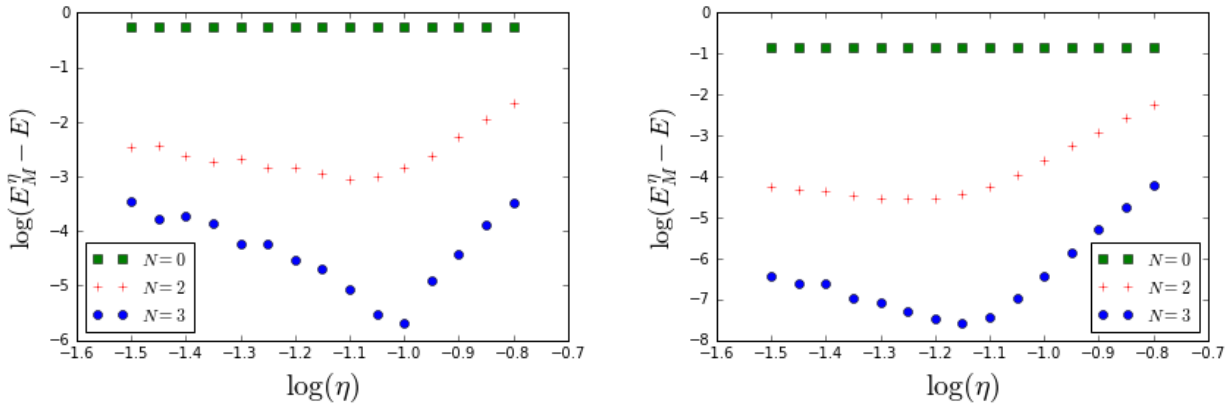
Remark 3.30. *The estimate (3.4.5) does not seem optimal as shown in Figure 3.5.6. It seems that singularities of any order can be removed by the VPAW method.*

3.5 Numerical tests

The goal of this section is to compare the theoretical estimates determined in Sections 3.2 and 3.3 to numerical simulations and show that they are optimal.

All numerical simulations are carried out with $Z_0 = Z_a = 10$ and $a = 0.4$. The Fourier coefficients are evaluated by a very accurate numerical integration.

It is interesting to compare the results (Figure 3.5.1) obtained by a direct expansion of the wave function ψ (here displayed by the points $N = 0$) and the VPAW method. Recall that N is the number of pseudo wave functions used to build the operator T. The smoothness of the pseudo wave functions is set to $d = N$.



(a) Error on the 8-th eigenvalue for $M = 64$ basis functions

(b) Error on the 8-th eigenvalue for $M = 256$ basis functions

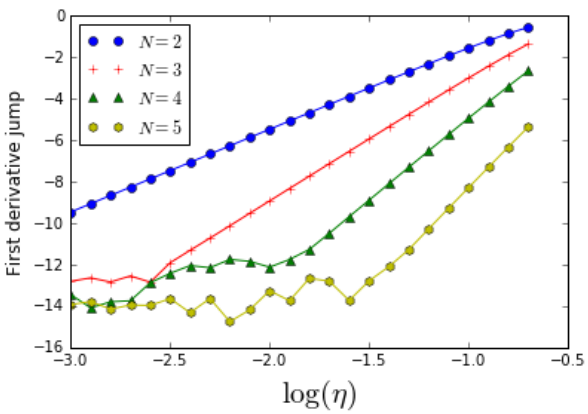
Figure 3.5.1 – The VPAW method compared to a direct calculation for the 8-th eigenvalue

Given a number M of basis functions, the VPAW method is much more accurate than the direct method although it is quite sensitive to the choice of η. More comments on this behavior will be made in Section 3.5.3. We do not report the computing times for the VPAW method because in this study, each time a simulation is run, we generate all the pseudo wave functions $\tilde{\phi}$, the projector functions $\tilde{p}$ and compute their Fourier coefficients. In practice, these data are precomputed and stored in a file. Thus, the only additional cost compared to the direct method comes from the assembly of the matrices $(\mathrm{Id} + T)^* H (\mathrm{Id} + T)$ and $(\mathrm{Id} + T)^* (\mathrm{Id} + T)$.

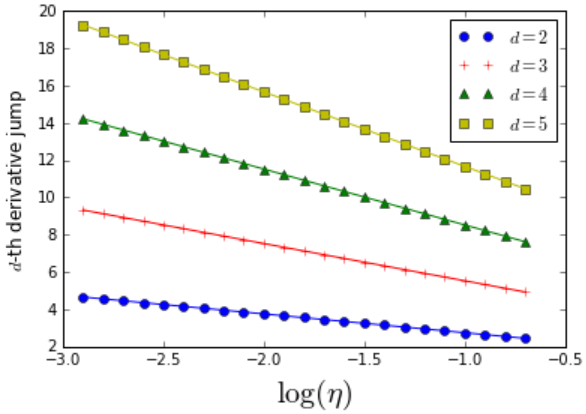
3.5.1 Derivative jumps

Since ψ and the functions ϕ_i are known analytically, it is possible to evaluate the derivative jumps of $\tilde{\psi}$ at 0 and $\pm\eta$ (Figure 3.5.2 and Table 3.5.1). The plots are given for the eigenfunction associated to the lowest eigenvalue of H. The behavior is similar for other eigenfunctions.

These numerical results are in remarkable agreement with Propositions 3.4 and 3.5.



(a) First derivative jump at 0 as a function of η in log-log scale ($d = N$).



(b) d-th derivative jump at $\pm\eta$ as a function of η in log-log scale ($N = 2$).

Figure 3.5.2 – Derivative jumps of the pseudo wave function $\tilde{\psi}$

N	Numerics	Theory
2	3.90	4
3	5.94	6
4	7.85	8
5	9.85	10

(a) Numerical and theoretical slopes for the first derivative jump at 0.

d	Numerics	Theory
2	-1.005	-1
3	-2.000	-2
4	-3.000	-3
5	-4.000	-4

(b) Numerical and theoretical slopes for the d-th derivative jump at $\pm\eta$.

Table 3.5.1 – Comparison of the theoretical and numerical results for the derivative jumps

3.5.2 Comparison of the PAW and VPAW methods in pre-asymptotic regime

The simulations are run for a fixed value of $d = 6$ and two different values of η ($\eta = 0.1$ and $\eta = 0.2$). In Figure 3.5.3, E is the lowest eigenvalue of the 1D-Schrödinger operator H given by (3.1.1).

Recall that our theoretical estimate on the eigenvalue given by the VPAW method is :

$$|E_M^\eta - E| \leq C \left(\frac{\eta^{4N}}{M} + \frac{1}{\eta^{2d-2}} \frac{1}{M^{2d-1}} \right). \tag{3.5.1}$$

To transpose the PAW method to our one-dimensional setting, we need to account for the use of a pseudo-potential. For this purpose, we replace the Dirac delta potential by some smooth function

in Equation (3.1.1). We choose the 1-periodic function χ_ϵ such that

$$\chi_\epsilon(x) = \begin{cases} \frac{C}{\epsilon} \exp\left(-\frac{1}{1-\left(\frac{x}{\epsilon}\right)^2}\right), & x \in [-\epsilon, \epsilon], \\ 0, & x \in [-1/2, 1/2] \setminus [-\epsilon, \epsilon]. \end{cases}$$

where C ensures that $\int_{-\epsilon}^{\epsilon} \chi_\epsilon = 1$. As ϵ goes to 0, χ_ϵ converges to the 1-periodized Dirac potential in $H^{-1}_{\text{per}}(0,1)$.

As expected, the PAW method quickly converges to a wrong value of E. It is interesting to notice that asymptotically, the VPAW convergence is of order $\mathcal{O}\left(\frac{1}{M}\right)$ but for small enough values of M and η, the second term in the RHS of (3.5.1) dominates.

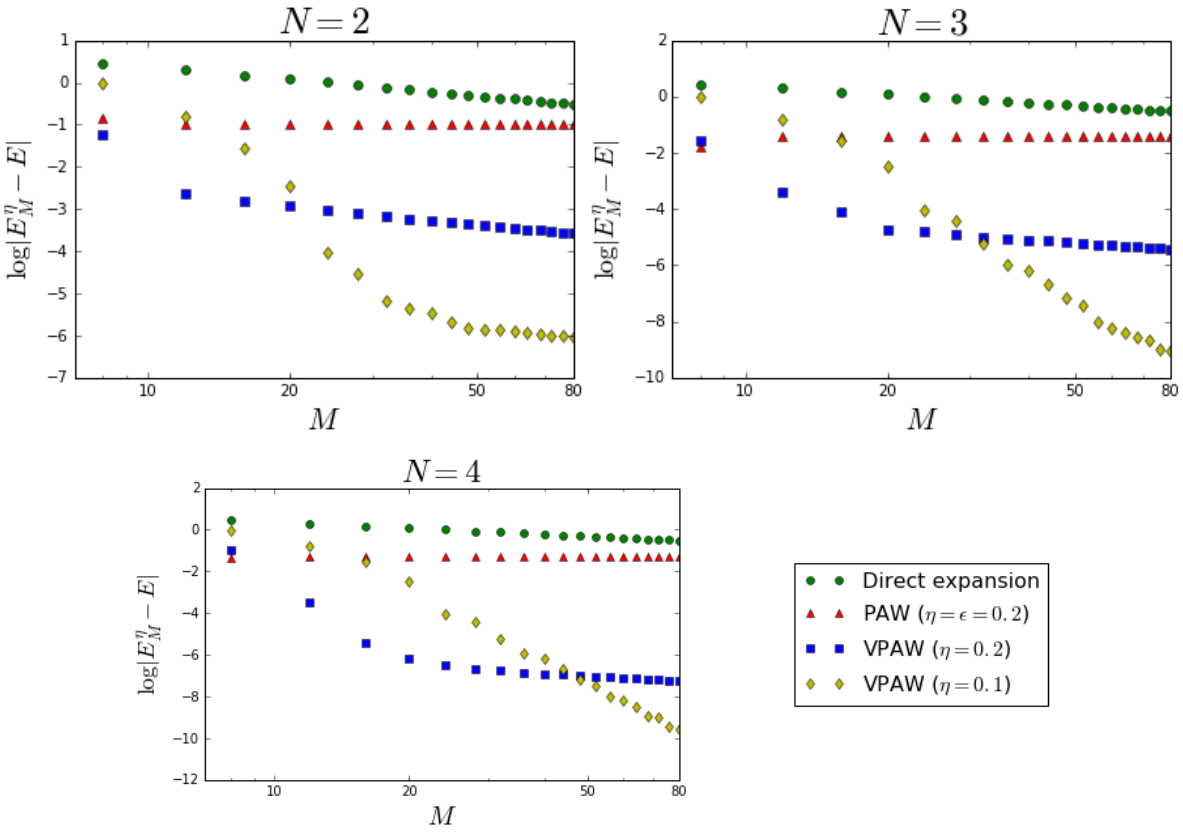


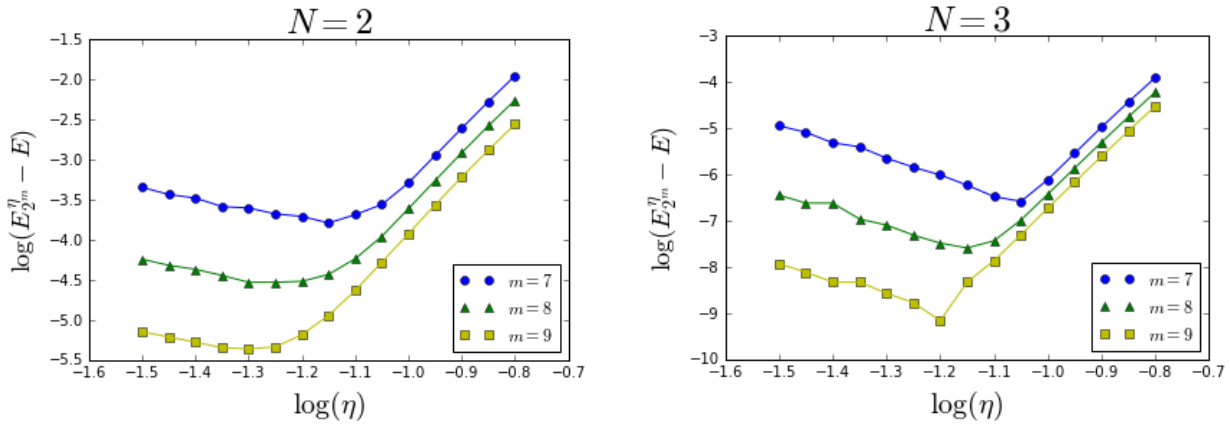
Figure 3.5.3 – Comparison between the PAW and VPAW methods for the lowest eigenvalue

3.5.3 Asymptotic regime

Behavior in the plane-wave cut-off M

The next numerical tests (Figure 3.5.4 and Table 3.5.2) are run with $d = N$ and $N = 2$, $N = 3$. The pseudo wave function $\tilde{\psi}$ is expanded in $M = 2^m$ plane-waves, $m = 7$ to 9.

Here, we can clearly see two regimes : for η small (resp. η large), the leading term in the error is dominated by the d-th derivative jumps at $k \pm \eta$ and $k + a \pm \eta$, $k \in \mathbb{Z}$ (resp. the first derivative



(a) Error on the 9-th eigenvalue with $N = 2$ (b) Error on the 9-th eigenvalue with $N = 3$

Figure 3.5.4 – Error on the eigenvalue for different values of M

jump at k and $k+a$, $k \in \mathbb{Z}$). In each regime, the gaps between the decreasing and increasing slopes seem constant and their evaluation gives the correct orders of convergence in M (see Table 3.5.2).

	Numerics	Theory
Decreasing lines	0.30	$\log(2) \simeq 0.30$
Increasing lines	0.90	$3\log(2) \simeq 0.90$

(a) Gaps for $N = 2$

	Numerics	Theory
Decreasing lines	0.32	$\log(2) \simeq 0.30$
Increasing lines	1.50	$5\log(2) \simeq 1.50$

(b) Gaps for $N = 3$

Table 3.5.2 – Estimation of the order of convergence in M

Dependence of the convergence rate in η on N and d

In each graph of Figure 3.5.5, we have kept M constant to track the dependence of the convergence rate in η. By Theorem 3.7, the logarithm of error on the eigenvalue is given by

$$\log(E_M^\eta - E) = \log(C) + \log\left(\frac{\eta^{4N}}{M} + \frac{1}{\eta^{2d-2}M^{2d-1}}\right).$$

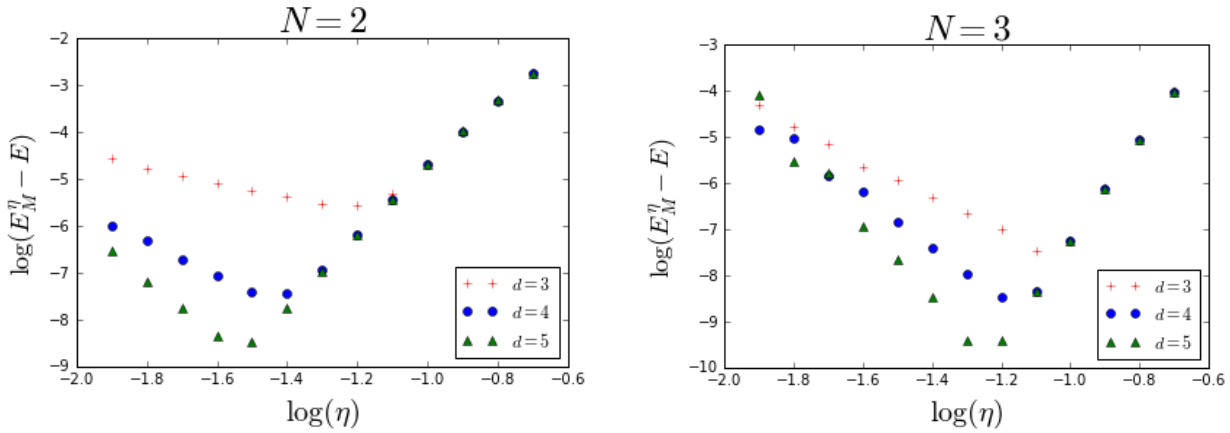
Hence, when η is large, we have

$$\log(E_M^\eta - E) \simeq \log(C) + 4N\log\eta - \log(M),$$

and when η is small, we have

$$\log(E_M^\eta - E) \simeq \log(C) - (2d-2)\log\eta - (2d-1)\log M.$$

Notice that in each graph, for η large, the parameter d has a negligible effect on the error on the eigenvalues, in agreement with our theoretical estimates.



(a) Error on the 8-th eigenvalue with $N = 2$, $M = 256$

(b) Error on the 8-th eigenvalue with $N = 3$, $M = 128$

Figure 3.5.5 – Error on the eigenvalue for different values of d

d	Numerics	Theory
2	6.5	8
3	6.9	8
4	7.2	8

(a) $N = 2$

d	Numerics	Theory
3	10.6	12
4	10.7	12
5	10.9	12

(b) $N = 3$

Table 3.5.3 – Estimation of the increasing slopes in Figure 3.5.5

There is a small discrepancy between the theoretical and numerical values of the increasing slope. A possible explanation could be that the estimates we have given for the first derivative jumps are valid asymptotically as η goes to 0, but the increasing slopes are observed for relatively large values of η.

d	Numerics	Theory
2	-1.6	-2
3	-3.6	-4
4	-6.0	-6

(a) $N = 2$

d	Numerics	Theory
3	-3.8	-4
4	-5.4	-6
5	-7.8	-8

(b) $N = 3$

Table 3.5.4 – Estimation of the decreasing slopes in Figure 3.5.5

For the decreasing slopes, our estimate is in very good agreement with the numerical simulations.

3.5.4 Perturbation by a continuous potential

In this subsection, we study the VPAW method applied to the Hamiltonian (3.4.1) with $W(x) = 10\sin(2\pi x + 0.2)$. Since this model is not exactly solvable, we use a P2 finite elements method to compute very accurately the eigenvalues (the relative error on the computed eigenvalue is less than 10^{-10}).

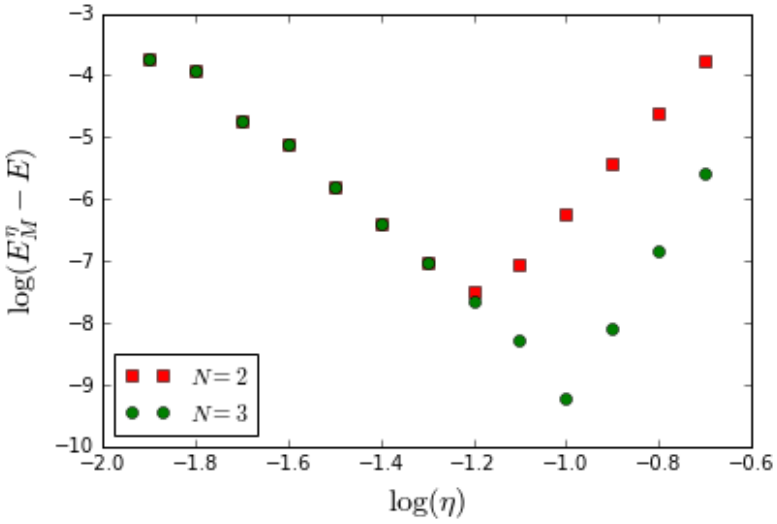


Figure 3.5.6 – Error on the first eigenvalue as a function of η ($M = 128, d = 4$)

N	Numerics	Theory
2	8.2	8
3	12	10

(a) Increasing slopes

	Numerics	Theory
$N = 2$ and $N = 3$	-5.7	-6

(b) Decreasing slopes

Table 3.5.5 – Estimation of the slopes in Figure 3.5.6

For $N = 3$, the increasing part of the curve has a slope which is very close to the theoretical estimation of Theorem 3.7 (that is with $W = 0$). This seems to indicate that the VPAW method removes the singularity at the nucleus up to the fifth order, but we are unable to support this observation with rigorous numerical analysis arguments.

CHAPTER 4

PROJECTOR AUGMENTED-WAVE IN A ONE-DIMENSIONAL SETTING

In this chapter, based on [Dup17], the PAW method is applied to the one-dimensional double Dirac potential Hamiltonian. The eigenfunctions of this model display a cusp at the location of the Dirac potentials that is reminiscent of the Kato cusp condition [Kat57]. Error estimates on the lowest PAW eigenvalue are proved for several choices of PAW parameters. The present analysis relies on some results on the variational PAW method (VPAW method) [BCD17a, BCD17b] which is a slight modification of the original PAW method. Contrary to the PAW method, the VPAW generalized eigenvalue problem is in one-to-one correspondence with the original eigenvalue problem. By estimating the difference between the PAW and VPAW generalized eigenvalue problems, error estimates on the lowest PAW generalized eigenvalue are found.

This chapter is organized as follows. The PAW formalism applied to the one-dimensional periodic Schrödinger operator is presented in Section 4.1. Estimates on the PAW truncation error for the lowest eigenvalue of this model can be found in Section 4.2. Proofs are gathered in Section 4.3 and numerical tests are given in Section 4.4.

4.1 The PAW method in a one-dimensional setting

A general overview of the VPAW and PAW methods for 3-D electronic Hamiltonians may be found in [BCD17a] for the molecular setting and in [BCD17b] for crystals. Here, the presentation of the VPAW and PAW methods is limited to the application to the 1-D periodic Schrödinger operator with double Dirac potentials.

4.1.1 The double Dirac potential Schrödinger operator

We are interested in the lowest eigenvalue of the 1-D periodic Schrödinger operator H on $L^2_{\mathrm{per}}(0,1) := \{f \in L^2_{\mathrm{loc}}(\mathbb{R}) \mid f \text{ 1-periodic}\}$ with form domain $H^1_{\mathrm{per}}(0,1) := \{f \in H^1_{\mathrm{loc}}(\mathbb{R}) \mid f \text{ 1-periodic}\}$:

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k - Z_a \sum_{k\in\mathbb{Z}} \delta_{k+a}, \tag{4.1.1}$$

where $0 < a < 1$, $Z_0, Z_a > 0$.

A mathematical analysis has been carried out in [CD17]. There are two negative eigenvalues $E_0 = -\omega_0^2$ and $E_1 = -\omega_1^2$ which are given by the zeros of the function

$$f(\omega) = 2\omega^2(1-\cosh(\omega)) + (Z_0+Z_a)\omega\sinh(\omega) - Z_0Z_a\sinh(a\omega)\sinh((1-a)\omega).$$

The corresponding eigenfunctions are

$$\psi_k(x) = \begin{cases} A_{1,k}\cosh(\omega_k x) + B_{1,k}\sinh(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cosh(\omega_k x) + B_{2,k}\sinh(\omega_k x)\ , & a \le x \le 1, \end{cases}$$

where the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a.

There is an infinity of positive eigenvalues $E_{k+2} = \omega_{k+2}^2$ which are given by the k-th zero of the function :

$$f(\omega) = 2\omega^2(1-\cos(\omega)) + (Z_0+Z_a)\omega\sin(\omega) + Z_0Z_a\sin(a\omega)\sin((1-a)\omega),$$

and the corresponding eigenfunctions $H\psi_k = \omega_k^2\psi_k$ are

$$\psi_k(x) = \begin{cases} A_{1,k}\cos(\omega_k x) + B_{1,k}\sin(\omega_k x)\ , & 0 \le x \le a, \\ A_{2,k}\cos(\omega_k x) + B_{2,k}\sin(\omega_k x)\ , & a \le x \le 1, \end{cases} \tag{4.1.2}$$

where again the coefficients $A_{1,k}$, $A_{2,k}$, $B_{1,k}$ and $B_{2,k}$ are determined by the continuity conditions and the derivative jumps at 0 and a. Notice that the eigenfunctions of H have a first derivative jump that is similar to the Kato cusp condition satisfied by the solutions of 3D electronic Hamiltonian [Kat57]:

$$\psi_k'(0_+) - \psi_k'(0_-) = -Z_0\psi_k(0).$$

4.1.2 The PAW method

General principle

The PAW method consists in replacing the original eigenvalue problem $H\psi = E\psi$ by the generalized eigenvalue problem

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T)\widetilde{\psi} = E(\mathrm{Id}+T^*)(\mathrm{Id}+T)\widetilde{\psi}, \tag{4.1.3}$$

where $\mathrm{Id}+T$ is an invertible operator. It is clear that (4.1.3) is equivalent to $H\psi = E\psi$ where $\psi = (\mathrm{Id}+T)\widetilde{\psi}$.

The transformation T is the sum of two operators acting in regions near the atomic sites that do not overlap (*i.e.* $T_0T_a = T_aT_0 = 0$)

$$T = T_0 + T_a, \quad T_0 = \sum_{i=0}^{\infty} (\phi_i^0 - \widetilde{\phi}_i^0) \left\langle \widetilde{p}_i^0 \,, \cdot \right\rangle, \quad T_a = \sum_{i=0}^{\infty} (\phi_i^a - \widetilde{\phi}_i^a) \left\langle \widetilde{p}_i^a \,, \cdot \right\rangle,$$

where $\langle \cdot \,, \cdot \rangle$ denotes the $L^2_{\mathrm{per}}(0,1)$ scalar product.

The atomic wave functions $(\phi_j^0)_{j\in\mathbb{N}}$ are solutions of an atomic eigenvalue problem

$$H_0\phi_j^0 := -\frac{\mathrm{d}^2\phi_j^0}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k \phi_j^0 = \epsilon_j^0 \phi_j^0,$$

and the pseudo wave functions $(\widetilde{\phi}_j^0)_{j\in\mathbb{N}}$ and the projector functions $(\widetilde{p}_j^0)_{j\in\mathbb{N}}$ satisfy the following conditions :

1. for each $j \in \mathbb{N}$,
   - for $x \in \mathbb{R} \setminus \bigcup_{k\in\mathbb{Z}} [-\eta + k, \eta + k]$, $\widetilde{\phi}_j^0(x) = \phi_j^0(x)$;
   - $\widetilde{\phi}_j^0$ restricted to $\bigcup_{k\in\mathbb{Z}} [-\eta + k, \eta + k]$ is a smooth function;
2. for each $j \in \mathbb{N}$, $\mathrm{supp}\, \widetilde{p}_j^0 \subset \bigcup_{k\in\mathbb{Z}} [-\eta + k, \eta + k]$;
3. the families $(\widetilde{\phi}_j^0|_{[-\eta,\eta]})_{j\in\mathbb{N}}$ and $(\widetilde{p}_j^0|_{[-\eta,\eta]})_{j\in\mathbb{N}}$ form a Riesz basis of $L^2(-\eta,\eta)$, *i.e.*

$$\forall\, j,k \in \mathbb{N}, \quad \int_{-\eta}^{\eta} \widetilde{p}_k^0(x)\widetilde{\phi}_j^0(x)\,\mathrm{d}x = \delta_{kj},$$

and for any $f \in L^2(-\eta,\eta)$, we have

$$\sum_{k=0}^{\infty} \left\langle \widetilde{p}_k^0 \,, f \right\rangle \widetilde{\phi}_k^0(x) = f(x), \quad \text{for a.a. } x \in \bigcup_{k\in\mathbb{Z}} [-\eta + k, \eta + k]. \tag{4.1.4}$$

Similarly, $(\phi_i^a)_{i\in\mathbb{N}^*}$ are eigenfunctions of the operator $H_a = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_{a+k}$, the pseudo wave functions $(\widetilde{\phi}_j^a)_{j\in\mathbb{N}^*}$ and the projector functions $(\widetilde{p}_j^a)_{j\in\mathbb{N}^*}$ are defined as above.

The relation (4.1.4) enables one to write the expression of $(\mathrm{Id}+T^*)H(\mathrm{Id}+T)$ and $(\mathrm{Id}+T^*)(\mathrm{Id}+T)$ as

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T) = H + \sum_{\substack{i,j=0 \\ I=\{0,a\}}}^{\infty} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, H\widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{4.1.5}$$

and

$$(\mathrm{Id}+T^*)(\mathrm{Id}+T) = \mathrm{Id} + \sum_{\substack{i,j=0\\ I=\{0,a\}}}^{\infty} \widetilde{p}_i^I \left(\langle \phi_i^I \,,\, \phi_j^I \rangle - \left\langle \widetilde{\phi}_i^I \,,\, \widetilde{\phi}_j^I \right\rangle \right) \langle \widetilde{p}_j^I \,,\, \cdot \rangle \,. \tag{4.1.6}$$

Introduction of a pseudopotential

A further modification is possible. As the pseudo wave functions $\widetilde{\phi}_i^0$ (resp. $\widetilde{\phi}_i^a$) are equal to ϕ_i^0 (resp. ϕ_i^a) outside $\bigcup_{k\in\mathbb{Z}} [-\eta+k, \eta+k]$ (resp. $\bigcup_{k\in\mathbb{Z}} [a-\eta+k, a+\eta+k]$), the integrals appearing in (4.1.5) can be truncated to the interval $(-\eta,\eta)$ (resp. $(a-\eta, a+\eta)$). Doing so, another expression of $(\mathrm{Id}+T^*)H(\mathrm{Id}+T)$ can be obtained :

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T) = H + \sum_{\substack{i,j=0\\ I=\{0,a\}}}^{\infty} \widetilde{p}_i^I \left(\langle \phi_i^I \,,\, H\phi_j^I \rangle_{I,\eta} - \left\langle \widetilde{\phi}_i^I \,,\, H\widetilde{\phi}_j^I \right\rangle_{I,\eta} \right) \langle \widetilde{p}_j^I \,,\, \cdot \rangle \,,$$

where

$$\langle f \,,\, g \rangle_{I,\eta} = \begin{cases} \int_{-\eta}^{\eta} f(x)g(x)\,\mathrm{d}x, & \text{when } I=0, \\ \int_{a-\eta}^{a+\eta} f(x)g(x)\,\mathrm{d}x, & \text{when } I=a. \end{cases}$$

Using this expression of the operator H^{PAW}, it is possible to introduce a smooth 1-periodic potential $\chi_\epsilon = \sum_{k\in\mathbb{Z}} \frac{1}{\epsilon}\chi\left(\frac{\cdot-k}{\epsilon}\right)$ with $\epsilon \leq \eta$, such that

1. χ is a smooth nonnegative function with support $[-1,1]$ and $\int_{-1}^{1}\chi(x)\,\mathrm{d}x = 1$;
2. $\chi_\epsilon \underset{\epsilon\to 0}{\longrightarrow} \sum_{k\in\mathbb{Z}} \delta_k$ in $H^{-1}_{\mathrm{per}}(0,1)$.

The potential χ_ϵ will be called a *pseudopotential* in the following.

The expression of $(\mathrm{Id}+T^*)H(\mathrm{Id}+T)$ becomes

$$(\mathrm{Id}+T^*)H(\mathrm{Id}+T) = H_{\mathrm{ps}} + \sum_{\substack{i,j=0\\ I=\{0,a\}}}^{\infty} \widetilde{p}_i^I \left(\langle \phi_i^I \,,\, H\phi_j^I \rangle_{I,\eta} - \left\langle \widetilde{\phi}_i^I \,,\, H_{\mathrm{ps}}\widetilde{\phi}_j^I \right\rangle_{I,\eta} \right) \langle \widetilde{p}_j^I \,,\, \cdot \rangle \,, \tag{4.1.7}$$

with

$$H_{\mathrm{ps}} = \frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0\chi_\epsilon - Z_a\chi_\epsilon(\cdot - a).$$

4.1.3 The PAW method in practice

In practice, the double sums appearing in the operators (4.1.5), (4.1.6) and (4.1.7) have to be truncated to some level N. Doing so, the identity $\psi = (\mathrm{Id}+T)\widetilde{\psi}$ is lost and the eigenvalues of the truncated equations are not equal to those of the original operator H (4.1.1). The PAW method introduces an error that will be estimated in the rest of chapter. First, we define the PAW functions appearing in (4.1.5), (4.1.6) and (4.1.7).

Generation of the PAW functions

For the double Dirac potential Hamiltonian, the PAW functions are defined as follows.

Atomic wave functions ϕ_k^0 As mentioned earlier, the atomic wave functions $(\phi_k^0)_{1\leq k\leq N}$ are eigenfunctions of the Hamiltonian H_0

$$H_0 = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k.$$

By parity, each eigenfunction of this operator is either even or odd. The odd eigenfunctions are in fact $x \mapsto \sin(2\pi k x)$ and the even ones are the 1-periodic functions such that

$$\begin{cases} \phi_0^0(x) := \cosh(\omega_0(x-\frac{1}{2})) & \text{for } x\in[0,1], \\ \phi_k^0(x) := \cos(\omega_k(x-\frac{1}{2})) & \text{for } x\in[0,1],\ k\in\mathbb{N}^*, \end{cases}$$

In the sequel (and in particular in (4.1.9) and (4.1.12) below), only the non-smooth thus even eigenfunctions $(\phi_i^0)_{1\leq i\leq N}$ are selected. The corresponding eigenvalues are denoted by $(\epsilon_i^0)_{1\leq i\leq N}$:

$$H_0\phi_i^0 = \epsilon_i^0\phi_i^0.$$

Pseudo wave function $\widetilde{\phi}_i^0$ The pseudo wave functions $(\widetilde{\phi}_i^0)_{1\leq i\leq N} \in \left(H^1_{\mathrm{per}}(0,1)\right)^N$ are defined as follows:

1. for $x \notin \bigcup_{k\in\mathbb{Z}} [-\eta+k, \eta+k]$, $\widetilde{\phi}_i^0(x) = \phi_i^0(x)$.
2. for $x \in \bigcup_{k\in\mathbb{Z}} [-\eta+k, \eta+k]$, $\widetilde{\phi}_i^0$ is an even polynomial of degree at most $2d-2$, $d \geq N$.
3. $\widetilde{\phi}_i^0$ is C^{d-1} at η *i.e.* $(\widetilde{\phi}_i^0)^{(k)}(\eta) = (\phi_i^0)^{(k)}(\eta)$ for $0 \leq k \leq d-1$.

Projector functions $\widetilde{p}_i^0$ Let ρ be a positive, smooth function with support included in $[-1,1]$ and $\rho_\eta(t) = \sum_{k\in\mathbb{Z}} \rho\left(\frac{t-k}{\eta}\right)$. The projector functions $(\widetilde{p}_i^0)_{1\leq i\leq N}$ are obtained by an orthogonalization procedure from the functions $p_i^0(t) = \rho_\eta(t)\widetilde{\phi}_i^0(t)$ in order to satisfy the duality condition :

$$\left\langle \widetilde{p}_i^0 \,, \widetilde{\phi}_j^0 \right\rangle = \delta_{ij}.$$

More precisely, the matrix $B_{ij} := \left\langle p_i^0 \,, \widetilde{\phi}_j^0 \right\rangle$ is computed and inverted to obtain the projector functions

$$\widetilde{p}_k^0 = \sum_{j=1}^{N} (B^{-1})_{kj} p_j^0.$$

The matrix B is the Gram matrix of the functions $(\widetilde{\phi}_j^0)_{1\leq j\leq N}$ for the weight ρ_η. The orthogonalization is possible only if the family $(\widetilde{\phi}_i^0)_{1\leq i\leq N}$ is linearly independent - thus necessarily $d \geq N$.

The eigenvalue problems

For the case *without* pseudopotentials, the PAW eigenvalue problem is given by

$$H^N f = E^{(\eta)} S^N f, \tag{4.1.8}$$

where

$$H^N = H + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, H\widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{4.1.9}$$

and

$$S^N = \mathrm{Id} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, \phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle. \tag{4.1.10}$$

The practical interest in solving the eigenvalue problem (4.1.8) is very limited since this version of the PAW method does not remove the singularity caused by the Dirac potentials. The next eigenvalue problem where the Dirac potentials are replaced by smoother potentials is closer to the implementation of the PAW method in practice.

For the case *with* pseudopotentials, the PAW eigenvalue problem becomes

$$H^{PAW} f = E^{PAW} S^{PAW} f, \tag{4.1.11}$$

where

$$H^{PAW} = H_{\mathrm{ps}} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, H\phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, H_{\mathrm{ps}}\widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle, \tag{4.1.12}$$

and

$$S^{PAW} = S^N = \mathrm{Id} + \sum_{\substack{i,j=1 \\ I=\{0,a\}}}^{N} \widetilde{p}_i^I \left(\left\langle \phi_i^I \,, \phi_j^I \right\rangle - \left\langle \widetilde{\phi}_i^I \,, \widetilde{\phi}_j^I \right\rangle \right) \left\langle \widetilde{p}_j^I \,, \cdot \right\rangle. \tag{4.1.13}$$

If the projector functions $(\widetilde{p}_i)_{1 \le i \le N}$ are smooth, then the eigenfunctions f in (4.1.11) are smooth as well, and their plane-wave expansions converge very quickly. Thus, if the difference $|E^{PAW} - E|$ is smaller than a desired accuracy, it is more interesting to solve (4.1.11) than the original eigenvalue problem. However, an estimate on the difference $|E^{PAW} - E|$ is needed in order to justify the use of the PAW method.

To the best of our knowledge, there exists no estimation of this error except a heuristic analysis in the seminal work of Blöchl ([Blo94], Sections VII.B and VII.C). However, his analysis relies on an expansion of the eigenvalue in $f - \sum_{i=1}^{N} \langle \widetilde{p}_i \,, f \rangle \, \widetilde{\phi}_i$ which goes to 0 if the families $(\widetilde{p}_i)_{i \in \mathbb{N}^*}$ and $(\widetilde{\phi}_i)_{i \in \mathbb{N}^*}$ form a Riesz basis, but a convergence rate of the expansion of f in this Riesz basis is not given. Moreover the inclusion of a pseudopotential in the PAW treatment is not taken into account.

The goal of this chapter is to provide error estimates on the lowest PAW eigenvalue of problems (4.1.8) and (4.1.11). To prove this result, the PAW method is interpreted as a perturbation of the VPAW method introduced in [BCD17a, BCD17b] which has the same eigenvalues as the original problem. In the following, when we refer to the PAW method, it will be to the truncated equations (4.1.8) or (4.1.11).

4.1.4 The VPAW method

The analysis of the PAW method relies on the connexion between the VPAW and the PAW methods. A brief description of the VPAW method is given in this subsection.

Like the PAW method, the principle of the VPAW method consists in replacing the original eigenvalue problem

$$H\psi = E\psi,$$

by the generalized eigenvalue problem:

$$(\mathrm{Id} + T_N^*)H(\mathrm{Id} + T_N)\widetilde{\psi} = E(\mathrm{Id} + T_N)(\mathrm{Id} + T_N)\widetilde{\psi}, \tag{4.1.14}$$

where $\mathrm{Id} + T_N$ is an invertible operator. Thus both problems have the same eigenvalues and it is straightforward to recover the eigenfunctions of the former from the generalized eigenfunctions of the latter:

$$\psi = (\mathrm{Id} + T_N)\widetilde{\psi}.$$

Again, T_N is the sum of two operators acting near the atomic sites

$$T_N = T_{0,N} + T_{a,N}. \tag{4.1.15}$$

To define $T_{0,N}$, we fix an integer N and a radius $0 < \eta < \min(\frac{a}{2}, \frac{1-a}{2})$ so that $T_{0,N}$ and $T_{a,N}$ act on two disjoint regions $\bigcup_{k\in\mathbb{Z}}[-\eta + k, \eta + k]$ and $\bigcup_{k\in\mathbb{Z}}[a - \eta + k, a + \eta + k]$ respectively.

The operators $T_{0,N}$ and $T_{a,N}$ are given by

$$T_{0,N} = \sum_{i=1}^{N}(\phi_i^0 - \widetilde{\phi}_i^0)\left\langle \widetilde{p}_i^0\,, \cdot \right\rangle, \qquad T_{a,N} = \sum_{i=1}^{N}(\phi_i^a - \widetilde{\phi}_i^a)\left\langle \widetilde{p}_i^a\,, \cdot \right\rangle\,, \tag{4.1.16}$$

with the same functions ϕ_i^I, $\widetilde{\phi}_i^I$ and $\widetilde{p}_i^I$, $I = 0, a$ as in Section 4.1.2. The only difference with the PAW method is that the sums appearing in (4.1.16) are *finite*, thereby avoiding a truncation error.

In the following, the VPAW operators are denoted by

$$\widetilde{H} = (\mathrm{Id} + T_N^*)H(\mathrm{Id} + T_N), \tag{4.1.17}$$

and

$$\widetilde{S} = (\mathrm{Id} + T_N^*)(\mathrm{Id} + T_N), \tag{4.1.18}$$

The full analysis of the VPAW method can be found in Chapter 3. We proved that the cusps

at 0 and a of the eigenfunctions $\widetilde{\psi}$ are reduced by a factor η^{2N} but the d-th derivative jumps introduced by the pseudo wave functions $\widetilde{\phi}_k$ blow up as η goes to 0 at the rate η^{1-d}. Using Fourier methods to solve (4.1.14), we observe an acceleration of convergence that can be tuned by the VPAW parameters η -the cut-off radius- N -the number of PAW functions used at each site- and d -the smoothness of the PAW pseudo wave functions.

4.2 Main results

The PAW method is well-posed if the projector functions $(\widetilde{p}_i^I)_{1\leq i\leq N}$ are well-defined. This question has already been addressed in Chapter 3 where it is shown that we simply need to take $\eta < \eta_0$ for some positive η_0.

Assumption 4.1. *Let $\eta_0 > 0$ such that for all $0 < \eta < \eta_0$, the projector functions $(\widetilde{p}_i)_{1\leq i\leq N}$ in Section 4.1.3 are well-defined.*

Moreover since the analysis of the PAW error requires the VPAW method to be well-posed, the matrix $\left(\langle \widetilde{p}_j^I, \phi_k^I\rangle\right)_{1\leq j,k\leq N}$ is assumed to be invertible for $0 < \eta \leq \eta_0$.

Assumption 4.2. *For all $0 < \eta < \eta_0$, the matrix $\left(\langle \widetilde{p}_j^I, \phi_k^I\rangle\right)_{1\leq j,k\leq N}$ is invertible.*

Under these assumptions, the following theorems are established. Proofs are gathered in Section 4.3.

4.2.1 PAW method without pseudopotentials

Theorem 4.1. *Let ϕ_i^I, $\widetilde{\phi}_i^I$ and $\widetilde{p}_i^I$, for $i = 1, \ldots, N$ and $I = 0, a$ be the functions defined in Section 4.1.3. Suppose $\eta_0 > 0$ satisfies Assumption 4.1 and Assumption 4.2. Let $E^{(\eta)}$ be the lowest eigenvalue of the generalized eigenvalue problem (4.1.8). Let E_0 be the lowest eigenvalue of H (4.1.1). Then there exists a positive constant C independent of η such that for all $0 < \eta \leq \eta_0$*

$$-C\eta \leq E^{(\eta)} - E_0 \leq C\eta^{2N}. \tag{4.2.1}$$

The constant C appearing in (4.2.1) (and in the theorems that will follow) depends on the other PAW parameters N and d in a nontrivial way. The upper bound is proved by using the VPAW eigenfunction $\widetilde{\psi}$ associated to the lowest eigenvalue E_0 for which we have precise estimates of the difference between the operators H^{PAW} and $\widetilde{H}$. As expected (and confirmed by numerical simulations in Section 4.4.1) the PAW method without pseudopotentials is *not* variational. Moreover as the Dirac delta potentials are not removed, Fourier methods applied to the eigenvalue problem (4.1.8) converge slowly.

4.2.2 PAW method with pseudopotentials

The following theorems are stated for $\epsilon = \eta$, *i.e.* when the support of the pseudopotential is equal to the acting region of the PAW method. Indeed, in the proof of Theorem 4.2, it appears that worse estimates are obtained when a pseudopotential χ_ϵ with $\epsilon < \eta$ is used.

Theorem 4.2. *Let ϕ_i^I, $\widetilde{\phi}_i^I$ and $\widetilde{p}_i^I$, for $i = 1, \dots, N$ and $I = 0, a$ be the functions defined in Section 4.1.3. Suppose $\eta_0 > 0$ satisfies Assumption 4.1 and Assumption 4.2. Let E^{PAW} the lowest eigenvalue of the generalized eigenvalue problem (4.1.11). Let E_0 be the lowest eigenvalue of H (4.1.1). Then there exists a positive constant C independent of η such that for all $0 < \eta \leq \eta_0$*

$$-C\eta \leq E^{PAW} - E_0 \leq C\eta^2. \tag{4.2.2}$$

Introducing a pseudopotential in H^{PAW} worsens the upper bound on the PAW eigenvalue. This is due to our construction of the PAW method in Section 4.1.2 where only even PAW functions are considered. Incorporating odd PAW functions in the PAW treatment, it is possible to improve the upper bound on the PAW eigenvalue and recover the bound in Theorem 4.1 (see Section 4.3.3).

As the cut-off radius η goes to 0, the lowest eigenvalue of the truncated PAW equations is closer to the exact eigenvalue. This is also observed in different implementations of the PAW method and is in fact one of the main guidelines: a small cutoff radius yields more accurate results [JTH14, **?**].

Theorem 4.3. *Let ϕ_i^I, $\widetilde{\phi}_i^I$ and $\widetilde{p}_i^I$, for $i = 1, \dots, N$ and $I = 0, a$ be the functions defined in Section 4.1.3. Suppose $\eta_0 > 0$ satisfies Assumption 4.1 and Assumption 4.2. Let E_M^{PAW} be the lowest eigenvalue of the variational approximation of (4.1.11), with H^{PAW} given by (4.1.12) in a basis of M plane waves. Let E_0 be the lowest eigenvalue of H (4.1.1). There exists a positive constant C independent of η and M such that for all $0 < \eta < \eta_0$ and for all $n \in \mathbb{N}^*$*

$$\left|E_M^{PAW} - E_0\right| \leq C\left(\eta + \frac{\eta^2}{(\eta M)^n}\right).$$

According to Theorem 4.3, if we want to compute E_0 up to a desired accuracy ε, then it suffices to choose the PAW cut-off radius η equal to $\frac{1}{C\varepsilon}$ and solve the PAW eigenvalue problem (4.1.11) with $M \geq \frac{1}{\eta}$ plane-waves.

Remark 4.4. *Using more PAW functions does not improve the bound on the computed eigenvalue. It is due to the poor lower bound in Theorems 4.2 and 4.20. Should the PAW method with odd functions (Section 4.3.3) be variational, we would know a priori that $E^{PAW} \geq E_0$. Therefore, we could prove the estimate*

$$0 < E_M^{PAW} - E_0 \leq C\left(\eta^{2N} + \frac{\eta^2}{(\eta M)^n}\right).$$

Hence taking a plane wave cut-off $M \geq \frac{1}{\eta}$ would ensure that the eigenvalue E_0 is computed up to an error of order $\mathcal{O}(\eta^{2N})$.

4.3 Proofs

4.3.1 Useful lemmas

We introduce some notation used in the below proofs. Let $I \in \{0, a\}$ and

$$\begin{aligned}
p^I(t) &:= (p_1^I(t), \dots, p_N^I(t))^T \in \mathbb{R}^N, \\
\widetilde{p}^I(t) &:= (\widetilde{p}_1^I(t), \dots, \widetilde{p}_N^I(t))^T \in \mathbb{R}^N, \\
\left\langle \widetilde{p}^I, f \right\rangle &:= \left(\left\langle \widetilde{p}_1^I, f \right\rangle, \dots, \left\langle \widetilde{p}_N^I, f \right\rangle \right)^T \in \mathbb{R}^N, \forall\, f \in L^2_{\mathrm{per}}(0,1), \\
\Phi_I(t) &:= (\phi_1^I(t), \dots, \phi_N^I(t))^T \in \mathbb{R}^N, \\
\widetilde{\Phi}_I(t) &:= (\widetilde{\phi}_1^I(t), \dots, \widetilde{\phi}_N^I(t))^T \in \mathbb{R}^N, \\
A_I &:= (\langle p_i^I, \phi_j^I \rangle)_{1 \le i,j \le N} \in \mathbb{R}^{N \times N}.
\end{aligned}$$

For $p \in [1, \infty]$, we denote by

$$\|f\|_{p,\eta,I} = \begin{cases} \|f\|_{L^p(-\eta,\eta)}, & \text{if } I = 0 \\ \|f\|_{L^p(a-\eta,a+\eta)}, & \text{if } I = a \end{cases}.$$

First, we recall some results of [BCD17b] that are useful for the proofs of Theorems 4.1 to 4.3.

Lemma 4.5. *Let $\widetilde{\psi}$ be an eigenfunction of (4.1.1) associated to the lowest eigenvalue E_0 and $\widetilde{\psi}_e$ be its even part. Let $\psi = (\mathrm{Id} + T_N)\widetilde{\psi}$ where T_N is the operator (4.1.15) and ψ_e be the even part of ψ. Suppose $\eta_0 > 0$ satisfies Assumption 4.1 and Assumption 4.2. Then there exists a constant C independent of η such that for any $0 < \eta \le \eta_0$ we have*

$$\left\| \widetilde{\psi}_e - \left\langle \widetilde{p}^I, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \right\|_{\infty,\eta,I} \le C\eta^{2N},$$

and

$$\left\| E_0 \psi_e - \left\langle A_I^{-1} p^I, \psi \right\rangle \cdot \mathcal{E}^I \Phi_I \right\|_{\infty,\eta,I} \le C\eta^{2N-2},$$

where $\mathcal{E}^I$ is the $N \times N$ diagonal matrix with entries $(-\epsilon_1^I, \dots, -\epsilon_N^I)$.

Proof. We have

$$\widetilde{\psi} - \left\langle \widetilde{p}^I, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I = \psi - \left\langle A_I^{-1} p, \psi \right\rangle \cdot \Phi_I, \tag{4.3.1}$$

and in combination with Lemmas 4.2 and 4.6 in [BCD17b], we obtain

$$\left\| \widetilde{\psi}_e - \left\langle \widetilde{p}^I, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \right\|_{\infty,\eta,I} \le C\eta^{2N},$$

where $C > 0$ is independent of η.

The second estimate is proved the same way. □

Lemma 4.6. *Let $P_k(t) = \frac{1}{2^k k!}(t^2-1)^k$ and $P(t) = (P_0(t), \dots, P_{d-1}(t))^T$. Let $C_\eta^{(P)} \in \mathbb{R}^{N\times d}$ be the matrix such that for $t \in (-\eta, \eta)$,*

$$\widetilde{\Phi}_I(t) = C_\eta^{(P)} P(\tfrac{t}{\eta}).$$

Let $C_1 \in \mathbb{R}^{N\times N}$ and $C_2 \in \mathbb{R}^{N\times(d-N)}$ be the matrices such that

$$C_\eta^{(P)} = \Big(C_1 \;\Big|\; C_2\Big).$$

Let M_η be the matrix

$$M_\eta = \left(C_\eta^{(P)}\right)^T \left(C_\eta^{(P)} G(P) \left(C_\eta^{(P)}\right)^T\right)^{-1} C_\eta^{(P)},$$

where $G(P)$ is the matrix $\int_{-1}^1 \rho(t)P(t)P(t)^T \,\mathrm{d}t$.

Then the following statements hold.

1. *the norm of the matrix M_η is uniformly bounded in η.*
2. *for all $x \in (-\eta, \eta)$*

$$\left\langle \widetilde{p}^I, f\right\rangle^T \Phi_I(x) = \left(M_\eta \int_{-1}^1 \rho(t) f(\eta t) P(t)\,\mathrm{d}t\right)^T \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi_I(x),$$

and

$$\left\langle \widetilde{p}^I, f\right\rangle^T \widetilde{\Phi}_I(x) = \left(M_\eta \int_{-1}^1 \rho(t) f(\eta t) P(t)\,\mathrm{d}t\right)^T P(x/\eta).$$

3. *for all $0 < \eta \le \eta_0$ and $x \in (-\eta, \eta)$*

$$C_1^{-1}\Phi_I(x) = \begin{pmatrix} 1 \\ * \end{pmatrix} + \mathcal{O}(\eta) \quad \text{and} \quad C_1^{-1}\Phi_I'(x) = \frac{1}{\eta}\begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(1),$$

where $\begin{pmatrix} 1 \\ * \end{pmatrix}$ and $\begin{pmatrix} 0 \\ * \end{pmatrix}$ are uniformly bounded in η and x.

Proof. Proofs of these statements can be found in the proof of Lemma 4.13 and 4.14 in [BCD17b]. □

Lemma 4.7. *There exists a positive constant C independent of f and η such that we have the following estimates*

1. *for all $f \in H^1_{\mathrm{per}}(0,1)$, $0 < \eta \le \eta_0$ and $x \in (-\frac{1}{2}, \frac{1}{2})$, we have*

$$\left|\left\langle \widetilde{p}^I, f\right\rangle^T (\Phi_I(x) - \widetilde{\Phi}_I(x))\right| \le C\eta \|f\|_{H^1_{\mathrm{per}}} \quad \text{and} \quad \left|\left\langle \widetilde{p}^I, f\right\rangle^T (\Phi_I'(x) - \widetilde{\Phi}_I'(x))\right| \le C\|f\|_{H^1_{\mathrm{per}}};$$

2. *for all $f \in L^2_{\mathrm{per}}(0,1)$, $0 < \eta \le \eta_0$ and $x \in (-\frac{1}{2}, \frac{1}{2})$, we have*

$$\left|\left\langle \widetilde{p}^I, f\right\rangle^T (\Phi_I(x) - \widetilde{\Phi}_I(x))\right| \le \frac{C}{\eta^{1/2}} \|f\|_{L^2_{\mathrm{per}}};$$

3. *for all* $f \in H^1_{\mathrm{per}}(0,1)$, $0 < \eta \leq \eta_0$ *and* $x \in (-\eta, \eta)$, *we have*

$$\left|\left\langle \widetilde{p}^I \,, f \right\rangle^T \widetilde{\Phi}_I(x)\right| \leq C\|f\|_{L^\infty} \quad \textit{and} \quad \left|\left\langle \widetilde{p}^I \,, f \right\rangle^T \Phi_I(x)\right| \leq C\|f\|_{L^\infty};$$

4. *for all* $f \in H^1_{\mathrm{per}}(0,1)$, $0 < \eta \leq \eta_0$ *and* $x \in (-\eta, \eta)$, *we have*

$$\left|\left\langle \widetilde{p}^I \,, f \right\rangle^T \widetilde{\Phi}'_I(x)\right| \leq C\|f\|_{H^1_{\mathrm{per}}} \quad \textit{and} \quad \left|\left\langle \widetilde{p}^I \,, f \right\rangle^T \Phi'_I(x)\right| \leq C\|f\|_{H^1_{\mathrm{per}}}.$$

Proof. 1. Proof of this statement can be found in [BCD17b] (Lemmas 4.12 and 4.14).

2. By Lemma 4.6,

$$\left\langle \widetilde{p}^I \,, f \right\rangle^T \left(\Phi_I(x) - \widetilde{\Phi}_I(x)\right) = \left(M_\eta \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t\right)^T \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi_I(x) - P(x/\eta)\right).$$

Applying the Cauchy-Schwarz inequality to $\int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t$ suffices to prove the estimate.

3. By item 2 of Lemma 4.6,

$$\left\langle \widetilde{p}^I \,, f \right\rangle^T \widetilde{\Phi}_I(x) = \left(M_\eta \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t\right)^T P(x/\eta).$$

Thus the first inequality follows from the uniform boundedness of M_η with respect to η (item 1 of Lemma 4.6). For the second inequality, we proceed the same way and conclude using item 3 of Lemma 4.6.

4. For the first inequality, we simply replace Step 1 in the proof of Lemma 4.12 in [BCD17b] by

(a) $\frac{1}{\eta} P'(x/\eta) = \frac{1}{\eta} \begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(1)$

and keep on the proof. For the second inequality, we replace Step 1 in the proof of Lemma 4.12 in [BCD17b] by item 3 of Lemma 4.6.

□

4.3.2 PAW method without pseudopotentials

The main idea of the proof is to use that the PAW operator H^N (4.1.9) (respectively S^N (4.1.10)) is close to the VPAW operator $\widetilde{H}$ (4.1.17) (resp. $\widetilde{S}$ (4.1.18)), in a sense that will be clearly stated. Then it is possible to use this connexion and bound the error on the PAW eigenvalue $E^{(\eta)}$, since the VPAW generalized eigenvalue problem (4.1.14) has the same eigenvalues as (4.1.1).

Proposition 4.8. *Let* H^N, S^N, $\widetilde{H}$ *and* $\widetilde{S}$ *be defined by Equations (4.1.9), (4.1.10),* (4.1.17) *and* (4.1.18) *respectively. Then we have for* $f \in H^1_{\mathrm{per}}(0,1)$

$$\left\langle f \,, \widetilde{H} f \right\rangle = \left\langle f \,, H^N f \right\rangle + 2 \sum_{I=\{0,a\}} \left\langle \left\langle \widetilde{p}^I \,, f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \,, H \left(f - \left\langle \widetilde{p}^I \,, f \right\rangle^T \widetilde{\Phi}_I \right) \right\rangle, \tag{4.3.2}$$

and

$$\left\langle f\,,\widetilde{S}f\right\rangle = \langle f\,,S^N f\rangle + 2\sum_{I=\{0,a\}}\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,f-\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle. \tag{4.3.3}$$

Proof. Using that $T_{0,N}$ and $T_{a,N}$ act on strictly distinct region, we have for $f\in H^1_{\mathrm{per}}(0,1)$

$$\begin{aligned}\left\langle f\,,\widetilde{H}f\right\rangle &= \left\langle f+\sum_{I=\{0,a\}}\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,H\Big(f+\sum_{I=\{0,a\}}\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\Big)\right\rangle\\ &= \langle f\,,Hf\rangle+\sum_{I=\{0,a\}}2\left\langle f\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\\ &\qquad+\sum_{I=\{0,a\}}\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\\ &= \langle f\,,Hf\rangle+\sum_{I=\{0,a\}}2\left\langle f\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle+\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\right\rangle\\ &\qquad-2\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\right\rangle+\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle.\end{aligned}$$

Notice that for each I, we have

$$\begin{aligned}\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\right\rangle &= \left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\\ &\qquad+\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle.\end{aligned}$$

Hence

$$\begin{aligned}\left\langle f\,,\widetilde{H}f\right\rangle &= \langle f\,,Hf\rangle+\sum_{I=\{0,a\}}\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\Phi_I\right\rangle-\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle\\ &\qquad+2\left\langle f-\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\\ &= \left\langle f\,,H^N f\right\rangle+\sum_{I=\{0,a\}}2\left\langle f-\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\,,H\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle.\end{aligned}$$

The second identity is proved the same way. □

Before proving Theorem 4.2, we will state some properties of the operators $\widetilde{S}$ and S^N.

Lemma 4.9. *The operators $\widetilde{S}$ and S^N satisfies the following properties*

1. *there exists a constant C independent of η such that for all $f\in H^1_{\mathrm{per}}(0,1)$;*

$$\left|\left\langle f\,,\widetilde{S}f\right\rangle\right|\le C\|f\|^2_{L^2_{\mathrm{per}}}.$$

2. *there exists a constant C independent of η such that for all $f\in H^1_{\mathrm{per}}(0,1)$;*

$$|\left\langle f\,,S^N f\right\rangle|\le C\|f\|^2_{L^2_{\mathrm{per}}}.$$

3. *there exists a constant C independent of η such that for all $f \in H^1_{\mathrm{per}}(0,1)$;*

$$\left|\left\langle f\,,\widetilde{S}f\right\rangle - \left\langle f\,,S^N f\right\rangle\right| \leq C\eta^2\|f\|^2_{H^1_{\mathrm{per}}}.$$

4. *let $\widetilde{\psi}$ be a generalized eigenfunction of (4.1.14), then there exists a positive constant C independent of η such that*

$$\left|\left\langle \widetilde{\psi}\,,\widetilde{S}\widetilde{\psi}\right\rangle - \left\langle \widetilde{\psi}\,,S^N\widetilde{\psi}\right\rangle\right| \leq C\eta^{2N+2}\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}}.$$

5. *there exists a constant C independent of η such that for all $f \in H^1_{\mathrm{per}}(0,1)$;*

$$\left|\left\langle f\,,S^N f\right\rangle - \left\langle f\,,f\right\rangle\right| \leq C\eta\|f\|^2_{H^1_{\mathrm{per}}}.$$

Proof. 1. By item 2 of Lemma 4.7, there exists a constant C independent of η and x such that for all $x \in (-\frac{1}{2},\frac{1}{2})$ and for all $0 < \eta \leq \eta_0$

$$\left|\left\langle \widetilde{p}^I\,,f\right\rangle^T\left(\Phi_I(x) - \widetilde{\Phi}_I(x)\right)\right| \leq \frac{C}{\eta^{1/2}}\|f\|_{L^2_{\mathrm{per}}}.$$

Then, we have

$$\begin{aligned}\|T_{0,N}f\|^2_{L^2_{\mathrm{per}}} &= \int_0^1 \left|\left\langle \widetilde{p}\,,f\right\rangle^T\left(\Phi(x) - \widetilde{\Phi}(x)\right)\right|^2 \mathrm{d}x\\ &\leq \int_{-\eta}^{\eta} \left|\left\langle \widetilde{p}\,,f\right\rangle^T\left(\Phi(x) - \widetilde{\Phi}(x)\right)\right|^2 \mathrm{d}x\\ &\leq C\|f\|^2_{L^2_{\mathrm{per}}}.\end{aligned}$$

Similarly, $\|T_{a,N}f\|_{L^2_{\mathrm{per}}} \leq C\|f\|_{L^2_{\mathrm{per}}}$ and the result follows.

2. By Proposition 4.8, for all $f \in H^1_{\mathrm{per}}(0,1)$

$$\left\langle f\,,S^N f\right\rangle = \left\langle f\,,\widetilde{S}f\right\rangle - 2\sum_{I=\{0,a\}}\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T\left(\Phi_I - \widetilde{\Phi}_I\right), f - \left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle.$$

From items 1 and 2 of Lemma 4.6, it is easy to show that there exists a constant C independent of η and x such that for all $x \in (-\eta,\eta)$, $0 < \eta \leq \eta_0$ and $f \in H^1_{\mathrm{per}}(0,1)$

$$\left|\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I(x)\right| \leq \frac{C}{\eta^{1/2}}\|f\|_{L^2_{\mathrm{per}}}.$$

Hence

$$\begin{aligned}\left|\left\langle f\,,S^N f\right\rangle\right| &\leq \left|\left\langle f\,,\widetilde{S}f\right\rangle\right| + 2\sum_{I\in\{0,a\}}\left|\left\langle \left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,f-\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\rangle\right| \\ &\leq C\|f\|^2_{L^2_{\mathrm{per}}} + \sum_{I\in\{0,a\}}\left\|\left\langle \widetilde{p}^I\,,f\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\|_{L^2_{\mathrm{per}}}\left(\|f\|_{L^2_{\mathrm{per}}}+\left\|\left\langle \widetilde{p}^I\,,f\right\rangle^T\widetilde{\Phi}_I\right\|_{2,\eta,I}\right) \\ &\leq C\|f\|^2_{L^2_{\mathrm{per}}}.\end{aligned}$$

3. This is an easy consequence of Proposition 4.8 and items 2 and 3 of Lemma 4.7.
4. By Proposition 4.8

$$\left\langle\widetilde{\psi}\,,S^N\widetilde{\psi}\right\rangle = \left\langle\widetilde{\psi}\,,\widetilde{S}\widetilde{\psi}\right\rangle - 2\sum_{I\in\{0,a\}}\left\langle\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,\widetilde{\psi}-\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T\widetilde{\Phi}_I\right\rangle.$$

By Lemma 4.5, we have for each $I\in\{0,a\}$

$$\left\|\widetilde{\psi}-\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T\widetilde{\Phi}_I\right\|_{\infty,\eta,I}\leq C\eta^{2N},$$

where $C>0$ is independent of η. Hence, using item 1 of Lemma 4.7,

$$\begin{aligned}\left|\left\langle\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\,,\widetilde{\psi}-\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T\widetilde{\Phi}_I\right\rangle\right| &\leq \left\|\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\|_{1,\eta,I}\left\|\widetilde{\psi}-\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T\widetilde{\Phi}_I\right\|_{\infty,\eta,I} \\ &\leq C\eta^{2N+2}\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}}.\end{aligned}$$

and the result follows.

5. By item 3 of Lemma 4.9, we have for all $f\in H^1_{\mathrm{per}}(0,1)$

$$\left|\left\langle f\,,\widetilde{S}f\right\rangle - \left\langle f\,,S^N f\right\rangle\right|\leq C\eta^2\|f\|^2_{H^1_{\mathrm{per}}},$$

where C is a constant independent of η and f.
By item 1 of Lemma 4.7, we can easily show that

$$\left|\left\langle f\,,\widetilde{S}f\right\rangle - \left\langle f\,,f\right\rangle\right|\leq C\eta\|f\|^2_{H^1_{\mathrm{per}}},$$

with a constant C independent of η and f. By a triangular inequality, the result follows.

□

Before moving to the proof of the upper bound on the PAW eigenvalue (4.1.8), we show that there exists a constant independent of η that bounds the H^1_{per}-norm of L^2_{per}-normalized generalized eigenfunctions $\widetilde{\psi}$ associated to the first generalized eigenvalue of $\widetilde{H}$ for all $0<\eta\leq\eta_0$.

Lemma 4.10. *Let $\widetilde{\psi}$ be an L^2_{per}-normalized generalized eigenfunction associated to the lowest eigenvalue of (4.1.14). Then there exists a positive constant C independent of η such that for all*

$0 < \eta \leq \eta_0$

$$\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}} \leq C.$$

Proof. The operator H defined in (4.1.1) is coercive. A proof of this statement can be found in [CD17]. Let $\alpha > 0$ be such that for all $f \in H^1_{\mathrm{per}}(0,1)$

$$\langle f\,, Hf\rangle + \alpha \langle f\,, f\rangle \geq \frac{1}{2}\|f\|^2_{H^1_{\mathrm{per}}}.$$

Then

$$\left\langle \widetilde{\psi}\,, \widetilde{H}\widetilde{\psi}\right\rangle + \alpha \left\langle \widetilde{\psi}\,, \widetilde{S}\widetilde{\psi}\right\rangle \geq \frac{1}{2}\|(\mathrm{Id}+T)\widetilde{\psi}\|^2_{H^1_{\mathrm{per}}}.$$

By item 1 of Lemma 4.7, we have

$$\|T\widetilde{\psi}\|_{H^1_{\mathrm{per}}} \leq C\eta^{1/2}\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}},$$

for some positive constant C independent of η. Hence, for η sufficiently small, there exists a positive constant C independent of η such that

$$(E_0+\alpha)\left\langle \widetilde{\psi}\,, \widetilde{S}\widetilde{\psi}\right\rangle \geq C\|\widetilde{\psi}\|^2_{H^1_{\mathrm{per}}}.$$

Using item 1 of Lemma 4.9, we obtain

$$C\|\widetilde{\psi}\|^2_{L^2_{\mathrm{per}}} \geq \|\widetilde{\psi}\|^2_{H^1_{\mathrm{per}}},$$

and the result follows from the normalization of the eigenfunctions $\widetilde{\psi}$. □

We now have all the necessary tools to prove the upper bound of Theorem 4.2.

Proof of the upper bound of Theorem 4.2. Let $\widetilde{\psi}$ be an L^2_{per}-normalized eigenvector of the lowest eigenvalue of $\widetilde{H}\widetilde{\psi} = E_0\widetilde{S}\widetilde{\psi}$. Then by Proposition 4.8,

$$\left\langle \widetilde{\psi}\,, \widetilde{H}\widetilde{\psi}\right\rangle = \left\langle \widetilde{\psi}\,, H^N\widetilde{\psi}\right\rangle + 2\sum_{I=\{0,a\}} \left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I\,, \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T H(\Phi_I - \widetilde{\Phi}_I)\right\rangle.$$

Recall that

$$\widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I = \psi - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \Phi_I,$$

which with Equation (4.3.1) yields

$$\widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I = \psi - \left\langle A_I^{-1}p^I\,, \psi\right\rangle^T \Phi_I$$

Thus we have :

$$\begin{aligned}\left\langle \widetilde{\psi}\,,\widetilde{H}\widetilde{\psi}\right\rangle &= \left\langle \widetilde{\psi}\,,H^N\widetilde{\psi}\right\rangle + 2\sum_{I=\{0,a\}}\left\langle \psi - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \Phi_I\,, H\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle \\ &= \left\langle \widetilde{\psi}\,,H^N\widetilde{\psi}\right\rangle + 2\sum_{I=\{0,a\}}\left\langle E_0\psi - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \mathcal{E}^I\Phi_I\,, \left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle, \qquad (4.3.4)\end{aligned}$$

where we used $H\Phi_I = \mathcal{E}^I\Phi_I$ in $(I-\eta, I+\eta)$ for $I\in\{0,a\}$. By Lemma 4.5,

$$\left\| E_0\psi_e - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \mathcal{E}^I\Phi_I\right\|_{\infty,\eta,I} \leq C\eta^{2N-2}.$$

So for each I,

$$\begin{aligned}&\left|\left\langle E_0\psi_e - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \mathcal{E}^I\Phi_I\,, \left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\right| \\ &\qquad\leq \left\| E_0\psi_e - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \mathcal{E}^I\Phi_I\right\|_{\infty,\eta,I}\left\|\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\|_{1,\eta,I}.\end{aligned}$$

By item 1 of Lemma 4.7, we have

$$\left\|\left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\|_{1,\eta,I} \leq C\eta^2\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}} \leq C\eta^2.$$

where we bound $\|\widetilde{\psi}\|_{H^1_{\mathrm{per}}}$ by means of Lemma 4.10. Hence, using Lemma 4.5, we obtain

$$\left|\left\langle E_0\psi - \left\langle A_I^{-1}p^I\,,\psi\right\rangle^T \mathcal{E}^I\Phi_I\,, \left\langle \widetilde{p}^I\,,\widetilde{\psi}\right\rangle^T(\Phi_I-\widetilde{\Phi}_I)\right\rangle\right| \leq C\eta^{2N}.$$

Going back to Equation (4.3.4),

$$\begin{aligned}E_0\left\langle \widetilde{\psi}\,,\widetilde{S}\widetilde{\psi}\right\rangle + C\eta^{2N} &\geq \left\langle \widetilde{\psi}\,,H^N\widetilde{\psi}\right\rangle \\ &\geq E^{(\eta)}\left\langle \widetilde{\psi}\,,S^N\widetilde{\psi}\right\rangle\end{aligned}$$

By Lemmas 4.9 and 4.10, we have

$$\left|\left\langle \widetilde{\psi}\,,\widetilde{S}\widetilde{\psi}\right\rangle - \left\langle \widetilde{\psi}\,,S^N\widetilde{\psi}\right\rangle\right| \leq C\eta^{2N+2},$$

which finishes the proof. □

Lemma 4.11. *Let f be an L^2_{per}-normalized generalized eigenfunction associated to the lowest generalized eigenvalue of (4.1.8). Then there exists a positive constant C independent of η such that for all $0<\eta\leq\eta_0$*

$$\|f\|_{H^1_{\mathrm{per}}} \leq C.$$

Proof. We proceed as in the proof of Lemma 4.10. Let α be the coercivity constant of H and f be an L^2_{per}-normalized eigenfunction associated to the lowest eigenvalue of (4.1.8). Then we have

$$\alpha \langle f , f \rangle + \langle f , Hf \rangle \geq \frac{1}{2} \|f\|^2_{H^1_{\mathrm{per}}}.$$

From Equation (4.1.9), it easy to see that we have

$$\left\langle f , H^N f \right\rangle = \langle f , Hf \rangle + \sum_{I \in \{0,a\}} \left\langle \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) , H \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\rangle .$$

Hence, we have

$$\alpha \langle f , f \rangle + \left\langle f , H^N f \right\rangle - \sum_{I \in \{0,a\}} \left\langle \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) , H \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\rangle \geq \frac{1}{2} \|f\|^2_{H^1_{\mathrm{per}}}$$

$$\alpha \langle f , f \rangle + \left\langle f , H^N f \right\rangle \geq \frac{1}{2} \|f\|^2_{H^1_{\mathrm{per}}} - C \sum_{I \in \{0,a\}} \| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) \|_{H^1,\eta,I} \| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \|_{H^1,\eta,I}.$$

From items 1, 3 and 4 of Lemma 4.7, it is easy to show that

$$\left\| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) \right\|_{H^1,\eta,I} \left\| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\|_{H^1,\eta,I} \leq C\eta \|f\|^2_{H^1_{\mathrm{per}}}. \tag{4.3.5}$$

Thus, for η sufficiently small, we have for a positive constant C independent of η,

$$\alpha \langle f , f \rangle + \left\langle f , H^N f \right\rangle \geq C \|f\|^2_{H^1_{\mathrm{per}}}. \tag{4.3.6}$$

Since f is a generalized eigenfunction of H^N, we have

$$\alpha \langle f , f \rangle + E^{(\eta)} \left\langle f , S^N f \right\rangle \geq C \|f\|^2_{H^1_{\mathrm{per}}}.$$

By item 5 of Lemma 4.9, we have

$$(E^{(\eta)} + \alpha) \langle f , f \rangle \geq C \|f\|^2_{H^1_{\mathrm{per}}},$$

which completes the proof. □

Proof of the lower bound of Theorem 4.2. Let f be an L^2_{per}-normalized eigenfunction associated to the lowest eigenvalue of $H^N f = E^{(\eta)} S^N f$. Then we have :

$$\begin{aligned}
\left\langle f , H^N f \right\rangle &= \langle f , Hf \rangle + \sum_{I = \{0,a\}} \left\langle \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) , H \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\rangle \\
&\geq E_0 \langle f , f \rangle - C \sum_{I = \{0,a\}} \| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I + \widetilde{\Phi}_I) \|_{H^1,\eta,I} \| \left\langle \widetilde{p}^I , f \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \|_{H^1,\eta,I} \\
&\geq E_0 \langle f , f \rangle - C\eta \|f\|_{H^1_{\mathrm{per}}},
\end{aligned}$$

where we used (4.3.5) in the last inequality.

It remains to show that $|\left\langle f\,,S^N f\right\rangle - \langle f\,,f\rangle\,| \leq C\eta\|f\|^2_{H^1_{\mathrm{per}}}$ which is precisely item 5 of Lemma 4.9. We then conclude the proof by Lemma 4.11. □

4.3.3 PAW method with pseudopotentials

In this section, we focus on the truncated equations (4.1.11) where a pseudopotential is used. First, we see how H^{PAW} and $\widetilde{H}$ are related.

Lemma 4.12. *If $\epsilon \leq \eta$, then*

$$H^{PAW} = H^N + \delta V - \sum_{I\in\{0,a\}} (\widetilde{p}^I)^T \left\langle \widetilde{\Phi}_I\,, \delta V \widetilde{\Phi}_I^T \right\rangle_{I,\eta} \langle \widetilde{p}^I\,, \cdot\rangle\,. \tag{4.3.7}$$

where $\delta V = -Z_0\chi_\epsilon - Z_a\chi^a_\epsilon + Z_0\sum_{k\in\mathbb{Z}}\delta_k + Z_a\sum_{k\in\mathbb{Z}}\delta_{k+a}$.

Proof. By definition of the pseudo wave functions $\widetilde{\phi}_i$, we have

$$\langle \phi^I_i\,, H\phi^I_j\rangle - \left\langle \widetilde{\phi}^I_i\,, H\widetilde{\phi}^I_j\right\rangle = \langle \phi^I_i\,, H\phi^I_j\rangle_{I,\eta} - \left\langle \widetilde{\phi}^I_i\,, H\widetilde{\phi}^I_j\right\rangle_{I,\eta}. \tag{4.3.8}$$

By definition of δV, $H_{\mathrm{ps}} = H + \delta V$ thus we have the result. □

Proposition 4.13. *Let $g \in H^1_{\mathrm{per}}(0,1)$. Then*

$$\begin{aligned}\langle g\,, H^{PAW} g\rangle = \left\langle g\,, \widetilde{H} g\right\rangle - 2\sum_{I\in\{0,a\}} &\left\langle g - \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\,, \langle \widetilde{p}^I\,, g\rangle^T \left(H\Phi_I - (H+\delta V)\widetilde{\Phi}_I\right)\right\rangle \\ &+ \sum_{I\in\{0,a\}} \left\langle g - \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\,, \delta V\left(g - \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\right)\right\rangle_{I,\eta}\end{aligned} \tag{4.3.9}$$

Proof. By Lemma 4.12, we have

$$\langle g\,, H^{PAW} g\rangle = \langle g\,, H^N g\rangle + \langle g\,, \delta V g\rangle - \sum_{I\in\{0,a\}} \left\langle \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\,, \delta V \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\right\rangle_{I,\eta}.$$

Applying Proposition 4.8, we obtain

$$\begin{aligned}\langle g\,, H^{PAW} g\rangle = \left\langle g\,, \widetilde{H} g\right\rangle - 2\sum_{I\in\{0,a\}} &\left\langle g - \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\,, \langle \widetilde{p}^I\,, g\rangle^T H(\Phi_I - \widetilde{\Phi}_I)\right\rangle \\ &+ \langle g\,, \delta V g\rangle - \sum_{I\in\{0,a\}} \left\langle \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\,, \delta V \langle \widetilde{p}^I\,, g\rangle^T \widetilde{\Phi}_I\right\rangle.\end{aligned}$$

Now, using $H_{\rm ps} = H + \delta V$, we get

$$\left\langle g\,, H^{PAW} g\right\rangle = \left\langle g\,, \widetilde{H} g\right\rangle - 2\sum_{I\in\{0,a\}} \left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \left\langle \widetilde{p}^I\,, g\right\rangle^T (H\Phi_I - H_{\rm ps}\widetilde{\Phi}_I)\right\rangle$$
$$-2\sum_{I\in\{0,a\}} \left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right\rangle_{I,\eta} + \langle g\,, \delta V g\rangle - \sum_{I\in\{0,a\}} \left\langle \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right\rangle. \tag{4.3.10}$$

Notice that for each I,

$$\begin{aligned}
&-2\left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right\rangle_{I,\eta} + \langle g\,, \delta V g\rangle_{I,\eta} - \left\langle \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right\rangle \\
&= \langle g\,, \delta V g\rangle_{I,\eta} - 2\left\langle g\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I)\right\rangle_{I,\eta} + \left\langle \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right\rangle_{I,\eta} \\
&= \left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left(g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\right)\right\rangle_{I,\eta}.
\end{aligned}$$

Injecting this expression in (4.3.10), we have the result. □

Proof of the upper of Theorem 4.2

Proof of the upper bound of Theorem 4.2. We start by estimating $\left\langle \widetilde{\psi}\,, H^{PAW}\widetilde{\psi}\right\rangle$ where $\widetilde{\psi}$ is the generalized eigenfunction associated to the lowest eigenvalue: $\widetilde{H}\widetilde{\psi} = E_0\widetilde{S}\widetilde{\psi}$. Thus we have :

$$\left\langle \widetilde{\psi}\,, H^{PAW}\widetilde{\psi}\right\rangle = \left\langle \widetilde{\psi}\,, \widetilde{H}\widetilde{\psi}\right\rangle - 2\sum_{I\in\{0,a\}} \left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I\,, \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \left(H\Phi_I - (H+\delta V)\widetilde{\Phi}_I\right)\right\rangle$$
$$+ \sum_{I\in\{0,a\}} \left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I\,, \delta V \left(\widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I\right)\right\rangle_{I,\eta}.$$

By Equation (4.3.1), we have for each I

$$\widetilde{\psi} - \left\langle \widetilde{p}^I\,, \widetilde{\psi}\right\rangle^T \widetilde{\Phi}_I = \psi - \left\langle A_I^{-1} p^I\,, \psi\right\rangle^T \Phi_I,$$

so for each I

$$\begin{aligned}
&\left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle \cdot \widetilde{\Phi}_I \,, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \left(H\Phi_I - (H+\delta V)\widetilde{\Phi}_I \right) \right\rangle \\
&\qquad = \left\langle \psi - \left\langle A_I^{-1} p^I \,, \psi \right\rangle^T \Phi_I \,, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \left(H\Phi_I - (H+\delta V)\widetilde{\Phi}_I \right) \right\rangle \\
&\qquad = \left\langle E_0\psi - \left\langle A_I^{-1} p^I \,, \psi \right\rangle^T \mathcal{E}^I \Phi_I \,, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\rangle \\
&\qquad\quad + \left\langle \psi - \left\langle A_I^{-1} p^I \,, \psi \right\rangle^T \Phi_I, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \delta V \widetilde{\Phi}_I \right\rangle_{I,\eta} .
\end{aligned}$$

We have already proved in the proof of the upper bound of Theorem 4.1 that

$$\left| \left\langle E_0\psi - \left\langle A_I^{-1} p^I \,, \psi \right\rangle^T \mathcal{E}^I \Phi_I \,, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T (\Phi_I - \widetilde{\Phi}_I) \right\rangle \right| \leq C\eta^{2N}.$$

Moreover by Lemma 4.5 and item 3 of Lemma 4.7, we have

$$\begin{aligned}
\left| \left\langle \psi - \left\langle A_I^{-1} p^I \,, \psi \right\rangle^T \Phi_I \,, \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \delta V \widetilde{\Phi}_I \right\rangle_{I,\eta} \right| &\leq C \| \psi_e - \left\langle A_I^{-1} p^I \,, \psi \right\rangle \cdot \Phi_I \|_{\infty,\eta,I} \| \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \|_{\infty,\eta,I} \\
&\leq C\eta^{2N}.
\end{aligned}$$

Again using Lemma 4.5, we obtain

$$\left| \left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \,, \delta V \left(\widetilde{\psi} - \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \right) \right\rangle_{I,\eta} \right| \leq C\eta^{2N} + \int_{-\eta}^{\eta} \chi_\epsilon(x) |\psi_o(x)|^2 \, \mathrm{d}x, \tag{4.3.11}$$

where ψ_o is the odd part of ψ. By Lemma 4.2 in [BCD17b], we know that for $|x| \leq \eta$, there exists a constant independent of η such that:

$$|\psi_o(x)|^2 \leq C\eta^2,$$

hence

$$\left| \left\langle \widetilde{\psi} - \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \,, \delta V \left(\widetilde{\psi} - \left\langle \widetilde{p}^I \,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}_I \right) \right\rangle_{I,\eta} \right| \leq C\eta^2.$$

Thus

$$E^{PAW} \left\langle \widetilde{\psi} \,, S^{PAW} \widetilde{\psi} \right\rangle \leq E_0 \left\langle \widetilde{\psi} \,, \widetilde{S}\widetilde{\psi} \right\rangle + C\eta^2,$$

and we conclude using item 4 of Lemma 4.9 (recall that $S^{PAW} = S^N$). □

Proof of the lower bound of Theorem 4.2

The core of the proof of the error on the lowest PAW eigenvalue lies on the estimation of $f - \sum_{i=1}^{N} \langle \widetilde{p}_i \, , f \rangle \, \widetilde{\phi}_i$, which is of the order of the best approximation of f by the family of pseudo wave functions $(\widetilde{\phi}_i)_{1 \leq i \leq N}$. In order to give estimates of the best approximation, we analyze the behavior of the PAW eigenfunction f, but first, we need an estimate on the PAW eigenvalue.

Lemma 4.14. *Let E^{PAW} be the lowest generalized eigenvalue of (4.1.11). Then as η goes to 0, E^{PAW} is bounded by below.*

Proof. Let f be an L^2_{per}-normalized generalized eigenfunction of (4.1.11) associated to E^{PAW}. By (4.3.6), we have

$$\alpha \langle f \, , f \rangle + \left\langle f \, , H^N f \right\rangle \geq C \| f \|^2_{H^1_{\mathrm{per}}},$$

where C is some positive constant, α the coercivity constant of H (4.1.1) and H^N the truncated PAW operator (4.1.9). By Lemma 4.12, we have

$$\alpha \langle f \, , f \rangle + \left\langle f \, , H^{PAW} f \right\rangle \geq C \| f \|_{H^1_{\mathrm{per}}} - \langle f \, , \delta V f \rangle + \sum_{I \in \{0, a\}} \left\langle \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \, , \delta V \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \right\rangle. \quad (4.3.12)$$

We have

$$\begin{aligned} \left| \langle f \, , \delta V f \rangle_{0,\eta} \right| &\leq Z_0 \left| \int_{-\epsilon}^{\epsilon} \chi_\epsilon(x) (|f(x)|^2 - |f(0)|^2) \, \mathrm{d}x \right| \\ &\leq C \int_{-\epsilon}^{\epsilon} \chi_\epsilon(x) |f(x) + f(0)| |f(x) - f(0)| \, \mathrm{d}x \\ &\leq C \| f \|_{\infty,\eta} \| f - f(0) \|_{\infty,\eta} \\ &\leq C \eta^{1/2} \| f \|^2_{H^1_{\mathrm{per}}}, \end{aligned} \quad (4.3.13)$$

where in the second inequality, we used $\int_{-\epsilon}^{\epsilon} \chi_\epsilon(x) \, \mathrm{d}x = 1$ and $\epsilon \leq \eta$ and in the last inequality, $\| f - f(0) \|_{\infty,\eta} \leq C \eta^{1/2} \| f \|_{H^1_{\mathrm{per}}}$ and the Sobolev embedding $\| f \|_{L^\infty} \leq C \| f \|_{H^1_{\mathrm{per}}}$.

Similarly, we have

$$\left| \left\langle \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \, , \delta V \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \right\rangle \right| \leq C \eta^{1/2} \| \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \|^2_{H^1_{\mathrm{per}}},$$

thus by items 3 and 4 of Lemma 4.7, we obtain

$$\left| \left\langle \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \, , \delta V \left\langle \widetilde{p}^I \, , f \right\rangle^T \widetilde{\Phi}_I \right\rangle \right| \leq C \eta \| f \|^2_{H^1_{\mathrm{per}}}. \quad (4.3.14)$$

Thus injecting (4.3.13) and (4.3.14) in (4.3.12), we get for η sufficiently small and a positive constant C,

$$\alpha \langle f \, , f \rangle + \left\langle f \, , H^{PAW} f \right\rangle \geq C \| f \|^2_{H^1_{\mathrm{per}}}.$$

Thus

$$\alpha \langle f \, , f \rangle + E^{PAW} \left\langle f \, , S^{PAW} f \right\rangle \geq C \| f \|^2_{H^1_{\mathrm{per}}}, \quad (4.3.15)$$

and we conclude the proof using item 5 of Lemma 4.9. □

Lemma 4.15. *Let f be a generalized eigenfunction of (4.1.11) and $k \in \mathbb{N}^*$. Then there exists a constant C independent of η, ϵ and f such that*

$$\|f^{(k)}\|_{\infty,\eta,I} \leq C\left(\frac{1}{\eta^{k-1}} + \frac{1}{\epsilon^{k-1}}\right)\|f\|_{\infty,\eta,I} \tag{4.3.16}$$

Proof. This lemma is proved by iteration. We show the lemma for $I = 0$ and drop the index I.

Initialization To get the desired estimate for f', we integrate (4.1.11) on $(-\eta, x)$ where $x \in (-\eta, \eta)$:

$$\begin{aligned} -f''(x) + \frac{1}{\epsilon}\chi\left(\tfrac{x}{\epsilon}\right) f(x) + \langle \widetilde{p}, f\rangle^T \left(\left\langle \Phi, H\Phi^T\right\rangle_\eta - \left\langle \widetilde{\Phi}, H_{\mathrm{ps}}\widetilde{\Phi}^T\right\rangle_\eta\right)\widetilde{p}^I(x) \\ = E^{PAW}\left(f(x) + \langle \widetilde{p}, f\rangle^T \left(\left\langle \Phi, \Phi^T\right\rangle_\eta - \left\langle \widetilde{\Phi}, \widetilde{\Phi}^T\right\rangle_\eta\right)\widetilde{p}(x)\right). \end{aligned} \tag{4.3.17}$$

First, we bound $f'(\pm\eta)$ and $f'(a \pm \eta)$. For $x \in \bigcup_{k\in\mathbb{Z}} (\eta + k, a - \eta + k)$ and $x \in \bigcup_{k\in\mathbb{Z}} (a + \eta + k, 1 - \eta + k)$, f satisfies

$$-f''(x) = E^{PAW} f(x).$$

From Section 4.3.3, we already know that

$$E^{PAW} \leq E_0 + C\eta^2.$$

Since $E_0 < 0$, then for η sufficiently small, $E^{PAW} < 0$. Thus, outside the intervals $(-\eta, \eta)$ and $(a - \eta, a + \eta)$, f can be written as

$$f(x) = a_1 \cosh\left(\sqrt{-E^{PAW}}x\right) + a_2 \sinh\left(\sqrt{-E^{PAW}}x\right).$$

The coefficients a_1 and a_2 are determined by the continuity of f at $\pm\eta$ and $a \pm \eta$. By Lemma 4.14, E^{PAW} is bounded from below as η goes to 0, hence $|f'(\pm\eta)|$ and $f'(a \pm \eta)$ are uniformly bounded with respect to η as η goes to 0.

We now prove that $f'(x)$ is uniformly bounded with respect to η and ϵ as $\eta, \epsilon \to 0$ for $x \in \bigcup_{k\in\mathbb{Z}} (-\eta + k, \eta + k)$ and $x \in \bigcup_{k\in\mathbb{Z}} (a - \eta + k, a + \eta + k)$. $\chi\left(\frac{\cdot}{\epsilon}\right)$ is a bounded function supported in $(-\epsilon, \epsilon)$, we have

$$\left|\frac{1}{\epsilon}\int_{-\eta}^{x} \chi\left(\tfrac{t}{\epsilon}\right) f(t)\,\mathrm{d}t\right| \leq C\|f\|_{\infty,\eta}.$$

To finish the proof, it suffices to show that the remaining terms are at most of order $\mathcal{O}\left(\frac{\|f\|_{\infty,\eta}}{\eta}\right)$ with respect to the ∞-norm. These terms will be treated separately.

1. For $\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, \Phi^T \right\rangle_\eta \widetilde{p}(x)$, by item 2 of Lemma 4.6, we have

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, \Phi^T \right\rangle_\eta \widetilde{p}(x) = \left(M_\eta \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t \right)^T \left\langle \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi\,, \Phi^T \left(C_1^{-T} \,\middle|\, 0 \right) \right\rangle_\eta M_\eta \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right).$$

According to item 3 of Lemma 4.6, we already know that

$$\left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi \right\|_{\infty,\eta} \leq C,$$

thus

$$\left| \langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, \Phi^T \right\rangle_\eta \widetilde{p}(x) \right| \leq C \|f\|_{\infty,\eta} \left| \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right) \right|.$$

2. Using item 2 of Lemma 4.6, the term $\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}\,, \widetilde{\Phi}^T \right\rangle_\eta \widetilde{p}(x)$ can be written as

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}\,, \widetilde{\Phi}^T \right\rangle_\eta \widetilde{p}(x) = \left(M_\eta \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t \right)^T \left\langle P\left(\tfrac{\cdot}{\eta}\right), P^T\left(\tfrac{\cdot}{\eta}\right) \right\rangle_\eta M_\eta \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right).$$

Hence, we obtain

$$\left| \langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}\,, \widetilde{\Phi}^T \right\rangle_\eta \widetilde{p}^I(x) \right| \leq C \|f\|_{\infty,\eta} \left| \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right) \right|.$$

3. On the LHS of (4.3.17), the term $\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, H\Phi^T \right\rangle_\eta \widetilde{p}(x)$ is given by

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, H\Phi^T \right\rangle_\eta \widetilde{p}(x) = \langle \widetilde{p}\,, f\rangle^T \left\langle \Phi'\,, \Phi'^T \right\rangle_\eta \widetilde{p}(x) - Z_0 \langle \widetilde{p}\,, f\rangle^T \Phi(0)\Phi(0)^T \widetilde{p}(x).$$

Like in item 1 above, we can show that

$$\left| \langle \widetilde{p}\,, f\rangle^T \Phi(0)\Phi(0)^T \widetilde{p}(x) \right| \leq C \|f\|_{\infty,\eta} \left| \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right) \right|. \tag{4.3.18}$$

Using item 3 of Lemma 4.6,

$$\left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \Phi' \right\|_{\infty,\eta} \leq \frac{C}{\eta},$$

we get

$$\left| \langle \widetilde{p}\,, f\rangle^T \left\langle \Phi'\,, \Phi'^T \right\rangle_\eta \widetilde{p}(x) \right| \leq \frac{C}{\eta} \|f\|_{\infty,\eta} \left| \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right) \right|. \tag{4.3.19}$$

4. Finally, for $\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}\,, H_{\mathrm{ps}}\widetilde{\Phi}^T\right\rangle_\eta \widetilde{p}(x)$, we have

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}\,, H_{\mathrm{ps}}\widetilde{\Phi}^T\right\rangle_\eta \widetilde{p}(x) = \langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}'\,, \widetilde{\Phi}'^T\right\rangle_\eta \widetilde{p}(x) - \frac{Z_0}{\epsilon}\langle \widetilde{p}\,, f\rangle^T \int_{-\epsilon}^{\epsilon} \chi\left(\tfrac{t}{\epsilon}\right) P(\tfrac{t}{\eta})P(\tfrac{t}{\eta})^T \,\mathrm{d}t\, \widetilde{p}(x).$$

Since $\epsilon \le \eta$, $\left|\int_{-\epsilon}^{\epsilon} \chi\left(\frac{t}{\epsilon}\right) P(\frac{t}{\eta})P(\frac{t}{\eta})^T \,\mathrm{d}t\right| \le C\epsilon$ where C is independent of η and ϵ. Moreover,

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}'\,, \widetilde{\Phi}'^T\right\rangle_\eta \widetilde{p}(x) = \frac{1}{\eta^2}\left(M_\eta \int_{-1}^{1} \rho(t) f(\eta t) P(t)\,\mathrm{d}t\right)^T \left\langle P'(\tfrac{\cdot}{\eta})\,, P'(\tfrac{\cdot}{\eta})^T\right\rangle_\eta M_\eta \rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right),$$

hence

$$\left|\langle \widetilde{p}\,, f\rangle^T \left\langle \widetilde{\Phi}'\,, \widetilde{\Phi}'^T\right\rangle_\eta \widetilde{p}(x)\right| \le \frac{C}{\eta}\|f\|_{\infty,\eta}\left|\rho\left(\tfrac{x}{\eta}\right) P\left(\tfrac{x}{\eta}\right)\right|.$$

Iteration Suppose the statement is true for any $k \le n$. We derivate (4.3.17) $(n-1)$ times

$$\begin{aligned} -f^{(n+1)}(x) + \frac{1}{\epsilon}\left(\chi\left(\tfrac{\cdot}{\epsilon}\right) f\right)^{(n-1)}(x) + \langle \widetilde{p}\,, f\rangle^T \left(\left\langle \Phi\,, H\Phi^T\right\rangle_\eta - \left\langle \widetilde{\Phi}\,, H_{\mathrm{ps}}\widetilde{\Phi}^T\right\rangle_\eta\right)\widetilde{p}^{(n-1)}(x) \\ = E^{PAW}\left(f^{(n-1)}(x) + \langle \widetilde{p}\,, f\rangle^T \left(\left\langle \Phi\,, \Phi^T\right\rangle_\eta - \left\langle \widetilde{\Phi}\,, \widetilde{\Phi}^T\right\rangle_\eta\right)\widetilde{p}^{(n-1)}(x)\right). \end{aligned} \tag{4.3.20}$$

By the induction hypothesis and since $\epsilon \le \eta$, we have

$$\left|\frac{1}{\epsilon}\left(\chi\left(\tfrac{\cdot}{\epsilon}\right) f\right)^{(n-1)}(x)\right| \le C\left(\frac{\|f\|_{\infty,\eta}}{\epsilon^n} + \sum_{k=1}^{n-1}\frac{\|f^{(k)}\|_{\infty,\eta}}{\epsilon^{n-k}}\right) \le C\frac{\|f\|_{\infty,\eta}}{\epsilon^n}. \tag{4.3.21}$$

We simply give an estimate of the term

$$\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi\,, H\Phi^T\right\rangle_\eta \widetilde{p}^{(n-1)}(x),$$

since the other terms appearing in (4.3.20) can be treated the same way. By (4.3.18), we already know that

$$\left|\langle \widetilde{p}\,, f\rangle^T \Phi(0)\Phi(0)^T \widetilde{p}^{(n-1)}(x)\right| \le \frac{C}{\eta^{n-1}}\|f\|_{\infty,\eta}\left|(\rho P)^{(n-1)}(\tfrac{x}{\eta})\right| \le \frac{C}{\eta^{n-1}}\|f\|_{\infty,\eta}.$$

By (4.3.19), we have

$$\left|\langle \widetilde{p}\,, f\rangle^T \left\langle \Phi'\,, \Phi'^T\right\rangle_\eta \widetilde{p}^{(n-1)}(x)\right| \le \frac{C}{\eta^n}\|f\|_{\infty,\eta}\left|(\rho P)^{(n-1)}(\tfrac{x}{\eta})\right| \le \frac{C}{\eta^n}\|f\|_{\infty,\eta}. \tag{4.3.22}$$

Injecting (4.3.21) and (4.3.22) in (4.3.20) finishes the proof. □

First, an estimation of the best approximation by $(\widetilde{\phi}_i)_{1\le i\le N}$ of the even part f_e of the PAW eigenfunction f is proved.

Lemma 4.16. *Let f be an eigenfunction associated to the lowest eigenvalue of (4.1.11) and let f_e be the even part of f. Suppose that $\epsilon \leq \eta$. Then there exists a family of coefficients $(\alpha_i)_{1\leq i\leq N}$ and C independent of η and ϵ such that*

$$\left\| f_e - \sum_{i=1}^{N} \alpha_i \widetilde{\phi}_i^I \right\|_{\infty,\eta,I} \leq C\eta \left(\frac{\eta}{\epsilon}\right)^{2N-1} \|f\|_{\infty,\eta,I},$$

and for the same family of coefficients

$$\left\| f_e' - \sum_{i=1}^{N} \alpha_i \widetilde{\phi}_i^{I\prime} \right\|_{\infty,\eta,I} \leq C \left(\frac{\eta}{\epsilon}\right)^{2N} \|f\|_{\infty,\eta,I}.$$

Proof. For clarity, we will drop the index I in this proof. First we write the Taylor expansion of f around 0, for $|x| \leq \eta$:

$$f_e(x) = \sum_{k=0}^{N-1} \frac{f^{(2k)}(0)}{(2k)!} x^{2k} + R_{2N}(f)(x),$$

where $R_{2N}(f)$ is the integral form of the remainder

$$R_{2N}(f)(x) = \int_0^x \frac{f^{(2N)}(t)}{(2N-1)!}(x-t)^{2N-1}\,\mathrm{d}t.$$

The remainder $R_{2N}(f)$ satisfies

$$\begin{aligned} |R_{2N}(f)(x)| &\leq C\eta^{2N} \left\|f^{(2N)}\right\|_{\infty,\eta} \\ &\leq C\eta \left(\tfrac{\eta}{\epsilon}\right)^{2N-1} \|f\|_{\infty,\eta}, \end{aligned}$$

where, in the second inequality, we used Lemma 4.15. Thus, the best approximation of f by a linear combination of $(\widetilde{\phi}_k)_{1\leq k\leq N}$ is at most of order η. In the remainder of the proof, we will show that this order is attainable. Setting $t = \frac{x}{\eta}$, we obtain

$$f_e(x) - \sum_{i=1}^{N} \alpha_i \widetilde{\phi}_i(x) = \sum_{k=0}^{N-1} \frac{f^{(2k)}(0)}{(2k)!} \eta^{2k} t^{2k} - \sum_{i=1}^{N} \alpha_i \widetilde{\phi}_i(\eta t) + R_{2N}(f)(\eta t).$$

By Lemma 4.15, we have for all $1 \leq k \leq N-1$:

$$\left| \frac{f^{(2k)}(0)}{(2k)!} \eta^{2k} \right| \leq C\eta \left(\frac{\eta}{\epsilon}\right)^{2k-1}.$$

The family $(\widetilde{\phi}_j)_{1\leq j\leq N}$ satisfies

$$\widetilde{\Phi}(x) = C_\eta^{(P)} P(\tfrac{x}{\eta}),$$

where $P(t)$ is the vector of polynomials $P_k(t) = \frac{1}{2^k k!}(t^2-1)^k$. By Lemma 4.9 in [BCD17b], we know

that $C_\eta^{(P)}$ can be written:

$$C_\eta^{(P)} = \Phi(\eta)e_0^T + \eta\Phi'(\eta)\beta_1^T + \mathcal{O}(\eta^2), \tag{4.3.23}$$

where β_1 is a vector of $\mathbb{R}^d$ uniformly bounded in η. Thus we have

$$\sum_{k=0}^{N-1} \frac{f^{(2k)}(0)}{(2k)!}\eta^{2k}t^{2k} - \sum_{i=1}^{N} \alpha_i\widetilde{\phi}_i(\eta t) = f(0) - \alpha^T\Phi(\eta) + \mathcal{O}\left(\eta\left(\frac{\eta}{\epsilon}\right)^{2N-1}\right).$$

To get the result, α has to be chosen such that $\alpha^T\Phi(\eta) = f(0)$, which is possible because $\Phi(\eta) \neq 0$.

For f_e', we proceed the same way. However, by Lemma 4.15, the remainder of the Taylor expansion of f_e' satisfies

$$|R_{2N}(f')(x)| \leq C\eta^{2N}\left\|f^{(2N+1)}\right\|_{\infty,\eta} \leq C\left(\tfrac{\eta}{\epsilon}\right)^{2N}\|f\|_{\infty,\eta}.$$

We simply have to check that $\|\widetilde{\Phi}'\|_{\infty,\eta}$ is bounded when η goes to 0. By (4.3.23) and because $P_0' = 0$,

$$\widetilde{\Phi}'(x) = \Phi'(\eta)\beta_1^T P'(\tfrac{x}{\eta}) + \mathcal{O}(\eta),$$

hence $\|\widetilde{\Phi}'\|_{\infty,\eta}$ is bounded when η goes to 0. □

We can now give an estimate for $f_e - \sum_{i=1}^{N} \langle\widetilde{p}\,, f\rangle\,\phi_i$.

Lemma 4.17. *Assume that f is the generalized eigenfunction of (4.1.11) associated the lowest generalized eigenvalue. Let f_e be the even part of f. Then*

$$\left\|f_e - \left\langle\widetilde{p}^I\,, f\right\rangle^T\widetilde{\Phi}_I\right\|_{\infty,\eta,I} \leq C\eta\left(\frac{\eta}{\epsilon}\right)^{2N-1}\|f\|_{\infty,\eta,I},$$

and

$$\left\|f_e' - \left\langle\widetilde{p}^I\,, f\right\rangle^T\widetilde{\Phi}_I'\right\|_{\infty,\eta,I} \leq C\left(\frac{\eta}{\epsilon}\right)^{2N-1}\|f\|_{\infty,\eta,I}.$$

Proof. For clarity, we will drop the index I. For any family $(\alpha_j)_{1\leq j\leq N}$, we have for $x \in (-\eta, \eta)$

$$\begin{aligned} f_e(x) - \langle\widetilde{p}\,, f\rangle^T\widetilde{\Phi}(x) &= f_e(x) - \left\langle\widetilde{p}\,, f_e - \sum_{j=1}^{N}\alpha_j\widetilde{\phi}_j + \sum_{j=1}^{N}\alpha_j\widetilde{\phi}_j\right\rangle^T\widetilde{\Phi}(x) \\ &= f_e(x) - \sum_{j=1}^{N}\alpha_j\widetilde{\phi}_j - \left\langle\widetilde{p}\,, f_e - \sum_{j=1}^{N}\alpha_j\widetilde{\phi}_j\right\rangle^T\widetilde{\Phi}(x). \end{aligned}$$

By Lemma 4.16, $(\alpha_j)_{1\leq j\leq N}$ can be chosen such that for any $x \in (-\eta, \eta)$

$$\left|f_e(x) - \sum_{j=1}^{N}\alpha_j\widetilde{\phi}_j(x)\right| \leq C\eta\left(\frac{\eta}{\epsilon}\right)^{2N-1}\|f\|_{\infty,\eta}.$$

Thus by item 3 of Lemma 4.7,

$$\left\| f_e - \langle \widetilde{p}\,, f\rangle^T \widetilde{\Phi} \right\|_{\infty,\eta} \leq C\eta \left(\frac{\eta}{\epsilon}\right)^{2N-1} \|f\|_{\infty,\eta}.$$

Similarly, we have by item4 of Lemma 4.7 for any function $g \in H^1_{\mathrm{per}}(0,1)$ with $g' \in L^\infty(-\eta,\eta)$,

$$\left| \langle \widetilde{p}\,, g\rangle^T \widetilde{\Phi}'(x) \right| \leq C\|g\|_{H^1,\eta} \leq C\eta^{1/2}(\|g\|_{\infty,\eta} + \|g'\|_{\infty,\eta}), \tag{4.3.24}$$

and with the same coefficients (α_j),

$$\left| f_e'(x) - \sum_{j=1}^N \alpha_j \widetilde{\phi}_j' \right| \leq C \left(\frac{\eta}{\epsilon}\right)^{2N-1} \|f\|_{\infty,\eta}.$$

So,

$$\begin{aligned}\left\| f_e' - \langle \widetilde{p}\,, f\rangle^T \widetilde{\Phi}' \right\|_{\infty,\eta} &\leq \left\| f_e' - \sum_{j=1}^N \alpha_j \widetilde{\phi}_j' \right\|_{\infty,\eta} + \left\| \left\langle \widetilde{p}\,, f_e - \sum_{j=1}^N \alpha_j \widetilde{\phi}_j \right\rangle^T \widetilde{\Phi}' \right\|_{\infty,\eta} \\ &\leq C \left(\frac{\eta}{\epsilon}\right)^{2N-1} \|f\|_{\infty,\eta},\end{aligned}$$

where in the last inequality, we used (4.3.24) with Lemma 4.16. □

In the proof of the lower bound of Theorem 4.2, we will need to bound terms of the form $\left\| f_e - \langle \widetilde{p}^I\,, f\rangle^T \widetilde{\Phi}_I \right\|_{\infty,\eta,I}$. If $\epsilon < \eta$, we will get worse bounds than by setting $\epsilon = \eta$. Hence, from now on, we fix $\epsilon = \eta$.

To estimate the term $\left\langle f - \langle \widetilde{p}^I\,, f\rangle^T \widetilde{\Phi}_I\,, \delta V \left(f - \langle \widetilde{p}^I\,, f\rangle^T \widetilde{\Phi}_I \right) \right\rangle_{I,\eta}$, we will need the following estimates.

Lemma 4.18. *Let f be an eigenfunction associated to the lowest generalized eigenvalue of (4.1.11). Then*

$$\left\| f - \langle \widetilde{p}^I\,, f\rangle^T \widetilde{\Phi}_I \right\|_{\infty,\eta,I} \leq C\eta \|f\|_{\infty,\eta,I},$$

and

$$\left\| f' - \langle \widetilde{p}^I\,, f\rangle^T \widetilde{\Phi}_I' \right\|_{\infty,\eta,I} \leq C \|f\|_{\infty,\eta,I},$$

Proof. This follows from Lemma 4.17 and that the odd part of f is bounded in $(-\eta,\eta)$ by $\eta\|f'\|_{L^\infty(-\eta,\eta)}$, which is itself bounded by $C\eta\|f\|_{L^\infty(-\eta,\eta)}$ according to Lemma 4.15. □

We need a uniform bound in η on the PAW eigenfunction f, in order to prove Theorem 4.2.

Lemma 4.19. *Let f be an L^2_{per}-normalized eigenfunctions associated to the first eigenvalue of (4.1.11). Then there exists a positive constant C independent of η such that for all $0 < \eta \leq \eta_0$*

$$\|f\|_{H^1_{\mathrm{per}}} \leq C.$$

Proof. This is a direct consequence of Equation (4.3.15). □

We now have all the elements to complete the proof of Theorem 4.2.

Proof of the lower bound in Theorem 4.2. Let f be an L^2_{per}-normalized generalized eigenfunction of the PAW eigenvalue problem (4.1.11). By Proposition 4.13, we have

$$\begin{aligned}\left\langle f\,,H^{PAW}f\right\rangle = \left\langle f\,,\widetilde{H}f\right\rangle - 2\sum_{I\in\{0,a\}}\left\langle f-\langle\widetilde{p}^I\,,f\rangle^T\widetilde{\Phi}_I\,,\langle\widetilde{p}^I\,,f\rangle^T\left(H\Phi_I-(H+\delta V)\widetilde{\Phi}_I\right)\right\rangle \\ + \sum_{I\in\{0,a\}}\left\langle f-\langle\widetilde{p}^I\,,f\rangle^T\widetilde{\Phi}_I\,,\delta V\left(f-\langle\widetilde{p}^I\,,f\rangle^T\widetilde{\Phi}_I\right)\right\rangle_{\eta,I}. \quad (4.3.25)\end{aligned}$$

We simply bound terms with $I=0$ as the terms with $I=a$ are treated exactly the same way. First, we estimate $\left\langle f-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}\,,\delta V\left(f-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}\right)\right\rangle_{I,\eta}$. By Lemma 4.17, we have:

$$\begin{aligned}&\left|\left\langle f-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}\,,\delta V\left(f-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}\right)\right\rangle_{\eta}\right| \\ &\quad= Z_0\left|\left(f(0)-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}(0)\right)^2-\int_{-\eta}^{\eta}\chi_\eta(x)\left(f(x)-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}(x)\right)^2\mathrm{d}x\right| \\ &\quad= Z_0\left|\int_{-\eta}^{\eta}\chi_\eta(x)\left(\left(f(x)-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}(x)\right)^2-\left(f(0)-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}(0)\right)^2\right)\mathrm{d}x\right| \\ &\quad\le C\eta\left\|f'-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}'\right\|_{\infty,\eta}\left\|f-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}\right\|_{\infty,\eta} \\ &\quad\le C\eta^2\|f\|^2_{\infty,\eta}, \quad (4.3.26)\end{aligned}$$

where in the last inequality, we applied Lemma 4.18.

We then estimate $\left\langle f'-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}'\,,\langle\widetilde{p}\,,f\rangle^T(\Phi'-\widetilde{\Phi}')\right\rangle$:

$$\begin{aligned}&\left|\left\langle f'-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}'\,,\langle\widetilde{p}\,,f\rangle^T(\Phi'-\widetilde{\Phi}')\right\rangle\right| \\ &\quad=\left|\int_{-\eta}^{\eta}\left(f_e'(x)-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}'(x)\right)\langle\widetilde{p}\,,f\rangle^T(\Phi'-\widetilde{\Phi}')(x)\,\mathrm{d}x\right| \\ &\quad\le C\eta\left\|f_e'-\langle\widetilde{p}\,,f\rangle^T\widetilde{\Phi}'\right\|_{\infty,\eta}\|f\|_{H^1_{\mathrm{per}}} \\ &\quad\le C\eta\|f\|_{\infty,\eta}\|f\|_{H^1_{\mathrm{per}}}, \quad (4.3.27)\end{aligned}$$

where in the first inequality, we used item 1 of Lemma 4.7 and in the second, Lemma 4.17. Finally,

it remains to estimate $\left\langle f - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}, \langle \widetilde{p}, f\rangle^T (\delta_0 \Phi - \chi_\eta \widetilde{\Phi}) \right\rangle$:

$$\begin{aligned}
&\left|\left\langle f - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}, \langle \widetilde{p}, f\rangle^T (\delta_0 \Phi - \chi_\eta \widetilde{\Phi}) \right\rangle\right| \\
&\quad \leq \left| \left(f(0) - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}(0) \right) \langle \widetilde{p}, f\rangle^T (\Phi(0) - \widetilde{\Phi}(0)) \right| \\
&\qquad + \left| \int_{-\eta}^{\eta} \chi_\eta(x) \left(\left(f_e(x) - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}(x) \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}(x) - \left(f_e(0) - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}(0) \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}(0) \right) \mathrm{d}x \right| \\
&\quad \leq C\eta^2 \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}} + C\eta \left\| \left(\left(f_e - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right)' \right\|_{\infty,\eta}.
\end{aligned}$$

We have

$$\begin{aligned}
&\left\| \left(\left(f_e - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right)' \right\|_{\infty,\eta} \\
&\quad \leq \left\| \left(f_e - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}' \right\|_{\infty,\eta} + \left\| \left(f_e' - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}' \right) \langle \widetilde{p}, f\rangle^T \widetilde{\Phi} \right\|_{\infty,\eta} \\
&\quad \leq C\eta \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}} + C \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}},
\end{aligned}$$

where we applied Lemma 4.17 and items 3 and 4 of Lemma 4.7. Thus,

$$\left|\left\langle f - \langle \widetilde{p}, f\rangle^T \widetilde{\Phi}, \langle \widetilde{p}, f\rangle^T (\delta_0 \Phi - \chi_\eta \widetilde{\Phi}) \right\rangle\right| \leq C\eta \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}}. \tag{4.3.28}$$

Injecting (4.3.26), (4.3.27) and (4.3.28), in (4.3.25), we obtain

$$\begin{aligned}
\langle f, H^{PAW} f \rangle &\geq \left\langle f, \widetilde{H} f \right\rangle - C\eta^2 \|f\|_{L^\infty}^2 - C\eta \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}} \\
&\geq E_0 \left\langle f, \widetilde{S} f \right\rangle - C\eta^2 \|f\|_{L^\infty}^2 - C\eta \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}}.
\end{aligned}$$

Using item 3 of Lemma 4.9, we obtain

$$\begin{aligned}
E_0 \langle f, S^{PAW} f \rangle - C\eta^2 \|f\|_{L^\infty}^2 - C\eta \|f\|_{\infty,\eta} \|f\|_{H^1_{\mathrm{per}}} &\leq \langle f, H^{PAW} f \rangle \\
&\leq E^{PAW} \langle f, S^{PAW} f \rangle,
\end{aligned}$$

and the result follows from Lemma 4.19 and the Sobolev embedding $\|f\|_{L^\infty} \leq C \|f\|_{H^1_{\mathrm{per}}}$. □

Improvement of the model

The critical term yielding the upper bound of Theorem 4.2 is due to the poor approximation of f by the pseudo wave functions $\widetilde{\phi}_k$. The latter are only even polynomials inside the cut-off region, hence incorporating odd functions to the PAW treatment should improve the upper bound on the PAW eigenvalue E^{PAW}.

The odd atomic wave functions are the functions

$$\widetilde{\theta}_k(x) = \sin(2\pi kx), \quad k \in \mathbb{N}^*, \tag{4.3.29}$$

which are eigenfunctions of the atomic Hamiltonian $-\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k$. As these functions are already smooth, there is no need to take pseudo wave functions different from the atomic wave functions.

To define the corresponding projector functions $\widetilde{q}_k$, first we denote by

$$G = \left(\int_{-\eta}^{\eta} \rho_\eta(t) \sin(2\pi jt) \sin(2\pi kt) \, \mathrm{d}t \right)_{1\leq j,k\leq N}, \tag{4.3.30}$$

where ρ_η is the smooth cut-off function defined in Section 4.1.4. G is an invertible matrix since it is the Gram matrix of the linearly independent family of functions $(\sin(2\pi kx))_{1\leq k\leq N}$. Now let $\widetilde{q}_k$ be defined by

$$\widetilde{q}_k(x) = \rho_\eta(x) \sum_{j=1}^{N} (G^{-1})_{jk} \widetilde{\theta}_j(x), \tag{4.3.31}$$

so the functions $(\widetilde{\theta}_k)_{1\leq k\leq N}$ and $(\widetilde{q}_k)_{1\leq k\leq N}$ satisfy

$$\left\langle \widetilde{q}_j \, , \widetilde{\theta}_k \right\rangle = \delta_{jk}.$$

The functions $(\widetilde{\theta}^a_k)_{1\leq k\leq N}$ are equal to $(\widetilde{\theta}_k(\cdot - a))_{1\leq k\leq N}$ and the projector functions $(\widetilde{q}^a_k)_{1\leq k\leq N}$ denotes the shifted projector functions $(\widetilde{q}_k(\cdot - a))_{1\leq k\leq N}$.

Since $\widetilde{\theta}_k$ is an eigenfunction of $-\frac{\mathrm{d}^2}{\mathrm{d}x^2} - Z_0 \sum_{k\in\mathbb{Z}} \delta_k$, for all $1 \leq i, j \leq N$ and $I = 0, a$,

$$\left\langle \widetilde{\theta}^I_i \, , H\widetilde{\theta}^I_i \right\rangle - \left\langle \widetilde{\theta}^I_i \, , H_{\mathrm{ps}} \widetilde{\theta}^I_i \right\rangle = - \left\langle \widetilde{\theta}^I_i \, , -Z_I \chi_\eta \widetilde{\theta}^I_i \right\rangle .$$

Hence, the new expression of H^{PAW} is given by

$$\begin{aligned} H^{PAW} = H_{\mathrm{ps}} + & \sum_{\substack{i,j=1 \\ I\in\{0,a\}}}^{N} \widetilde{p}^I_i \left(\left\langle \phi^I_i \, , H\phi_j \right\rangle_{I,\eta} - \left\langle \widetilde{\phi}^I_i \, , H_{\mathrm{ps}} \widetilde{\phi}^I_j \right\rangle_{I,\eta} \right) \left\langle \widetilde{p}^I_j \, , \cdot \right\rangle \\ & - \sum_{\substack{i,j=1 \\ I\in\{0,a\}}}^{N} \widetilde{q}^I_i \left\langle \widetilde{\theta}^I_i \, , -Z_I \chi_\eta \widetilde{\theta}_j \right\rangle_{I,\eta} \left\langle \widetilde{q}^I_j \, , \cdot \right\rangle , \end{aligned} \tag{4.3.32}$$

and S^{PAW} remains unchanged.

We denote by $\widetilde{q}^I$ the vector of functions $(\widetilde{q}^I_1, \ldots, \widetilde{q}^I_N)^T$ and $\widetilde{\Theta}_I$ the vector of functions $(\widetilde{\theta}^I_1, \ldots, \widetilde{\theta}^I_N)^T$.

Using the functions $(\widetilde{\theta}^I_k)_{1\leq k\leq N}$ and $(\widetilde{q}^I_k)_{1\leq k\leq N}$ in the PAW treatment, we have the following theorem on the lowest PAW eigenvalue.

Theorem 4.20. *Let ϕ^I_i, $\widetilde{\phi}^I_i$ and $\widetilde{p}^I_i$, for $i = 1, \ldots, N$ and $I = 0, a$ be the functions defined in Section*

4.1.3. Suppose $\eta_0 > 0$ satisfies Assumption 4.1 and Assumption 4.2. Let $(\widetilde{\theta}_k^I)_{1\le k\le N}$ be the functions given by (4.3.29) and $(\widetilde{q}_k^I)_{1\le k\le N}$ be the functions given by (4.3.31). Let E^{PAW} the lowest eigenvalue of the generalized eigenvalue problem $H^{PAW}f = E^{PAW}S^{PAW}f$ with H^{PAW} defined in (4.3.32). Let E_0 be the lowest eigenvalue of H (4.1.1). Then there exists a positive constant C independent of η such that for all $0 < \eta \le \eta_0$

$$-C\eta \le E^{PAW} - E_0 \le C\eta^{2N}. \tag{4.3.33}$$

The proof of Theorem 4.20 follows the same steps of the proof of Theorem 4.2. First, we prove that for $g \in H^1_{\mathrm{per}}$, the quantity $\left\langle g\,, H^{PAW}g\right\rangle$ is equal to $\left\langle g\,, \widetilde{H}g\right\rangle$ and error terms of the form $g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I - \left\langle \widetilde{q}^I\,, g\right\rangle^T \widetilde{\Theta}_I$ that needs to be estimated.

Proposition 4.21. *Let $g \in H^1_{\mathrm{per}}(0,1)$. Then*

$$\begin{aligned}\left\langle g\,, H^{PAW}g\right\rangle = \left\langle g\,, \widetilde{H}g\right\rangle &- 2\sum_{I\in\{0,a\}} \left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I\,, \left\langle \widetilde{p}^I\,, g\right\rangle^T \left(H\Phi_I - (H+\delta V)\widetilde{\Phi}_I\right)\right\rangle \\ &+ 2\sum_{I\in\{0,a\}} \left\langle g - \left\langle \widetilde{q}^I\,, g\right\rangle^T \widetilde{\Theta}_I\,, \left\langle \widetilde{q}^I\,, g\right\rangle^T \delta V\widetilde{\Theta}_I\right\rangle_{I,\eta} \\ &+ \sum_{I\in\{0,a\}} \left\langle g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I - \left\langle \widetilde{q}^I\,, g\right\rangle^T \widetilde{\Theta}_I\,, \delta V\left(g - \left\langle \widetilde{p}^I\,, g\right\rangle^T \widetilde{\Phi}_I - \left\langle \widetilde{q}^I\,, g\right\rangle^T \widetilde{\Theta}_I\right)\right\rangle_{I,\eta}.\end{aligned}$$

Proof. The proof is similar to the proof of Proposition 4.13. □

Lemma 4.22. *There exists a constant C independent of η such that for all $f \in H^1_{\mathrm{per}}(0,1)$ for x in $(-\eta,\eta)$,*

$$\left|\left\langle \widetilde{q}^I\,, f\right\rangle^T \widetilde{\Theta}_I(x)\right| \le C\|f\|_{\infty,\eta,I}.$$

Proof. For clarity, we will drop the index I. For $0 \le j \le N-1$, let

$$v_j = (2\pi\eta)^{2j+1}\begin{pmatrix}1\\ 2^{2j+1}\\ \vdots\\ N^{2j+1}\end{pmatrix}, \qquad \hat{v}_j = \frac{1}{\eta^{2j+1}}v_j.$$

Let $(\hat{w}_j)_{0\le j\le N-1}$ be the dual basis of $(\hat{v}_j)_{0\le j\le N-1}$ and $w_j = \frac{1}{\eta^{2j+1}}\hat{w}_j$. Let M be the matrix such that for all $0 \le j,k \le N-1$,

$$M_{jk} = \frac{(-1)^{j+k}}{(2j+1)!(2k+1)!}\int_{-1}^{1}\rho(t)t^{2j+2k+2}\,\mathrm{d}t.$$

By a Taylor expansion, we obtain for $t \in (-1,1)$,

$$\widetilde{\Theta}(\eta t) = \begin{pmatrix}\sin(2\pi\eta t)\\ \vdots\\ \sin(2\pi\eta N t)\end{pmatrix} = \sum_{k=0}^{N-1}\frac{(-1)^k(2\pi\eta t)^{2k+1}}{(2k+1)!}\begin{pmatrix}1\\ 2^{2j+1}\\ \vdots\\ N^{2j+1}\end{pmatrix} + R_{\widetilde{\Theta}}(\eta t),$$

where $|R_{\widetilde{\Theta}}(\eta t)| \leq C\eta^{2N+1}$. Then, we can rewrite the matrix G given by (4.3.30)

$$\begin{aligned} G &= \eta \int_{-1}^{1} \rho(t) \left(\sum_{j=0}^{N-1} \frac{(-1)^j \eta^{2j+1}}{(2j+1)!} \hat{v}_j t^{2j+1} + R_{\widetilde{\Theta}}(\eta t) \right) \left(\sum_{k=0}^{N-1} \frac{(-1)^k \eta^{2k+1}}{(2k+1)!} \hat{v}_k t^{2k+1} + R_{\widetilde{\Theta}}(\eta t) \right)^T \mathrm{d}t \\ &= \eta \sum_{j,k=0}^{N-1} M_{jk} v_j v_k^T + \eta \int_{-1}^{1} \sum_{j=0}^{N-1} \frac{(-1)^j}{(2j+1)!} t^{2j+1} \left(v_j R_{\widetilde{\Theta}}(\eta t)^T + R_{\widetilde{\Theta}}(\eta t) v_j^T \right) \mathrm{d}t + \mathcal{O}(\eta^{4N+3}). \end{aligned}$$

Hence, we have for $0 \leq j, k \leq N-1$,

$$w_j^T G w_k = \eta M_{jk} + \eta w_j^T \mathcal{R}_k + \eta \mathcal{R}_j^T w_k + \mathcal{O}(\eta^5),$$

where

$$\mathcal{R}_k = \int_{-1}^{1} \rho(t) \frac{(-1)^k}{(2k+1)!} t^{2k+1} R_{\widetilde{\Theta}}(\eta t) \, \mathrm{d}t.$$

But $\|w_k\| = \mathcal{O}(\eta^{-2k-1})$ and $|R_{\widetilde{\Theta}}(\eta t)| \leq C\eta^{2N+1}$, hence $\mathcal{R}_j^T w_k = \mathcal{O}(\eta^2)$. Thus, if we denote by

$$W = \begin{pmatrix} w_0^T \\ \vdots \\ w_{N-1}^T \end{pmatrix}, \qquad V = \begin{pmatrix} v_0^T \\ \vdots \\ v_{N-1}^T \end{pmatrix},$$

we obtain

$$W G W^T = \eta M + \mathcal{O}(\eta^3),$$

and

$$W^{-T} G^{-1} W^{-1} = V G^{-1} V^T = \frac{1}{\eta} M^{-1} + \mathcal{O}(\eta). \tag{4.3.34}$$

Thus, we have for $f \in L^\infty(-\eta, \eta)$ and $x \in (-\eta, \eta)$

$$\begin{aligned} \langle \widetilde{q}, f \rangle^T \widetilde{\Theta}(x) = \eta \left(\int_{-1}^{1} \rho(t) f(\eta t) G^{-1} \left(\sum_{j=0}^{N-1} \frac{(-1)^j}{(2j+1)!} t^{2j+1} v_j + R_{\widetilde{\Theta}}(\eta t)^T \right) \mathrm{d}t \right)^T \\ \left(\sum_{j=0}^{N-1} \frac{(-1)^j}{(2j+1)!} \left(\frac{x}{\eta} \right)^{2j+1} v_j + R_{\widetilde{\Theta}}(x) \right). \end{aligned} \tag{4.3.35}$$

By expanding (4.3.35), three types of terms arise involving

1. $v_j^T G^{-1} v_k$: by (4.3.34), we have $|v_j^T G^{-1} v_k| = \mathcal{O}\left(\frac{1}{\eta}\right)$;
2. $v_j^T G^{-1} R_{\widetilde{\Theta}}(x)$: by (4.3.34), $\|v_j G^{-1}\| = \mathcal{O}\left(\frac{1}{\eta^{2N-1}}\right)$ and because $R_{\widetilde{\Theta}}(x) = \mathcal{O}(\eta^{2N+1})$, we have $|v_j^T G^{-1} R_{\widetilde{\Theta}}(x)| = \mathcal{O}(\eta^2)$;
3. $R_{\widetilde{\Theta}}(\eta t)^T G^{-1} R_{\widetilde{\Theta}}(x)$: by (4.3.34), we deduce that $\|G^{-1}\| = \mathcal{O}\left(\frac{1}{\eta^{4N-1}}\right)$, but $R_{\widetilde{\Theta}}(x) = \mathcal{O}(\eta^{2N+1})$, hence $|R_{\widetilde{\Theta}}(\eta t)^T G^{-1} R_{\widetilde{\Theta}}(x)| = \mathcal{O}(\eta^3)$.

Thus,

$$|\langle \widetilde{q}\,, f\rangle^T \widetilde{\Theta}(x)| \leq C\|f\|_{\infty,\eta}.$$

□

Lemma 4.23. *Let f be a smooth and odd function. Then we have*

$$\left\| f - \langle \widetilde{q}^I\,, f\rangle^T \widetilde{\Theta}_I \right\|_{\infty,\eta,I} \leq C\eta^{2N+3}\|f^{(2N+3)}\|_{\infty,\eta,I},$$

Proof. We simply write the Taylor expansion of f around 0. Then by expanding the functions θ_k around 0, it is easy to show that the difference between f and the best approximation in $(-\eta,\eta)$ of f by a linear combination of θ_k is bounded by the Taylor remainder of f and terms arising from the truncation of the expansions of the functions θ_k which are both of order $\mathcal{O}(\eta^{2N+3})$. We then conclude using Lemma 4.22. □

The presence of $\widetilde{\theta}_j$ and $\widetilde{q}_j$ (see (4.3.32) above) does not change the lower bound of the PAW eigenvalue as it does not improve the estimate of critical terms in the proof of lower bound in Theorem 4.2. However, we get a much better upper bound as it is the odd part of the wave function ψ which prevents to have a better bound. Thus introducing these odd functions in the PAW treatment, we have Theorem 4.20.

4.4 Numerical tests

In this section, some numerical tests are provided to confirm the bounds obtained in Theorems 4.1, 4.2 and 4.20. The simulations of the different PAW versions are done with $a = 0.4$ and $Z_0 = Z_a = 10$.

4.4.1 The PAW equations

Without pseudopotentials

We solve the generalized eigenvalue problem

$$H^N f = E^{(\eta)} S^N f,$$

where H^N and S^N are defined by Equations (4.1.9) and (4.1.10), by expanding f in 512 plane-waves. We study how $E^{(\eta)}$ behaves as a function of η. In our case, the PAW eigenvalue $E^{(\eta)}$ is smaller than E_0. For this regime, Theorem 4.1 states that $E^{(\eta)}$ converges at least linearly to E_0, which is what we observe in Figure 4.4.1.

With pseudopotentials

The eigenfunction f is expanded in 1000 plane waves for which convergence is reached. The integrals of plane-waves against PAW functions are computed with an accurate numerical integral scheme.

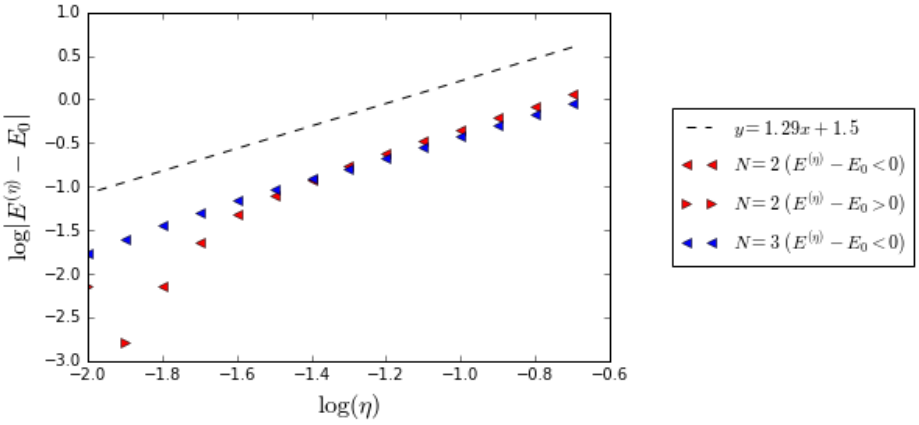


Figure 4.4.1 – Error on the lowest eigenvalue of the truncated PAW equations (4.1.8)

In view of Figure 4.4.2, the lower bound in Theorem 4.2 seems sharp. The use of odd PAW functions improves the error on the PAW eigenvalue (Figure 4.4.3) for a range of moderate values of the cut-off radius η. However, the use of odd PAW functions does not give a better lower bound.

Finally, the upper bound in Theorem 4.20 seems optimal (see Figure 4.4.3). For $N = 2$, we have a slope close to the theoretical value ($2N = 4$).

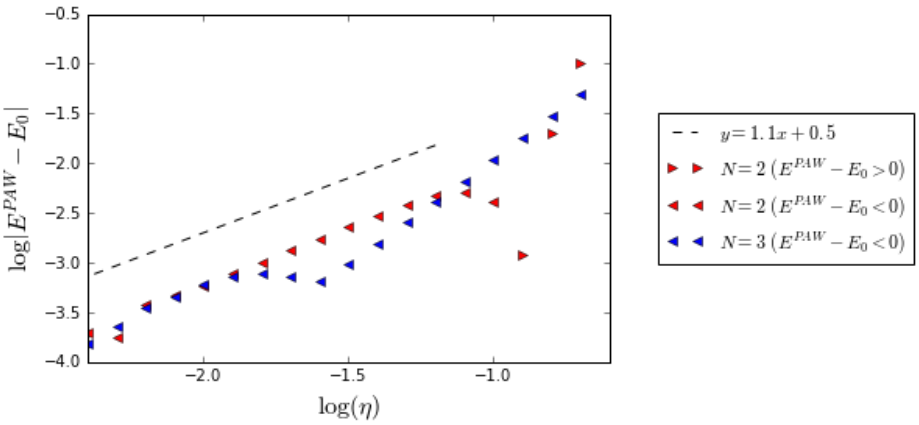


Figure 4.4.2 – Error on the lowest eigenvalue of the PAW equations (4.1.11) with pseudopotentials

4.4.2 Comparison between the PAW and VPAW methods in pre-asymptotic regime

The simulations are run for a fixed value of $d = 6$ and different values of $\eta = 0.1$ and $\eta = 0.2$. In Figure 4.4.4, E_0 is the lowest eigenvalue of the 1D-Schrödinger operator H. The PAW method considered in Figure 4.4.4 is the generalized eigenvalue problem (4.1.11).

Using Fourier methods to solve the VPAW eigenvalue problem (4.1.14), we have the following

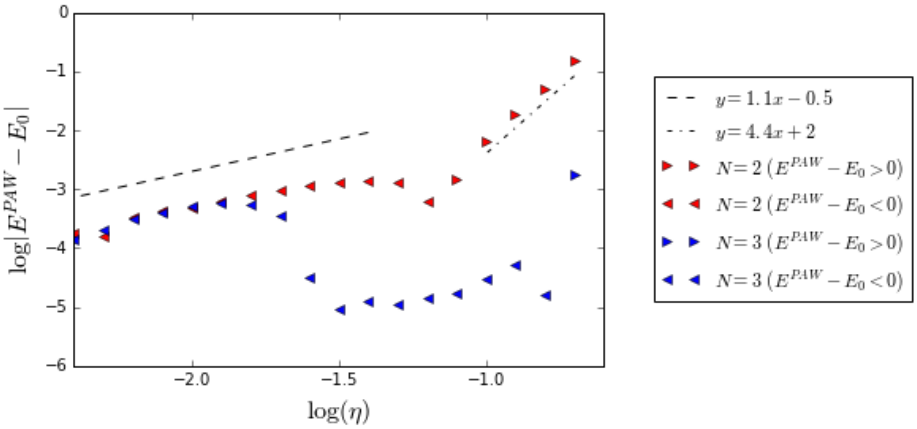


Figure 4.4.3 – Error on the lowest eigenvalue of the PAW equations with pseudopotentials including odd PAW functions

bound on the computed eigenvalue E_M^{VPAW} [BCD17b]:

$$0 < E_M^{\mathrm{VPAW}} - E_0 \leq C \left(\frac{\eta^{4N}}{M} + \frac{1}{\eta^{2d-2}} \frac{1}{M^{2d-1}} \right), \tag{4.4.1}$$

where M is the number of plane-waves, N the number of PAW functions and d the regularity of the PAW pseudo wave functions $\widetilde{\phi}_k$.

As expected, the PAW method quickly converges to E^{PAW} which, according to Theorem 4.2, is close but not equal to E_0. Although the VPAW method does not remove the Dirac singularities -which is why, asymptotically, the VPAW method convergence rate is of order $\mathcal{O}\left(\frac{1}{M}\right)$-, it converges faster to E_0 than the PAW method with pseudopotentials.

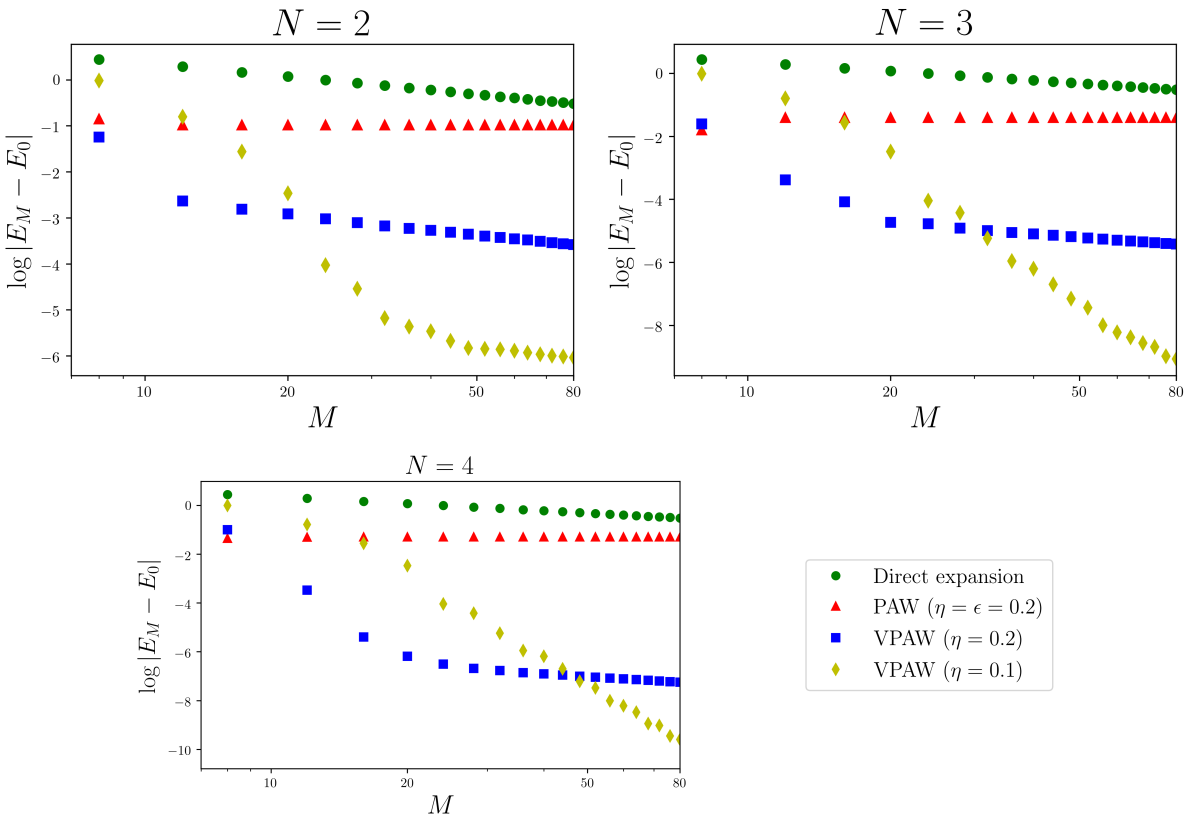


Figure 4.4.4 – Comparison between the PAW and VPAW methods

CHAPTER 5

THE VPAW METHOD FOR 3D HAMILTONIANS

In this chapter, we expose the results on the VPAW method applied to eigenvalue problems of periodic 3D linear Hamiltonians with Coulomb potentials [Dup18].

Similarly to the study of the VPAW method applied to the one-dimensional model with Dirac potentials, the cusp of the eigenfunction of the VPAW eigenvalue problem is significantly reduced. Hence, estimates on the eigenvalues obtained by a plane-wave discretization of the VPAW equations are similar to the estimates obtained in the one-dimensional model studied in Chapter 3.

This chapter is organized as follows. The VPAW method applied to periodic 3D linear Hamiltonians is presented in Section 5.1. Estimates on the eigenvalues of the plane-wave discretization of the VPAW equations are given in Section 5.2. Proofs of these results are gathered in Section 5.3. Numerical tests confirming the efficiency of the VPAW method can be found in Section 5.4.

5.1 VPAW method applied to linear 3D Hamiltonians

5.1.1 General setting

For simplicity, we restrict ourselves to the linear model. A quick overview of the spectral theory of periodic Hamiltonians can be found in [Gon15]. More thoroughful expositions of this theory are presented in [Eas73, Kuc12]. For extensions to nonlinear equations, the interested reader is referred to [CLBL02] for the Hartree model and to [CLBL01] for the Hartree-Fock model.

The crystal is modeled as an infinite periodic motif of N_{at} point charges at positions $\mathbf{R}_I$ in the unit cell

$$\Gamma = \left\{\alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \alpha_3\mathbf{a}_3, (\alpha_1,\alpha_2,\alpha_3) \in [-1/2,1/2)^3\right\}.$$

and repeated over a periodic lattice

$$\mathcal{R} = \mathbb{Z}\mathbf{a}_1 + \mathbb{Z}\mathbf{a}_2 + \mathbb{Z}\mathbf{a}_3.$$

where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are linearly independent vectors of $\mathbb{R}^3$.

The electronic properties of the crystal are determined by the spectrum of the periodic Hamil-

tonian H_{per} acting on $L^2(\mathbb{R}^3)$:

$$H_{\text{per}} = -\frac{1}{2}\Delta + V_{\text{per}} + W_{\text{per}}, \tag{5.1.1}$$

where V_{per} is an $\mathcal{R}$-periodic potential defined by

$$\begin{cases} -\Delta V_{\text{per}} = 4\pi \left(\sum\limits_{\mathbf{T}\in\mathcal{R}} \sum\limits_{I=1}^{N_{at}} Z_I \left(\delta_{\mathbf{R}_I}(\cdot + \mathbf{T}) - \frac{1}{|\Gamma|} \right) \right) \\ V_{\text{per}} \text{ is } \mathcal{R}\text{-periodic.} \end{cases} \tag{5.1.2}$$

In this paper, W_{per} is a smooth $\mathcal{R}$-periodic potential so that Equation (5.1.2) has a solution. In practice, W_{per} is a nonlinear potential depending on the model chosen to describe the electronic self-interaction (typically a Kohn-Sham potential).

The standard way to study the spectrum of H_{per} is through Bloch theory which will be outlined in the next few lines. Let $\mathcal{R}^*$ be the dual lattice

$$\mathcal{R}^* = \mathbb{Z}\mathbf{a}_1^* + \mathbb{Z}\mathbf{a}_2^* + \mathbb{Z}\mathbf{a}_3^*,$$

where $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ satisfies $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$. The reciprocal unit cell is defined by

$$\Gamma^* = \left\{ \alpha_1\mathbf{a}_1^* + \alpha_2\mathbf{a}_2^* + \alpha_3\mathbf{a}_3^*, (\alpha_1, \alpha_2, \alpha_3) \in [-1/2, 1/2)^3 \right\}.$$

As H_{per} commutes with $\mathcal{R}$-translations, H_{per} admits a Bloch decomposition in operators $H_{\mathbf{q}}$ acting on

$$L^2_{\text{per}}(\Gamma) = \{ f \in L^2_{\text{loc}}(\mathbb{R}^3) \mid f \text{ is } \mathcal{R}\text{-periodic} \},$$

with domain

$$H^2_{\text{per}}(\Gamma) = \{ f \in H^2_{\text{loc}}(\mathbb{R}^3) \mid f \text{ is } \mathcal{R}\text{-periodic} \}.$$

The operator $H_{\mathbf{q}}$ is given by:

$$H_{\mathbf{q}} = \frac{1}{2}|-i\nabla + \mathbf{q}|^2 + V_{\text{per}} + W_{\text{per}}, \quad \mathbf{q} \in \Gamma^*.$$

For each $\mathbf{q} \in \Gamma^*$, the operator $H_{\mathbf{q}}$ is self-adjoint, bounded below and with compact resolvent. Thus it has a discrete spectrum of infinite eigenvalues $E_{1,\mathbf{q}} \leq E_{2,\mathbf{q}} \leq \ldots, E_{n,\mathbf{q}} \to \infty$, counted with multiplicities, and the associated eigenfunctions $(\psi_{n,\mathbf{q}})_{n\in\mathbb{N}^*}$ form an orthonormal basis of $L^2_{\text{per}}(\Gamma)$:

$$H_{\mathbf{q}}\psi_{n,\mathbf{q}} = E_{n,\mathbf{q}}\psi_{n,\mathbf{q}}. \tag{5.1.3}$$

By Bloch theorem ([RS78], Chapter XIII), the spectrum of H_{per} is given by the union of the discrete spectra of an infinite number of eigenvalue problems parameterized by the vector $\mathbf{q}$ belonging to the reciprocal unit cell Γ^*:

$$\sigma(H_{\text{per}}; L^2(\mathbb{R}^3)) = \bigcup_{\mathbf{q}\in\Gamma^*} \sigma(H_{\mathbf{q}}; L^2_{\text{per}}(\Gamma)). \tag{5.1.4}$$

The VPAW method aims to ease the resolution of the eigenvalue problem (5.1.3). For clarity, we will only present the case $\mathbf{q} = 0$ and denote H_0 by H as this example contains all the main difficulties encountered in the numerical resolution of Equation (5.1.3). Transposition to $\mathbf{q} \neq 0$ can be done without problem.

5.1.2 The VPAW method for solids

Following the idea of the PAW method, an invertible transformation $(\mathrm{Id} + T)$ is applied to the eigenvalue problem (5.1.3), where T is the sum of operators T_I acting locally around each nucleus. For each operator T_I, two parameters N_{paw} and r_c need to be fixed (r_c and N_{paw} may depend on the atomic site I):

1. N_{paw} is the number of PAW functions used to build T_I,
2. r_c is a cut-off radius which will set the acting domain of T_I, more precisely:
   - for all $f \in L^2_{\mathrm{per}}(\Gamma)$, $\mathrm{supp}(T_I f) \subset \bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{R}_I + \mathbf{T}, r_c)$, where $B(\mathbf{R}, r)$ is the closed ball of $\mathbb{R}^3$ with center $\mathbf{R}$ and radius r,
   - if $\mathrm{supp}(f) \bigcap \bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{R}_I + \mathbf{T}, r_c) = \emptyset$, then $T_I f = 0$.

The operator T_I is given by:

$$T_I = \sum_{\mathbf{T}\in\mathcal{R}} \sum_{k=1}^{N_{\mathrm{paw}}} \left(\phi_k^I(\mathbf{r} - \mathbf{R}_I) - \widetilde{\phi}_k^I(\mathbf{r} - \mathbf{R}_I)\right) \left\langle \widetilde{p}_k^I(\cdot - \mathbf{R}_I)\,, \bullet \right\rangle, \tag{5.1.5}$$

where $\langle \bullet\,, \bullet \rangle$ is the L^2-scalar product on the unit cell Γ and the functions ϕ_k^I, $\widetilde{\phi}_k^I$ and $\widetilde{p}_k^I$ are functions in $L^2_{\mathrm{per}}(\Gamma)$. The PAW functions $(\phi_k^I)_{1\leq k\leq N_{\mathrm{paw}}}$, $(\widetilde{\phi}_k^I)_{1\leq k\leq N_{\mathrm{paw}}}$ and $(\widetilde{p}_k^I)_{1\leq k\leq N_{\mathrm{paw}}}$ must satisfy the following essential properties:

1. $\mathrm{supp}\,(\phi_k^I - \widetilde{\phi}_k^I) \subset \bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{T}, r_c)$;
2. $\widetilde{\phi}_k^I$ restricted to $B(0, r_c)$ is smooth;
3. $\widetilde{p}_k^I$ are supported in $\bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{T}, r_c)$ and $\forall\, 1 \leq i, j \leq N_{\mathrm{paw}}$, $\left\langle \widetilde{p}_i\,, \widetilde{\phi}_j \right\rangle = \delta_{ij}$ (that is $(\widetilde{p}_j)_{1\leq j\leq N_{\mathrm{paw}}}$ is dual to $(\widetilde{\phi}_j)_{1\leq j\leq N_{\mathrm{paw}}}$).

The operators T_I act locally in $\bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{R}_I + \mathbf{T}, r_c)$.

Several schemes exist in the literature to generate the PAW functions. In this paper, the PAW functions are close to the Vanderbilt scheme [KJ99] where only the projector functions differ from ours. Numerical tests in Section 5.4 suggest that the Vanderbilt scheme is also efficient to compute the eigenvalues of (5.1.14). The Blöchl scheme [Blo94] is another popular way to generate PAW functions although the first seems to be preferred [JTH14]. See [BCD17b, JTH14] for more details on the generation of the PAW functions.

Atomic wave function Let $(\varphi_k^I)_{1\leq k\leq N_{\text{paw}}} \in (L^2(\mathbb{R}^3))^{N_{\text{paw}}}$ be eigenfunctions of an atomic *non-periodic* Hamiltonian

$$H_I\varphi_k^I = \epsilon_k\varphi_k^I, \quad \epsilon_1^I \leq \epsilon_2^I \leq \epsilon_3^I \leq \dots, \quad \int_{\mathbb{R}^3} \varphi_k^I\varphi_{k'}^I = \delta_{kk'},$$

with H_I defined by

$$H_I = -\frac{1}{2}\Delta - \frac{Z_I}{|\mathbf{r}|} + W(|\mathbf{r}|), \tag{5.1.6}$$

where W is a smooth bounded potential. The operator H_I is self-adjoint on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. Again, in practice, W is a radial nonlinear potential belonging to the same family of models as W_{per} in Equation (5.1.2). Since the atomic Hamiltonian is rotationnaly invariant, H_I is block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ associated with the eigenspaces of the operator $\mathbf{L}^2$ (the square of the angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p} = \mathbf{r}\times(-i\nabla)$). The eigenfunctions φ_k^I can be decomposed into a radial function and a spherical harmonics (see [RS78] XIII.3.B for further details):

$$\varphi_k^I(\mathbf{r}) = r^\ell R_{n\ell}(r)Y_{\ell m}(\hat{\mathbf{r}}), \tag{5.1.7}$$

where $Y_{\ell m}$ is the real spherical harmonics and $R_{n\ell}$ is a continuous function such that $\lim_{r\to 0}|R_{n\ell}(r)| < \infty$. For $\mathbf{r}\in\mathbb{R}^3$, we define $\hat{\mathbf{r}} := \frac{\mathbf{r}}{|\mathbf{r}|}$ and when there is no ambiguity we will denote by r the euclidean norm of $\mathbf{r}$. The decomposition (5.1.7) also holds for some nonlinear models, see [Sol91, CM14]. The functions $R_{n\ell}$ satisfies the following radial Schrödinger equation

$$\mathfrak{h}_\ell R_{n\ell}(r) = -\frac{1}{2}R_{n\ell}''(r) - \frac{\ell+1}{r}R_{n\ell}'(r) - \frac{Z_I}{r}R_{n\ell}(r) + W(r)R_{n\ell}(r) = \epsilon_{n\ell}R_{n\ell}(r). \tag{5.1.8}$$

The eigenvalues of $\mathfrak{h}_\ell$, if they exist, are all simple. The discrete spectrum of H_I is then the collection of all the eigenvalues of $\mathfrak{h}_\ell$.

The PAW atomic wave functions $(\phi_k^I)_{1\leq k\leq N_{\text{paw}}} \in (L^2_{\text{per}}(\Gamma))^{N_{\text{paw}}}$ are then defined by

— for $1\leq k\leq N_{\text{paw}}$ and $\mathbf{r}\in\Gamma$, $\phi_k^I(\mathbf{r}) = \varphi_k^I(\mathbf{r})$,

— ϕ_k^I is $\mathcal{R}$-periodic.

If $W\neq 0$, there is a minimal angular momentum ℓ_{adm} for which $\mathfrak{h}_\ell$ for all $\ell\geq\ell_{\text{adm}}$ has no eigenvalue (see Theorem XIII.8 in [RS78], [Sol91]). As an immediate consequence, PAW functions can only be selected for a finite range of angular momentum $\ell\leq\ell_{\text{adm}}$.

We denote by $(n_0, n_1, \dots, n_{\ell_{\max}})$ the number of PAW functions for each admissible angular momentum, *i.e.* there are n_0 PAW functions for the angular momentum $\ell = 0, m = 0$, n_1 PAW functions for $\ell = 1$, $|m|\leq 1$, ... The total number of PAW functions for one atomic site is thus given by $N_{\text{paw}} = \sum_{\ell=0}^{\ell_{\max}}(2\ell+1)n_\ell$.

Pseudo wave function The pseudo wave functions $\widetilde{\phi}_k^I$ are the $\mathcal{R}$-periodic functions given in the unit cell Γ by:

$$\forall\,\mathbf{r}\in\Gamma,\ \widetilde{\phi}_k^I(\mathbf{r}) = r^\ell\widetilde{R}_{n\ell}(r)\,Y_{\ell m}(\hat{\mathbf{r}}). \tag{5.1.9}$$

where k stands for the multiple index (n, ℓ, m). The radial functions $\widetilde{R}_{n\ell}$, $1 \leq n \leq n_\ell, 0 \leq \ell \leq \ell_{\max}$ are polynomial inside the augmentation region $B(0, r_c)$:

$$\widetilde{R}_{n\ell}(r) = \begin{cases} \sum_{k=0}^{d} c_{2k} r^{2k} & \text{for } 0 \leq r \leq r_c \\ R_{n\ell}(r) & \text{for } r > r_c \end{cases} \tag{5.1.10}$$

and the coefficients are chosen to match $R_{n\ell}$ and its first $(d-1)$ derivatives of $R_{n\ell}$ at r_c.

Projector functions The projector functions $(\widetilde{p}_k^I)_{1\leq k\leq N_{\text{paw}}}$ chosen here are the $\mathcal{R}$-periodic functions given in the unit cell Γ by:

$$\forall\, \mathbf{r} \in \Gamma,\ \widetilde{p}^I_{n\ell m}(\mathbf{r}) = r^\ell p_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}). \tag{5.1.11}$$

The functions $p_{n\ell}$ for $0 \leq \ell \leq \ell_{\max}, 1 \leq n \leq n_\ell$ are defined by

$$p_{n\ell}(r) = \sum_{n'=1}^{n_\ell} \left(B_\ell^{-1}\right)_{nn'} \chi(r) \widetilde{R}_{n'\ell}(r), \tag{5.1.12}$$

with χ a smooth positive cut-off function supported in $(0, r_c)$ and

$$B_\ell = \left(\int_0^{r_c} \chi(r) \widetilde{R}_{n\ell}(r) \widetilde{R}_{n'\ell}(r) r^{2+2\ell}\, \mathrm{d}r \right)_{1\leq n,n'\leq n_\ell}. \tag{5.1.13}$$

By definition, the projector functions $(\widetilde{p}_k^I)_{1\leq k\leq N_{\text{paw}}}$ are supported in $\bigcup_{\mathbf{T}\in\mathcal{R}} B(\mathbf{T}, r_c)$ and form a dual family to the pseudo wave functions $(\widetilde{\phi}_k^I)_{1\leq k\leq N_{\text{paw}}}$: $\left\langle \widetilde{p}_k^I, \widetilde{\phi}_{k'}^I \right\rangle = \delta_{kk'}$.

The VPAW equations to solve are then:

$$\widetilde{H}\widetilde{\psi} = E\widetilde{S}\widetilde{\psi},$$

where

$$\widetilde{H} = (\mathrm{Id} + T)^* H (\mathrm{Id} + T), \quad \widetilde{S} = (\mathrm{Id} + T)^* (\mathrm{Id} + T), \tag{5.1.14}$$

and

$$T = \sum_{I=1}^{N_{at}} T_I. \tag{5.1.15}$$

Thus if $(\mathrm{Id} + T)$ is invertible, it is easy to recover the eigenfunctions of H by the formula

$$\psi = (\mathrm{Id} + T)\widetilde{\psi}, \tag{5.1.16}$$

and the eigenvalues are identical to the original eigenvalue problem (5.1.3).

By construction, the operator $(\mathrm{Id} + T_I)$ maps the pseudo wave functions $\widetilde{\phi}$ to the atomic

eigenfunctions ϕ:

$$(\mathrm{Id} + T_I)\widetilde{\phi}_k^I(\cdot - \mathbf{R}_I) = \phi_k^I(\cdot - \mathbf{R}_I), \tag{5.1.17}$$

so if locally around each nucleus, the function ψ "behaves" like the atomic wave functions ϕ_k, we can hope that the cusp behavior of ψ is captured by the operator T. $\widetilde{\psi}$ is therefore smoother than ψ and the plane-wave expansion of $\widetilde{\psi}$ converges faster than the expansion of ψ.

5.1.3 Well-posedness of the VPAW method

To be well-posed the VPAW method requires

1. for each $0 \leq \ell \leq \ell_{\max}$, the family of pseudo wave functions $(\widetilde{R}_{n\ell})_{1\leq n\leq n_\ell}$ to be linearly independent in $[0, r_c]$, so that the projector functions $(p_{n\ell})_{1\leq n\leq n_\ell}$ are well defined;
2. $(\mathrm{Id} + T)$ to be invertible.

To fulfill the first condition, the following assertion is assumed.

Assumption 5.1. *For all $0 < r_c < r_{\min}$ and each $0 \leq \ell \leq \ell_{\max}$, $(\mathcal{R}^{(k)}(r_c))_{0\leq k\leq n_\ell - 1}$ is a linearly independent family, where $\mathcal{R}$ is the vector of the functions $(R_{1\ell}, \ldots, R_{n_\ell \ell})$.*

It is easy to check that this condition ensures that the family of pseudo-wave functions $\left(\widetilde{R}_{n\ell}\right)_{1\leq n\leq n_\ell}$ is linearly independent. This holds in the particular case of the hydrogenoid atom (see Lemma 5.22 in the appendix).

It can be shown that the second condition is equivalent to the invertibility of the matrix $\left(\langle p_j\,, r^\ell R_k\rangle\right)_{1\leq j,k\leq n_\ell}$ for all $0 \leq \ell \leq \ell_{\max}$. Since the proof of this statement is very close to the proof of Proposition 2.3 in [BCD17b], we will not reproduce it here. For the rest of the paper, we make the following assumption.

Assumption 5.2. *For all $0 < r_c < r_{\min}$ and any $0 \leq \ell \leq \ell_{\max}$, the matrix $(\langle p_{n\ell}\,, R_{n'\ell}\rangle)_{1\leq n,n'\leq n_\ell}$ is invertible.*

5.1.4 Singular expansion

It appears that the theory of weighted Sobolev spaces and the singular expansion of eigenfunctions of Hamiltonians with Coulomb potentials provides a nice framework to study the Fourier decay of the VPAW pseudo wave functions $\widetilde{\psi}$. The singular expansion gives a generalization of the Kato cusp condition [Kat57] to any order. This theory is closely linked to the b-calculus of pseudodifferential operators developed by Melrose [Mel93]. It has been applied successfully to characterize precisely the behaviour of the electronic wave function close the nucleus [FSS08, HNS08] and used in the analysis of the muffin-tin and LAPW methods [CS15]. The interested reader may refer to [KMR97, ES12] for a detailed exposition of this theory.

For simplicity, Γ denotes the cube $[-\frac{1}{2}, \frac{1}{2}]^3$. Let $\mathcal{S}$ be the set of the position of the nuclei:

$$\mathcal{S} = \{\mathbf{R}_I + \mathbf{T},\ I = 1, \ldots, N_{\mathrm{at}},\ \mathbf{T} \in \mathcal{R}\}.$$

Let ϱ be a $\mathcal{R}$-periodic continuous function such that $\varrho(\mathbf{R}_I + \mathbf{r}) = r$ for small r, $\varrho \in C^\infty_{\mathrm{loc}}(\mathbb{R}^3 \setminus \mathcal{S})$.

Definition 5.1. *Let $k \in \mathbb{N}$ and $\gamma \in \mathbb{R}$. We define the k-th weighted Sobolev space with index γ by:*

$$\mathcal{K}^{k,\gamma}(\Gamma) = \left\{ u \in L^2_{\mathrm{per}}(\Gamma) : \varrho^{|\alpha|-\gamma} \partial^\alpha u \in L^2_{\mathrm{per}}(\Gamma) \ \forall\ |\alpha| \leq k \right\}. \tag{5.1.18}$$

Consider a subspace of functions with the asymptotic expansions

$$\forall\, I = 1, \ldots, N_{\mathrm{at}},\ u(\mathbf{R}_I + \mathbf{r}) \sim \sum_{j \in \mathbb{N}} c_j(\hat{\mathbf{r}}) r^j \text{ as } r \to 0, \tag{5.1.19}$$

where c_j belongs to the finite dimensional subspace $M_j = \mathrm{span}\{Y_{\ell m}, 0 \leq \ell \leq j, |m| \leq \ell\}$.

We define the weighted Sobolev spaces with asymptotic type (5.1.19):

$$\mathscr{K}^{k,\gamma}(\Gamma) = \left\{ u \in \mathcal{K}^{k,\gamma}(\Gamma) \,\middle|\, \eta_N \in \mathcal{K}^{k,\gamma+N+1}(\Gamma) \text{ where } \eta_N \text{ is the } \Gamma\text{-periodic function defined in } \Gamma \text{ by} \right.$$
$$\left. \forall N \in \mathbb{N},\ \forall \mathbf{r} \in \Gamma,\ \eta_N(\mathbf{r}) = u(\mathbf{r}) - \sum_{I=1}^{N_{\mathrm{at}}} \omega(|\mathbf{r} - \mathbf{R}_I|) \sum_{j=0}^{N} c_j(\widehat{\mathbf{r} - \mathbf{R}_I}) |\mathbf{r} - \mathbf{R}_I|^j \right\}, \tag{5.1.20}$$

where ω is a smooth positive cutoff function, *i.e.* $\omega = 1$ near 0 and $\omega = 0$ outside some neighbourhood of 0.

The definition (5.1.20) slightly differs from the definition of the weighted Sobolev space given in [CS15] (Equation (2.6)). However, our definition is consistent with the results that can be found in [HNS08] (see Theorem I.1) and the original paper [FSS08] (see Proposition 1) from which the definition appearing in [CS15] is taken.

The expansion (5.1.19) can be viewed as a "regularity expansion". Let us suppose that the functions c_j in the singular expansion are constant. Then all the even terms appearing in (5.1.20) are smooth since for any $k \in \mathbb{N}$, $r \mapsto r^{2k}$ is smooth. For the odd terms in the expansion, the function $r \mapsto r$ is continuous but not differentiable at the origin, the function $r \mapsto r^3$ is C^2 but not C^3 and so on. Since the decay of the Fourier coefficients depends on the regularity of the function, this expansion enables one to characterize precisely this decay. A precise estimation of this decay for all the terms appearing in (5.1.20) is given in Lemma 5.11 below.

Definition 5.2. *A function u is asymptotically well-behaved if $u \in \mathscr{K}^{\infty,\gamma}(\Gamma)$ for $\gamma < 3/2$.*

Remark 5.3. *It is easy to see that if u is asymptotically well-behaved then by the definition of the weighted Sobolev space with asymptotic type (5.1.19), the remainder η_N is in the classical Sobolev space $H^{5/2+N-\varepsilon}_{\mathrm{per}}(\Gamma)$.*

The following result, stated in [HNS08, CS15], gives the regularity of the eigenfunction of (5.1.3) in terms of the previously defined weighted Sobolev space.

Theorem 5.4. *Let ψ be an eigenfunction of $H\psi = E\psi$ where H is defined in (5.1.3). Then ψ is asymptotically well-behaved.*

Theorem 5.4 enables to characterize precisely the singularity of the Hamiltonian wave function and generalizes the Kato cusp condition for eigenfunctions of 3D-Hamiltonians. Let V be the smooth potential such that in a neighborhood of $\mathbf{R}_I$,

$$V_{\mathrm{per}}(\mathbf{r}) = -\frac{Z}{|\mathbf{r}-\mathbf{R}_I|} + V(\mathbf{r}-\mathbf{R}_I), \tag{5.1.21}$$

and denote by $(v_k)_{k\geq \ell}$ the coefficients of the Taylor expansion of

$$V_{\ell m}(r) = \int_{S(0,1)} V(\mathbf{r}) Y_{\ell m}(\hat{\mathbf{r}})\, \mathrm{d}\hat{\mathbf{r}}. \tag{5.1.22}$$

Theorem 5.5. *Let $\ell \in \mathbb{N}$ and $|m| \leq \ell$. Let ψ be an eigenfunction of $H\psi = E\psi$ where H is defined in (5.1.3) and $(\psi_{j\ell m})_{j,\ell\leq j,|m|\leq \ell}$ be the coefficients of the singular expansion of ψ,* i.e. *for all $\varepsilon > 0$,*

$$\psi(\mathbf{r}) - \sum_{j=0}^{N} \sum_{|m|\leq \ell\leq j} c_{j\ell m} r^j Y_{\ell m}(\hat{\mathbf{r}}) \in \mathcal{K}^{\infty,\frac{5}{2}+N-\varepsilon}.$$

Let $(v_k)_{k\geq\ell}$ be the coefficients of the function $V_{\ell m}$ defined in (5.1.22). Then the sequence $(c_{j\ell m})_{j\geq\ell}$ satisfies

$$\forall\, j \geq \ell, \frac{(j+1)(j+2+2\ell)}{2}\psi_{j+1,\ell m} = -Z\psi_{j\ell m} + (v*c)_{j-1} - E\psi_{j-1,\ell m}, \tag{5.1.23}$$

where $v*c$ denotes the convolution

$$(v*c)_k = \sum_{j=\ell}^{k} v_{k-j}\psi_{k,\ell m}.$$

For $\ell = 0$, the Kato cusp condition is recovered since $\psi_{000} = \psi(0)$ and $\psi_{100} = \frac{\partial}{\partial r}\big|_{r=0} \int_{S(0,1)} \psi(\mathbf{r}) Y_{00}(\hat{\mathbf{r}})\, \mathrm{d}\hat{\mathbf{r}}$.

5.2 Main results

We focus on the analysis of the VPAW method restricted to a set of PAW functions associated to the lowest angular momentum $\ell = m = 0$, *i.e.* $\ell_{\max} = 0$. In this setting, we can prove the following theorem.

Theorem 5.6. *Let E_M be an eigenvalue of the variational approximation of (5.1.14) in a plane-wave basis with wavenumber $|\mathbf{K}| \leq M$, with n_0 PAW functions associated to the angular momentum $\ell = 0, m = 0$ with smoothness $d \geq n$ and cut-off radius r_c. Let E be the corresponding exact eigenvalue. Under Assumptions 5.1, 5.2, there exists a constant $C > 0$ independent of r_c and M such that for all $\varepsilon > 0$, and for all $\frac{1}{M} < r_c < r_{\min}$*

$$0 < E_M - E \leq C\left(\frac{{r_c}^{2\min(2n_0,5)-2\varepsilon}}{M^3} + \frac{{r_c}^{\min(2n_0,5)-\varepsilon}}{M^{4-\varepsilon}} + \frac{1}{M^5} + \frac{1}{{r_c}^{2d-2}}\frac{1}{M^{2d-1}} + o\left(\frac{1}{M^{7-\varepsilon}}\right)\right). \tag{5.2.1}$$

Theorem 5.6 holds for *any* eigenvalue of H given in (5.1.3), however numerical tests provided in Section 5.4 are restricted to the ground-state eigenvalue. They suggest that the VPAW method can be an efficient strategy to solve accurately the eigenvalue problem (5.1.3) (see Figures 5.4.1, 5.4.3).

Asymptotically, the same order of convergence as the direct plane-wave discretization of (5.1.3) is obtained, however, the prefactor is reduced by ${r_c}^{2\min(2n_0,5)-\varepsilon}$, improving the convergence for low plane-wave cut-offs. However, the VPAW method introduces a d-th order derivative jump which is reflected by the prefactor $\frac{1}{{r_c}^{2d-2}}$. This prevents one to choose a too low cut-off radius since this error can become predominant as r_c goes to 0 (see Figure 5.4.2).

Remark 5.7. *By incorporating n_1 functions for each angular momentum $\ell = 1$ and $m = -1, 0, 1$, we can improve the convergence estimate (5.2.1) to*

$$\forall \tfrac{1}{M} < r_c < r_{\min},\ 0 < E_M - E \leq C \left(\frac{{r_c}^{2\min(2n_0,5)-2\varepsilon}}{M^3} + \frac{{r_c}^{\min(2n_0,5)-\varepsilon}}{M^{4-\varepsilon}} + \frac{{r_c}^{2\min(2n_1,5)-\varepsilon}}{M^5} + \frac{1}{M^7} + \frac{1}{{r_c}^{2d-2}} \frac{1}{M^{2d-1}} + o\left(\frac{1}{M^{9-\varepsilon}} \right) \right). \quad (5.2.2)$$

*The only difference between (5.2.1) and (5.2.2) is the prefactor of $\frac{1}{M^5}$. In our example (Section **??**), improvements for the computation of ground-state are barely noticeable (see Figure 5.4.1 and 5.4.3). However, introducing PAW functions for $\ell = 1$ might be beneficial for higher eigenvalues where in a pre-asymtotic regime, the prefactor of $\frac{1}{M^5}$ may be preponderant.*

5.3 Proofs

A proof of Theorem 5.6 is given in this section with n PAW functions for the angular momentum $\ell = 0$ and $m = 0$. These functions are generated following the scheme presented in Section 5.1.2. Since only PAW functions for the angular momentum $\ell = 0$, $m = 0$ are considered, the 00 index in the PAW functions is dropped. The following notation is introduced

$$\begin{aligned}
p(r) &:= (p_1(r), \dots, p_n(r))^T \in \mathbb{R}^n, \\
\widetilde{p}(\mathbf{r}) &:= (\widetilde{p}_1(\mathbf{r}), \dots, \widetilde{p}_n(\mathbf{r}))^T \in \mathbb{R}^n, \\
\langle \widetilde{p}, f \rangle &:= (\langle \widetilde{p}_1, f \rangle, \dots, \langle \widetilde{p}_n, f \rangle)^T \in \mathbb{R}^n, \forall\, f \in L^2_{\text{per}}(\Gamma), \\
\Phi(\mathbf{r}) &:= (\phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r}))^T \in \mathbb{R}^n, \\
\widetilde{\Phi}(\mathbf{r}) &:= (\widetilde{\phi}_1(\mathbf{r}), \dots, \widetilde{\phi}_n(\mathbf{r}))^T \in \mathbb{R}^n, \\
\mathcal{R}(r) &:= (R_1(r), \dots, R_n(r))^T \in \mathbb{R}^n, \\
\widetilde{\mathcal{R}}(r) &:= (\widetilde{R}_1(r), \dots, \widetilde{R}_n(r))^T \in \mathbb{R}^n.
\end{aligned}$$

For a function $f \in L^2([-\frac{1}{2}, \frac{1}{2}]^3)$, we denote by $f_{\ell m}$ the averaged function

$$f_{\ell m}(r) = \int_{S(0,1)} f(\mathbf{r}) Y_{\ell m}(\hat{\mathbf{r}})\, \mathrm{d}\hat{\mathbf{r}}. \quad (5.3.1)$$

Let ω be a smooth nonnegative cut-off function such that $\omega(r) = g(\frac{r}{r_c})$ where g satisfies

— g is equal to 1 in $B(0, 1/4)$,

— $\mathrm{supp}(g) \subset B(0, 1/2)$.

Therefore, ω satisfies $\mathrm{supp}(\omega) \subset B(0, r_c/2)$, $\mathrm{supp}(1-\omega)^c \subset B(0, r_c/4)$ and $\|\omega^{(k)}\|_{L^\infty(0,r_c)} \leq \frac{C}{{r_c}^k}$.

Since the proof of Theorem 5.6 relies on the estimation of the singularities around each nucleus, we restrict the setting to a single atom of cahrge Z located at the origin in the unit cell Γ. Extension to the general case is straightforward.

The general idea of the proof is to isolate the main convergence difficulty which is the cusp located at each nucleus and see how the VPAW method reduces it. Although the VPAW method reduces the cusps of the pseudo wave function, it introduces a derivative jump on the augmentation spheres that blows up as the cut-off radius shrinks. As in [BCD17b], we split the pseudo wave function $\widetilde{\psi}$ into three parts using the singular expansion (5.1.20). Let $\eta \in \mathcal{K}^{\infty,\frac{5}{2}+N-\varepsilon}(\Gamma)$ be the remainder of the singular expansion (5.1.20) applied to ψ:

$$\eta(\mathbf{r}) = \psi(\mathbf{r}) - \omega(r) \sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j.$$

Then we have:

$$\begin{aligned}
\widetilde{\psi}(\mathbf{r}) &= \psi(\mathbf{r}) - \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi(\mathbf{r}) - \widetilde{\Phi}(\mathbf{r})), \\
&= \omega(r) \sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j + \eta(\mathbf{r}) - \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi(\mathbf{r}) - \widetilde{\Phi}(\mathbf{r})), \\
&= \omega(r) \left(\sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j - \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi(\mathbf{r}) - \widetilde{\Phi}(\mathbf{r})) \right) + (1-\omega(r)) \left(\left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi(\mathbf{r}) - \widetilde{\Phi}(\mathbf{r})) \right) + \eta(\mathbf{r}).
\end{aligned} \tag{5.3.2}$$

The first part corresponds to the cusp of the pseudo wave function in a neighborhood of a nucleus. The second part is the d-th derivative jump caused by the lack of regularity at the augmentation sphere. The last part is the remainder appearing in the singular expansion of the original wave function ψ. In this section, we analyze the decay of the Fourier coefficients of three parts separately and prove the following results. Since the proof is restricted to the case $\ell_{\max} = 0$, N can be set to 1.

Proposition 5.8. *Let c_j be the functions of the singular expansion (5.1.20) of ψ. Let $n \geq 1$ be the number of PAW functions associated to the angular momentum $\ell = 0, m = 0$. Then there exists a positive constant C independent of r_c and K such that for all $\varepsilon > 0$ and as K goes to ∞,*

$$\forall\, 0 < r_c < r_{\min}, \quad \left| \int_\Gamma \omega(r) \left(\sum_{j=0}^{1} c_j(\hat{\mathbf{r}}) r^j - \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi - \widetilde{\Phi})(\mathbf{r}) \right) e^{-i\mathbf{K}\cdot\mathbf{r}} \, \mathrm{d}\mathbf{r} \right| \leq \frac{C {r_c}^{\min(2n,5)-\varepsilon}}{K^4}. \tag{5.3.3}$$

This proposition states that, asymptotically, no regularity is gained, however, a prefactor of order ${r_c}^{\min(2n,5)-\varepsilon}$ is obtained.

Proposition 5.9. *There exists a positive constant C independent of r_c such that*

$$\forall\, 0 < r_c < r_{\min},\ \left| \int_\Gamma (1-\omega(r)) \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi - \widetilde{\Phi}) e^{-i\mathbf{K}\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \right| \leq \frac{C}{{r_c}^{d-1} K^{d+2}},\ \text{as } K \to \infty. \tag{5.3.4}$$

By reducing the cusp at a nucleus, the VPAW method introduces a derivative jump but for a higher order derivative.

Proposition 5.10. *Let η be the remainder of the expansion (5.1.20) for $N = 1$. Let η_M be the truncation to the wavenumber M of the plane-wave expansion of η. Then for all $\varepsilon > 0$, we have*

$$\|\eta_M - \eta\|_{H^1_{\mathrm{per}}} \leq \frac{1}{M^{5/2-\varepsilon}} \|\eta\|_{H^{7/2-\varepsilon}_{\mathrm{per}}}. \tag{5.3.5}$$

This is a direct consequence of the regularity of the remainder of the expansion (5.1.20) given by Theorem 5.4.

5.3.1 Cusp reduction

We recall the following identity that will be extensively used in the rest of the paper:

$$e^{-i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{|m|\leq \ell} i^\ell Y_{\ell m}(-\hat{\mathbf{K}}) Y_{\ell m}(\hat{\mathbf{r}}) j_\ell(Kr), \tag{5.3.6}$$

where j_ℓ is the spherical Bessel function of the first kind.

To prove Proposition 5.8, we start with a lemma that identifies the main issues in the plane-wave convergence of the molecular wave function.

Lemma 5.11. *Let ℓ and j be integers such that $\ell \leq j$. Let $K > 0$. Then, as K goes to ∞, if $j + \ell$ is even, we have for any positive integer $n \geq j + 3$,*

$$\int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j_\ell(Kr)\, \mathrm{d}r = \frac{\beta_{j,\ell}}{K^{j+3}} + o\left(\frac{1}{K^n}\right), \tag{5.3.7}$$

where

$$\beta_{j,\ell} = (-1)^{(j+\ell)/2} (j-\ell+1)! \prod_{k=0}^{\ell} (j-\ell+1+2k),$$

and if $j + \ell$ is odd, for any positive integer $n \geq j + 3$,

$$\int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j_\ell(Kr)\, \mathrm{d}r = o\left(\frac{1}{K^n}\right). \tag{5.3.8}$$

Proof. We prove the lemma by induction on ℓ. Let $a_{j+2,\ell}$ be defined by

$$a_{j+2,\ell} = \int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j_\ell(Kr)\,\mathrm{d}r. \tag{5.3.9}$$

Initialization For $\ell = 0$, we have

$$j_0(x) = \frac{\sin(x)}{x},$$

hence for any $j \in \mathbb{N}$,

$$a_{j+2,0} = \frac{1}{K}\mathrm{Im}\left(\int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} e^{iKr}\,\mathrm{d}r\right). \tag{5.3.10}$$

By integration by parts, we have

$$\begin{aligned}\int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} e^{iKr}\,\mathrm{d}r &= \frac{1}{iK}\underbrace{\left[-\omega(r) r^{j+1} e^{iKr}\right]_0^{\frac{r_c}{2}}}_{=0} - \frac{1}{iK}\int_0^{\frac{r_c}{2}} (\omega(r) r^{j+1})' e^{iKr}\,\mathrm{d}r \\ &= -\frac{1}{iK}\int_0^{\frac{r_c}{2}} \omega'(r) r^{j+1} e^{iKr}\,\mathrm{d}r - \frac{j+1}{iK}\int_0^{\frac{r_c}{2}} \omega(r) r^{j} e^{iKr}\,\mathrm{d}r.\end{aligned}$$

The function $r \mapsto r^{j+1}\omega'(r)$ belongs to $C_c^\infty(0, \frac{r_c}{2})$ hence we have for any $n > j+2$

$$\int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} e^{iKr}\,\mathrm{d}r = -\frac{(j+1)}{iK}\int_0^{\frac{r_c}{2}} \omega(r) r^{j} e^{iKr}\,\mathrm{d}r + o\left(\frac{1}{K^n}\right) \tag{5.3.11}$$

By integrating by parts j times and noticing that the functions $r \mapsto r^k\omega'(r)$, $k \in \mathbb{N}$ are in $C_c^\infty(0, \frac{r_c}{2})$, we obtain

$$\int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} e^{iKr}\,\mathrm{d}r = (-1)^{j+1}\frac{(j+1)!}{(iK)^{j+2}} + o\left(\frac{1}{K^n}\right). \tag{5.3.12}$$

Hence using (5.3.10), if j is even, $a_{j+2,0} = o\left(\frac{1}{K^n}\right)$ for all positive integer n, otherwise $a_{j+2,0} = (-1)^{j/2}\frac{(j+1)!}{K^{j+3}}$.

Iteration Using the recurrence relation

$$j_{\ell+1}(x) = -j_\ell'(x) + \frac{\ell j_\ell(x)}{x}, \tag{5.3.13}$$

we have the following recurrence relation on $(a_{j,\ell})$:

$$a_{j+2,\ell+1} = \int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j_{\ell+1}(Kr)\,\mathrm{d}r \tag{5.3.14}$$

$$= \int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} \left(-j'_\ell(Kr) + \frac{\ell j_\ell(Kr)}{Kr} \right) \mathrm{d}r \tag{5.3.15}$$

$$= \frac{\ell}{K} \int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} j_\ell(Kr)\,\mathrm{d}r - \int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j'_\ell(Kr)\,\mathrm{d}r. \tag{5.3.16}$$

By integration by parts, using that $r \mapsto r^{j+2}\omega'(r) \in C_c^\infty(0, \frac{r_c}{2})$, we have

$$\int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} j'_\ell(Kr)\,\mathrm{d}r = -\frac{j+2}{K} \int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} j_\ell(Kr)\,\mathrm{d}r + o\left(\frac{1}{K^n}\right).$$

Thus, we have by iteration,

$$\begin{aligned} a_{j+2,\ell+1} &= \frac{j+\ell+2}{K} \int_0^{\frac{r_c}{2}} \omega(r) r^{j+1} j_\ell(Kr)\,\mathrm{d}r + o\left(\frac{1}{K^n}\right) \\ &= \frac{j+\ell+2}{K} a_{j+1,\ell} + o\left(\frac{1}{K^n}\right) \\ &= \frac{\prod_{k=0}^{\ell+1}(j-\ell+2k)}{K^{\ell+1}} a_{j-\ell+1,0} + o\left(\frac{1}{K^n}\right). \end{aligned}$$

Hence if $j+\ell+1$ is odd, $a_{j+2,\ell+1} = o\left(\frac{1}{K^n}\right)$ for all positive integer n, else if $j+\ell+1$ is even, for any $n \geq j+3$,

$$a_{j+2,\ell+1} = (-1)^{(j-\ell+1)/2}(j-\ell)! \frac{\prod_{k=0}^{\ell+1}(j-\ell+2k)}{K^{j+3}} + o\left(\frac{1}{K^n}\right).$$

□

Lemma 5.12. *Let $N \in \mathbb{N}^*$. Let c_j be the functions of the singular expansion (5.1.20) of ψ. Let $c_{j\ell m}$ be the coefficients such that*

$$c_j(\hat{\mathbf{r}}) = \sum_{\ell=0}^{j} \sum_{|m|\leq\ell} c_{j\ell m} Y_{\ell m}(\hat{\mathbf{r}}).$$

Then, we have as K goes to ∞ and for any positive integer n,

$$\int_{[-\frac{1}{2},\frac{1}{2}]^3} \omega(r) \sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j e^{-i\mathbf{K}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r} = 4\pi \sum_{j=0}^{N} \sum_{\substack{\ell=0 \\ j+\ell\ odd}}^{j} \sum_{|m|\leq\ell} i^\ell Y_{\ell m}(-\hat{\mathbf{K}}) \frac{\beta_{j,\ell} c_{j\ell m}}{K^{j+3}} + o\left(\frac{1}{K^n}\right). \tag{5.3.17}$$

Proof. We have since $\mathrm{supp}(\omega) \subset (0, \frac{r_c}{2})$

$$\int_{[-\frac{1}{2},\frac{1}{2}]^3} \omega(r) \sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j e^{-i\mathbf{K}\cdot\mathbf{r}} \,\mathrm{d}\mathbf{r} = \int_0^{\frac{r_c}{2}} r^2 \omega(r) \sum_{j=0}^{N} r^j \sum_{\ell=0}^{j} \sum_{|m|\le\ell} c_{j\ell m} \int_{S(0,1)} Y_{\ell m}(\hat{\mathbf{r}}) e^{-i\mathbf{K}\cdot\mathbf{r}} \,\mathrm{d}\hat{\mathbf{r}} \,\mathrm{d}r. \tag{5.3.18}$$

Using the scattering expansion (5.3.6) and applying Lemma 5.11, we get

$$\int_{[-\frac{1}{2},\frac{1}{2}]^3} \omega(r) \sum_{j=0}^{N} c_j(\hat{\mathbf{r}}) r^j e^{-i\mathbf{K}\cdot\mathbf{r}} \,\mathrm{d}\mathbf{r} = 4\pi \sum_{j=0}^{N} \sum_{\ell=0}^{j} \sum_{|m|\le\ell} i^\ell Y^*_{\ell m}(-\hat{\mathbf{K}}) \int_0^{\frac{r_c}{2}} \omega(r) r^{j+2} c_{j\ell m} j_\ell(Kr) \,\mathrm{d}r \tag{5.3.19}$$

$$= 4\pi \sum_{j=0}^{N} \sum_{\substack{\ell=0 \\ j+\ell \text{ odd}}}^{j} \sum_{|m|\le\ell} i^\ell Y_{\ell m}(-\hat{\mathbf{K}}) \frac{\beta_{j,\ell} c_{j\ell m}}{K^{j+3}} + o\left(\frac{1}{K^n}\right). \tag{5.3.20}$$

□

j	ℓ	$\frac{1}{K}$
1	0	$\frac{1}{K^4}$
2	1	$\frac{1}{K^5}$
3	0	$\frac{1}{K^6}$
3	2	

Table 5.3.1 – Lowest decaying terms

According to Lemma 5.12, the slowest decaying term is the term associated to $j = 1$ and $\ell = 0$. Thus we need to analyze how the VPAW method reduces the coefficient c_{100} which is simply the cusp at 0 of the pseudo wave function $\widetilde{\psi}$.

Lemma 5.13. *Let ψ be an eigenfunction of $H\psi = E\psi$, with H defined in (5.1.3). Let n be the number of PAW functions associated to the angular momentum $\ell = 0, m = 0$.*

There exist coefficients $(\alpha_k)_{1\le k\le n}$ and a positive constant C independent of r_c such that

$$\|\psi_{00} - \alpha^T \mathcal{R}\|_{L^2(0,r_c)} \le C {r_c}^{1/2-\varepsilon+\min(2n,5)},$$

where ψ_{00} denotes the averaged function ψ according to (5.3.1). Moreover for these coefficients, we have

$$\psi_{00}(0) - \alpha^T \mathcal{R}(0) = 0.$$

Before proving this lemma, we start with a few intermediary results and introduce some notation.

Let $\psi_k \in \mathbb{R}$ and $\zeta_k \in \mathbb{R}^n$ be, respectively, the coefficients of the singular expansion of ψ_{00} and $\mathcal{R}$:

$$\psi_{00}(r) = \sum_{j=0}^{N} \psi_j r^j + \eta_{N+1}(r), \quad \eta_{N+1} \in \mathcal{K}^{\infty,\frac{5}{2}+N-\varepsilon}(\Gamma) \tag{5.3.21}$$

$$\mathcal{R}(r) = \sum_{j=0}^{N} \zeta_j r^j + \xi_{N+1}(r), \quad \xi_{N+1} \in \mathcal{K}^{\infty,\frac{5}{2}+N-\varepsilon}(\Gamma). \tag{5.3.22}$$

The external potentials V (5.1.21) and W (5.1.8) are smooth in a neighborhood of a nucleus, hence we have

$$V(r) = \sum_{k=0}^{N} v_{2k} r^{2k} + \mathcal{O}(r^{2N+2}), \tag{5.3.23}$$

$$W(r) = \sum_{k=0}^{N} w_{2k} r^{2k} + \mathcal{O}(r^{2N+2}). \tag{5.3.24}$$

Finally, we denote $\mathcal{E}$ the diagonal matrix with entries $(\epsilon_1, \dots, \epsilon_n)$.

Lemma 5.14. *Let $\mathcal{R} = (R_1, \dots, R_n)^T$ where R_k is defined in (5.1.7).*

There exists $(\mu_j^{(k)})_{0\le j\le k\le n-1}$ and $(\nu_j^{(k)})_{0\le j\le k\le n-1}$ such that

$$\zeta_{2k} = \sum_{j=0}^{k} \mu_j^{(k)} \mathcal{E}^j \zeta_0 \tag{5.3.25}$$

$$\zeta_{2k+1} = \sum_{j=0}^{k} \nu_j^{(k)} \mathcal{E}^j \zeta_0, \tag{5.3.26}$$

with $\mu_k^{(k)} \neq 0$ for any $0 \le k \le n-1$.

Moreover, ζ_0 has no null entry and the vectors $(\zeta_k)_{1\le k\le 5}$ satisfies

$$\begin{aligned}
\zeta_1 &= -Z\zeta_0 \\
\zeta_2 &= -\frac{1}{3}\mathcal{E}\zeta_0 + \frac{1}{3}(Z^2 + w_0)\zeta_0 \\
\zeta_3 &= \frac{2}{9}Z\mathcal{E}\zeta_0 - \left(\frac{Z^3}{18} + \frac{2}{9}Zw_0\right)\zeta_0 \\
\zeta_4 &= \frac{1}{30}\mathcal{E}^2\zeta_0 - \left(\frac{Z^2}{18} + \frac{w_0}{15}\right)\mathcal{E}\zeta_0 + \left(\frac{Z^4}{180} + \frac{Z^2 w_0}{18} + \frac{w_0^2}{30} + \frac{w_2}{10}\right)\zeta_0 \\
\zeta_5 &= -\frac{23}{1350}Z\mathcal{E}^2\zeta_0 + \left(\frac{Z^3}{135} + \frac{23}{675}w_0 Z\right)\mathcal{E}\zeta_0 - \left(\frac{Z^5}{2700} + \frac{Z^3 w_0}{135} + \frac{23}{1350}Zw_0^2 + \frac{11}{150}Zw_2\right)\zeta_0.
\end{aligned}$$

Proof. This lemma is proved by iteration using Equation (5.1.23) applied to each R_k, $k = 1, \dots, n$

$$\forall N \geq 1,\ \frac{(N+1)(N+2)}{2}\zeta_{N+1} = -Z\zeta_N + (w * \zeta)_{N-1} - \mathcal{E}\zeta_{N-1}.$$

Here $(w_k)_{k\geq 0}$ and $(\zeta_k)_{k\geq 0}$ are defined respectively by (5.3.22) and (5.3.24). Noticing that since W is smooth, we have

$$(w * \zeta)_{2k} = \sum_{j=0}^{k} w_{2k-2j}\zeta_{2j}, \quad (w * \zeta)_{2k+1} = \sum_{j=0}^{k} w_{2k-2j}\zeta_{2j+1}.$$

By iteration, it is easy to see that $\mu_k^{(k)} \neq 0$ for all $k \in \mathbb{N}$.

We have that $\zeta_0 = \mathcal{R}(0)$ and the radial wave functions R_k, $k = 1, \dots, n$ satisfy the radial Schrödinger equation (5.1.8)

$$\forall\, r > 0,\ -\frac{1}{2}R_k''(r) - \frac{1}{r}R_k'(r) - \frac{Z}{r}R_k(r) + W(r)R_k(r) = \epsilon_k R_k(r).$$

0 is a regular singular point and its indicial equation is $-\frac{1}{2}s(s-1) - s = 0$, with roots $s_1 = 0$ and $s_2 = -1$. By Fuch's theorem ([Tes12], Theorem 4.8), since $s_1 - s_2 \in \mathbb{N}$ the fundamental solutions are given by

$$\begin{cases} u_1(r) = h_1(r) \\ u_2(r) = \frac{h_2(r)}{r} + c\log(r)u_1(r), \end{cases}$$

with $h_1(0) \neq 0$ and $h_2(0) \neq 0$. Since R_k, $k = 1, \dots, n$, is square integrable, necessarily, we have $R_k = u_1$, thus, $R_k(0) \neq 0$. □

Proof of Lemma 5.13. To minimize $\|\psi_{00} - \alpha^T\mathcal{R}\|_{L^2(0,r_c)}$ with respect to α for r_c small, we need to determine how many successive terms in the singular expansion of ψ_{00} can be canceled with n functions $R_k, k = 1, \dots, n$, *i.e.* we need to determine for which $N_{\max} \leq 2n$ we have

$$\forall 0 \leq k \leq N_{\max},\ \alpha^T\zeta_k = \psi_k. \tag{5.3.27}$$

Expressing ζ_k (resp. ψ_k) as a linear combination of $(\zeta_0, \dots, \mathcal{E}^{\lceil \frac{N_{\max}}{2}\rceil - 1}\zeta_0)$ (resp. $(\psi_0, \dots, E^{\lceil \frac{N_{\max}}{2}\rceil - 1}\psi_0)$) using Lemma 5.14, the linear system (5.3.27) can be reformulated as

$$\begin{pmatrix} M_1 \\ M_2 \end{pmatrix} \begin{pmatrix} \zeta_0^T \\ \zeta_0^T\mathcal{E} \\ \vdots \\ \zeta_0^T\mathcal{E}^{\lceil N_{\max}/2\rceil - 1} \end{pmatrix} \alpha = \begin{pmatrix} N_1 \\ N_2 \end{pmatrix} \begin{pmatrix} \psi_0 \\ E\psi_0 \\ \vdots \\ E^{\lceil N_{\max}/2\rceil - 1}\psi_0 \end{pmatrix}, \tag{5.3.28}$$

where $M_1 = (\mu_j^{(k)})_{0\leq j,k\leq \lceil N_{\max}/2\rceil - 1}$, and $M_2 = (\nu_j^{(k)})_{0\leq j,k\leq \lceil N_{\max}/2\rceil - 1}$, with $\mu_j^{(k)}$ and $\nu_j^{(k)}$ given by Lemma 5.14. N_1 and N_2 the same matrices as M_1 and M_2 but where the coefficients $\mu_j^{(k)}$ and $\nu_j^{(k)}$ are generated using (v_{2k}) instead of (w_{2k}).

We will show that if $n \leq 2$, then $N_{\max} = 2n$, otherwise, $N_{\max} = 5$. Equation (5.3.28) is

equivalent to

$$\begin{cases} M_1(\zeta_0^T \mathcal{E}^k)_{0\le k\le \lceil N_{\max}/2\rceil -1}\alpha = N_1(E^k\psi_0)_{0\le k\le \lceil N_{\max}/2\rceil -1} \\ M_2(\zeta_0^T \mathcal{E}^k)_{0\le k\le \lceil N_{\max}/2\rceil -1}\alpha = N_2(E^k\psi_0)_{0\le k\le \lceil N_{\max}/2\rceil -1}, \end{cases}$$

hence Equation (5.3.28) has a solution if and only if

$$M_2M_1^{-1}N_1(E^k\psi_0)_{0\le k\le \lceil N_{\max}/2\rceil -1} = N_2(E^k\psi_0)_{0\le k\le \lceil N_{\max}/2\rceil -1}.$$

Since this holds for any value E, a necessary and sufficient condition to solve (5.3.28) is $M_2M_1^{-1}N_1 = N_2$.

For $n = 1$, $M_1 = N_1 = \begin{pmatrix}1\end{pmatrix}$ and $M_2 = N_2 = \begin{pmatrix}-Z\end{pmatrix}$ hence it is easy to see that (5.3.28) is solvable when $N_{\max} = 2$. The remainder $\psi_{00} - \alpha\mathcal{R}$ belongs to $\mathcal{K}^{\infty,\frac{7}{2}-\varepsilon}(\Gamma)$, hence by Lemma 5.19, there exists a constant C independent of r_c such that

$$\|\psi_{00} - \alpha\mathcal{R}\|_{L^2(0,r_c)} \le C{r_c}^{5/2-\varepsilon}.$$

For $n = 2$, we can check using Lemma 5.14 that

$$M_2M_1^{-1} = \begin{pmatrix} -Z & 0 \\ \frac{Z^3}{6} & -\frac{2Z}{3} \end{pmatrix}.$$

Thus $M_2M_1^{-1}N_1 = N_2$ and (5.3.28) has a solution (α_1, α_2) such that $\psi_{00}(r) - \alpha^T\mathcal{R}(r)$ belongs to $\mathcal{K}^{\infty,\frac{11}{2}-\varepsilon}(\Gamma)$, hence by Lemma 5.19, $\|\psi_{00}(r) - \alpha^T\mathcal{R}(r)\|_{L^2(0,r_c)} \le C{r_c}^{9/2-\varepsilon}$.

For $n \ge 3$, the dependence on W does not vanish in $M_2M_1^{-1}$. For example, the $(3,1)$ coordinate of the matrix $M_2M_1^{-1}$ has a term equal to $\frac{391}{6075}Z^3w_0$ which is unlikely to be compensated in general. For $n \ge 3$, we thus have:

$$\psi_{00}(r) - \alpha^T\mathcal{R}(r) = \mathcal{O}(r^5),$$

hence $\|\psi_{00}(r) - \alpha^T\mathcal{R}(r)\|_{L^2(0,r_c)} \le C{r_c}^{11/2}$ for a constant C independent of r_c. □

Proposition 5.15. *Let n be the number of PAW functions for $\ell = m = 0$. There exists a positive constant C independent of r_c such that*

$$\forall 0 < r_c < r_{\min},\ \left|\widetilde{\psi}'_{00}(0)\right| \le C{r_c}^{\min(2n,5)-\varepsilon}. \tag{5.3.29}$$

The proof of the proposition is very similar to the proof of the cusp reduction in [BCD17b] for the wave function of the 1D-Hamiltonian with the double Dirac potential as we manipulate 1D functions with similar properties.

Proof. We have

$$\widetilde{\psi}_{00}(r) = \psi_{00}(r) - \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)) \tag{5.3.30}$$

$$= \psi_{00}(r) - \alpha^T(\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)) - \left\langle \widetilde{p}, \widetilde{\psi} - \alpha^T\widetilde{\Phi} \right\rangle^T (\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)). \tag{5.3.31}$$

By construction, the PAW pseudo wave functions $\widetilde{R}_k$ do not have a cusp at 0, so

$$\begin{aligned}\widetilde{\psi}'_{00}(0) &= \psi'_{00}(0) - \alpha^T \mathcal{R}'(0) - \left\langle \widetilde{p}\,, \widetilde{\psi} - \alpha^T \widetilde{\Phi} \right\rangle^T \mathcal{R}'(0) \\ &= -Z \left(\psi_{00}(0) - \alpha^T \mathcal{R}(0) - \left\langle \widetilde{p}\,, \widetilde{\psi} - \alpha^T \widetilde{\Phi} \right\rangle^T \mathcal{R}(0) \right). \end{aligned} \tag{5.3.32}$$

First we rewrite $\left\langle \widetilde{p}\,, \widetilde{\psi} - \alpha^T \widetilde{\Phi} \right\rangle$ in a more convenient way. We have

$$\psi - \left\langle \widetilde{p}\,, \widetilde{\psi} \right\rangle^T \Phi = \widetilde{\psi} - \left\langle \widetilde{p}\,, \widetilde{\psi} \right\rangle^T \widetilde{\Phi}.$$

By multiplying by $\widetilde{p}_k$, $k = 1, .., n$ and integrating over the ball $B(0, r_c)$, we have

$$\langle \widetilde{p}_k\,, \psi \rangle - \left\langle \widetilde{p}\,, \widetilde{\psi} \right\rangle^T \langle \widetilde{p}_k\,, \Phi \rangle = 0,$$

so

$$\left\langle \widetilde{p}\,, \widetilde{\psi} \right\rangle = A^{-1} \langle \widetilde{p}\,, \psi \rangle\,,$$

where $A = (\langle \widetilde{p}_j\,, \phi_k \rangle)_{1 \le j,k \le n} = (\langle p_j\,, R_k \rangle_{[0,r_c]})_{1 \le j,k \le n}$ which is invertible by Assumption 5.1. By definition of the PAW functions, the 3D-integrals can be reduced to integrals on a segment

$$\left\langle \widetilde{p}\,, \widetilde{\psi} \right\rangle = A^{-1} \langle p\,, \psi_{00} \rangle_{[0,r_c]}\,,$$

where

$$\langle f\,, g \rangle_{[0,r_c]} = \int_0^{r_c} f(r) g(r) r^2 \,\mathrm{d}r.$$

By duality of the PAW functions, $\left\langle \widetilde{p}_j\,, \widetilde{\phi}_k \right\rangle = \delta_{jk}$, we have $\left\langle \widetilde{p}\,, \alpha^T \widetilde{\Phi} \right\rangle = A^{-1} \left\langle p\,, \alpha^T \mathcal{R} \right\rangle_{[0,r_c]}$. Hence,

$$\left\langle \widetilde{p}\,, \widetilde{\psi} - \alpha^T \widetilde{\Phi} \right\rangle = A^{-1} \left\langle p\,, \psi_{00} - \alpha^T \mathcal{R} \right\rangle_{[0,r_c]}.$$

By Lemma 5.25, there exists a constant C independent of r_c such that for any $r_c > 0$,

$$\left| \left\langle p\,, \psi_{00} - \alpha^T \mathcal{R} \right\rangle_{[0,r_c]}^T A^{-T} \mathcal{R}'(0) \right| \le \frac{C}{r_c^{3/2}} \|\psi_{00} - \alpha^T \mathcal{R}\|_{L^2(B(0,r_c))} \le \frac{C}{r_c^{1/2}} \|\psi_{00} - \alpha^T \mathcal{R}\|_{L^2(0,r_c)}. \tag{5.3.33}$$

From Lemma 5.13, we know that there exists $\alpha \in \mathbb{R}^n$ such that

$$\|\psi_{00} - \alpha^T \mathcal{R}\|_{L^2(0,r_c)} \le C r_c{}^{\frac{1}{2} - \varepsilon + \min(2n,5)} \quad \text{and} \quad \alpha^T \mathcal{R}(0) = \psi(0).$$

Inserting this equation into (5.3.32) finishes the proof. □

5.3.2 d-th derivative jump

An estimation of the derivative jump of the d-th derivative jump $\widetilde{R}_k$, $k = 1, \dots, n$ is needed. In fact, only the d-th derivative jump of $\left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T [\widetilde{\mathcal{R}}^{(d)}]_{r_c}$ needs to be estimated.

Lemma 5.16. *There exists a positive constant C independent of r_c such that*

$$\forall 0 < r_c < r_{\min}, \quad \left| \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T [\widetilde{\mathcal{R}}^{(d)}]_{r_c} \right| \leq \frac{C}{{r_c}^{d-1}},$$

and for any $k \in \mathbb{N}$, we have

$$\left\| \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T \left(\mathcal{R}^{(k)} - \widetilde{\mathcal{R}}^{(k)} \right) \right\|_{L^\infty(0, r_c)} \leq \frac{C}{{r_c}^k}.$$

The proof of this lemma is given in the appendix.

Proof of Proposition 5.9. Using the relation (5.3.6), we have

$$\int_{[-\frac{1}{2},\frac{1}{2}]^3} (1-\omega(r)) \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi - \widetilde{\Phi}) e^{-i\mathbf{K}\cdot\mathbf{r}} \, \mathrm{d}\mathbf{r} = 4\pi \int_0^{r_c} (1-\omega(r)) \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)) j_0(Kr) r^2 \, \mathrm{d}r. \tag{5.3.34}$$

Since ω is equal to 1 in a neighbourhood of 0, we can restrict the integral in the equation above to the interval $(r_c - \eta, r_c)$ for some $\eta > 0$. Recall that

$$j_0(x) = \frac{\sin(x)}{x},$$

thus

$$\int_{[-\frac{1}{2},\frac{1}{2}]^3} (1-\omega(r)) \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\Phi - \widetilde{\Phi}) e^{-i\mathbf{K}\cdot\mathbf{r}} \, \mathrm{d}\mathbf{r} = \frac{4\pi}{K} \left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T \int_{r_c-\eta}^{r_c} (1-\omega(r))(\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)) \sin(Kr) r \, \mathrm{d}r. \tag{5.3.35}$$

We denote by f the function $r \mapsto r(1-\omega(r))(\mathcal{R}(r) - \widetilde{\mathcal{R}}(r))$ and use

$$\int_{r_c-\eta}^{r_c} f(r) \sin(Kr) \, \mathrm{d}r = \mathrm{Im} \left(\int_{r_c-\eta}^{r_c} f(r) e^{iKr} \, \mathrm{d}r \right).$$

By definition of the cut-off function, for any $k \in \mathbb{N}$, we have

$$f^{(k)}(r_c - \eta) = 0, \tag{5.3.36}$$

and for $k \in \mathbb{N}^*$, $(1-\omega)^{(k)}(r_c) = 0$. Thus by integration by parts,

$$\int_{r_c-\eta}^{r_c} f(r) e^{iKr} \, \mathrm{d}r = \left[f(r) \frac{e^{iKr}}{iK} \right]_{r_c-\eta}^{r_c} - \frac{1}{iK} \int_{r_c-\eta}^{r_c} f'(r) e^{iKr} \, \mathrm{d}r = \frac{i}{K} \int_{r_c-\eta}^{r_c} f'(r) e^{iKr} \, \mathrm{d}r.$$

As $\mathcal{R} - \widetilde{\mathcal{R}}$ is C^{d-1} but not C^d at r_c, by integrating by parts d times, we have:

$$\int_{r_c-\eta}^{r_c} f(r)e^{iKr}\,\mathrm{d}r = \frac{i^{d+1}r_c}{K^{d+1}}[\widetilde{\mathcal{R}}^{(d)}]_{r_c}e^{iKr_c} - \frac{i^{d+1}}{K^{d+1}}\int_{r_c-\eta}^{r_c} f^{(d+1)}(r)e^{iKr}\,\mathrm{d}r. \tag{5.3.37}$$

Thus inserting the last equation in (5.3.35), we obtain

$$\begin{aligned}\int_{[-\frac{1}{2},\frac{1}{2}]^3}(1-\omega(r))\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T(\Phi-\widetilde{\Phi})e^{-i\mathbf{K}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r} &= \mathrm{Im}(i^{d+1}e^{iKr_c})\frac{4\pi r_c}{K^{d+2}}\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T[\widetilde{\mathcal{R}}^{(d)}]_{r_c}\\ &\quad - \mathrm{Im}\left(\frac{4\pi i^{d+1}}{K^{d+2}}\int_{r_c-\eta}^{r_c}\langle\widetilde{p},f\rangle^T f^{(d+1)}(r)e^{iKr}\,\mathrm{d}r\right).\end{aligned}$$

According to Lemma 5.16,

$$\left|\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T[\widetilde{\mathcal{R}}^{(d)}]_{r_c}\right| \leq \frac{C}{{r_c}^{d-1}}.$$

Furthermore, we have

$$\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T f^{(d+1)}(r) = r\left((1-\omega)\left\langle\widetilde{p},\widetilde{\psi}\right\rangle(\mathcal{R}-\widetilde{\mathcal{R}})\right)^{(d+1)} + \left((1-\omega)\left\langle\widetilde{p},\widetilde{\psi}\right\rangle(\mathcal{R}-\widetilde{\mathcal{R}})\right)^{(d)}.$$

By assumption on ω, we know that $\|\omega^{(k)}\|_{L^\infty(0,r_c)} \leq C{r_c}^{-k}$, hence

$$\begin{aligned}\left\|\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T f^{(d+1)}\right\|_{L^\infty(0,r_c)} &\leq r_c\sum_{k=0}^{d+1}\binom{d+1}{k}\left\|(1-\omega)^{(k)}(\mathcal{R}-\widetilde{\mathcal{R}})^{(d+1-k)}\right\|_{L^\infty(0,r_c)}\\ &\quad + \sum_{k=0}^{d}\binom{d}{k}\left\|(1-\omega)^{(k)}(\mathcal{R}-\widetilde{\mathcal{R}})^{(d-k)}\right\|_{L^\infty(0,r_c)}\\ &\leq \frac{C}{{r_c}^d},\end{aligned}$$

where we used Lemma 5.16. Thus, we obtain

$$\begin{aligned}\left|\int_{r_c-\eta}^{r_c}\langle\widetilde{p},f\rangle^T f^{(d+1)}(r)e^{iKr}\,\mathrm{d}r\right| &\leq r_c\left\|\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T f^{(d+1)}\right\|_{L^\infty(0,r_c)}\\ &\leq \frac{C}{{r_c}^{d-1}},\end{aligned}$$

which finishes the proof of this proposition. □

5.3.3 Convergence theorem

To prove the estimate on the eigenvalues, we will use the following classical result ([Wei74], p. 68).

Proposition 5.17. *Let H be a self-adjoint coercive H^1-bounded operator, $E_1 \leq \cdots \leq E_n$ be the lowest eigenvalues of H and $\psi_1, \ldots, \psi_n$ be L^2-normalized associated eigenfunctions. Let $E_1^{(M)} \leq$*

$\cdots \leq E_n^{(M)}$ *be the lowest eigenvalues of the Rayleigh quotient of* H *restricted to the subspace* V_M *of dimension* M.

Let $w_k \in V_M$ *for* $1 \leq k \leq n$ *be such that*

$$\sum_{k=1}^{n} \|w_k - \psi_k\|_{H^1}^2 < 1$$

Then there exists a positive constant C *which depends on the* H^1 *norm of* H *and the coercivity constant such that for all* $1 \leq k \leq n$

$$\left|E_k^{(M)} - E_k\right| \leq C \sum_{k=1}^{n} \|w_k - \psi_k\|_{H^1}^2$$

We would like to apply this result to $\psi_K = (\mathrm{Id} + T)\widetilde{\psi}_K$ where $\widetilde{\psi}_K$ is the truncation of the plane-wave expansion of f to the wave number K. In order to do this, we need to show that the H^1_{per}-norm of $(\mathrm{Id} + T)\widetilde{\psi}$ is bounded by a the H^1_{per}-norm of $\widetilde{\psi}$ independently of the cut-off radius r_c.

Lemma 5.18. *There exists a positive constant* C *independent of* r_c *such that for any function* $f \in H^1_{\mathrm{per}}([-\frac{1}{2}, \frac{1}{2}]^3)$

$$\|(\mathrm{Id} + T)f\|_{H^1_{\mathrm{per}}} \leq C\|f\|_{H^1_{\mathrm{per}}}.$$

Proof. By definition, we have

$$\begin{aligned}(\mathrm{Id} + T)f &= f + \langle \widetilde{p}\,, f\rangle^T (\Phi - \widetilde{\Phi}) \\ &= f + \langle p\,, f_{00}\rangle^T_{[0,r_c]} (\mathcal{R} - \widetilde{\mathcal{R}})Y_{00},\end{aligned}$$

where

$$f_{00}(r) = \int_{S(0,1)} f(\mathbf{r})Y_{00}(\hat{\mathbf{r}})\,\mathrm{d}\hat{\mathbf{r}}.$$

Thus

$$\begin{aligned}\|(\mathrm{Id} + T)f\|^2_{H^1_{\mathrm{per}}} \leq 2\|f\|^2_{H^1_{\mathrm{per}}} + 2\int_0^{r_c} \langle p\,, f_{00}\rangle^2_{[0,r_c]} (R(r) - \widetilde{R}(r))^2 r^2\,\mathrm{d}r \\ + 2\int_0^{r_c} \langle p\,, f_{00}\rangle^2_{[0,r_c]} (R'(r) - \widetilde{R}'(r))^2 r^2\,\mathrm{d}r. \quad (5.3.38)\end{aligned}$$

Unfortunately, we cannot directly use Lemmas 4.13 and 4.14 in [BCD17b] to complete the proof. Indeed, in doing, we would have

$$\|(\mathrm{Id} + T)f\|^2_{H^1_{\mathrm{per}}} \leq C\left(\|f\|^2_{H^1_{\mathrm{per}}} + \|f_{00}\|^2_{H^1(0,r_c)}\right),$$

but we do not have $\|f_{00}\|_{H^1(0,r_c)} \lesssim \|f\|_{H^1_{\mathrm{per}}}$.

By Lemma 5.24, we have

$$\langle \widetilde{p}\,, f\rangle^T (\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)) = C_{r_c}^T (C_{r_c} G(P) C_{r_c}^T)^{-1} C_{r_c} \int_0^1 \chi(t)P(t)f_{00}(r_c t)t^2\,\mathrm{d}t \cdot \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}(r) - P(\tfrac{r}{r_c})\right),$$

with $\left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}(r) \right\|_{L^\infty(0,r_c)}$ uniformly bounded with respect to r_c. Thus it suffices to study $\int_0^1 t^2 \chi(r_c t) f_{00}(r_c t) P(t)\,\mathrm{d}t$:

$$\begin{aligned}
\left| \int_0^1 t^2 \chi(r_c t) f_{00}(r_c t) P(t)^2\,\mathrm{d}t \right| &\leq \left(\int_0^1 t^2 \chi(r_c t)^2 P(t)\,\mathrm{d}t \right)^{1/2} \left(\int_0^1 t^2 f_{00}(r_c t)^2\,\mathrm{d}t \right)^{1/2} \\
&\leq \frac{C}{{r_c}^{3/2}} \left(\int_0^{r_c} r^2 f_{00}(r)^2\,\mathrm{d}r \right)^{1/2} \\
&\leq \frac{C}{{r_c}^{3/2}} \left(\int_0^{r_c} r^2 f_{00}(r)^6\,\mathrm{d}r \right)^{1/6} \left(\int_0^{r_c} r^2\,\mathrm{d}r \right)^{1/3} \\
&\leq \frac{C}{{r_c}^{1/2}} \|f\|_{L^6(B_{r_c})} \\
&\leq \frac{C}{{r_c}^{1/2}} \|f\|_{H^1(B_{r_c})}.
\end{aligned}$$

We obtain a weaker result than in

$$\left| \langle p\,, f_{00} \rangle_{[0,r_c]}^T \left(\mathcal{R}(r) - \widetilde{\mathcal{R}}(r) \right) \right| \leq \frac{C}{{r_c}^{1/2}} \|f\|_{H^1(B_{r_c})}.$$

Since $\left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}'(r) \right\|_{L^\infty(0,r_c)} = \mathcal{O}\left(\frac{1}{r_c}\right)$, we can prove similarly

$$\left| \langle p\,, f_{00} \rangle_{[0,r_c]}^T \left(\mathcal{R}'(r) - \widetilde{\mathcal{R}}'(r) \right) \right| \leq \frac{C}{{r_c}^{3/2}} \|f\|_{H^1(B_{r_c})}.$$

Thus inserting the last equations in (5.3.38) yields

$$\|(\mathrm{Id} + T) f\|_{H^1_{\mathrm{per}}} \leq C \|f\|_{H^1_{\mathrm{per}}}.$$

□

We have all the elements to prove the main convergence theorem.

Proof of Theorem 5.6. Using Equation (5.3.2), Propositions 5.8, 5.9 and 5.10, we have

$$\begin{aligned}
\|\widetilde{\psi}_M - \widetilde{\psi}\|_{H^1_{\mathrm{per}}} &\leq \left\| \widetilde{\psi}_M - \widetilde{\psi} - \eta_M + \eta \right\|_{H^1_{\mathrm{per}}} + \|\eta_M - \eta\|_{H^1_{\mathrm{per}}} \\
&\leq \left(\sum_{K \geq M, \mathbf{K} \in (2\pi\mathbb{Z})^3} (1 + K^2) \left(\frac{{r_c}^{\min(n,3)+1-\varepsilon}}{K^4} + \frac{1}{{r_c}^{d-1} K^{d+2}} \right)^2 \right)^{\frac{1}{2}} + o\left(\frac{1}{M^{5/2-\varepsilon}} \right).
\end{aligned}$$

By Proposition 5.17, we obtain

$$\begin{aligned}
|E_M - E| &\leq C\|(\mathrm{Id}+T)(\widetilde{\psi}_M - \widetilde{\psi})\|^2_{H^1_{\mathrm{per}}} \\
&\leq C\|\widetilde{\psi}_M - \widetilde{\psi}\|^2_{H^1_{\mathrm{per}}} \\
&\leq C\left(\left(\sum_{K\geq M, \mathbf{K}\in(2\pi\mathbb{Z})^3} (1+K^2)\left(\frac{{r_c}^{\min(2n,5)-\varepsilon}}{M^4} + \frac{1}{{r_c}^{d-1}M^{d+2}}\right)^2\right)^{1/2} + o\left(\frac{1}{M^{5/2-\varepsilon}}\right)\right)^2 \\
&\leq C\left(\frac{{r_c}^{2\min(2n,5)-2\varepsilon}}{M^3} + \frac{{r_c}^{\min(2n,5)-\varepsilon}}{M^{4-\varepsilon}} + \frac{1}{{r_c}^{2d-2}M^{2d-1}} + o\left(\frac{1}{M^{5-\varepsilon}}\right)\right).
\end{aligned}$$

□

5.4 Numerical results

In this section, we present some numerical results applied to the Hamiltonian H in $[-L/2, L/2]^3$

$$H = -\frac{1}{2}\Delta - \frac{Z}{\left|\mathbf{r} - \frac{\mathbf{R}}{2}\right|} - \frac{Z}{\left|\mathbf{r} + \frac{\mathbf{R}}{2}\right|}, \tag{5.4.1}$$

with periodic boundary conditions. The lowest eigenvalue is sought using iterative schemes, hence we are interested in the cost of the matrix-vector multiplication.

The problem is solved using plane-waves. The kinetic operator is diagonal in the reciprocal space. The potential is discretized using a radial grid around the nuclei and a uniform grid in the rest of the domain. For the VPAW method, the following integrals are pre-computed:

1. $\langle e_{\mathbf{K}}, \widetilde{p}\rangle$: since $\widetilde{p}(\mathbf{r}) = p(r)Y_{\ell m}(\hat{\mathbf{r}})$ using (5.3.6), $\langle e_{\mathbf{K}}, \widetilde{p}\rangle$ can be evaluated on a radial grid.
2. $\left\langle e_{\mathbf{K}}, \phi - \widetilde{\phi}\right\rangle$: we proceed like for $\langle e_{\mathbf{K}}, \widetilde{p}\rangle$ using a radial grid;
3. $\left\langle e_{\mathbf{K}}, H(\phi - \widetilde{\phi})\right\rangle$: $H(\phi - \widetilde{\phi})$ is decomposed into a radial and a non-radial part. The first is evaluated on a radial grid and the second on a uniform grid. For non-linear approximations (Hartree-Fock and Kohn-Sham DFT), this term can be critical since it may be necessary to re-compute these integrals regularly. This is the main drawback of the VPAW method compared to the PAW method where this term does not exist.
4. $\left\langle \phi - \widetilde{\phi}, \phi - \widetilde{\phi}\right\rangle$, $\left\langle \phi - \widetilde{\phi}, H(\phi - \widetilde{\phi})\right\rangle$: these integrals are computed using radial grids when possible or using 3D integration schemes. For nonlinear models, the last integral needs to be recomputed regularly, however, since there are N^2_{paw} of them, it is not too costly.

The numerical results using a Julia [BEKS17] homemade code are summarized in the following figures with $Z = 3$, $R = 1$ and $L = 5$. The atomic PAW function ϕ_k are the eigenfunctions of the hydrogenoid atom. "1s" denotes the VPAW method with one PAW function for $\ell = 0$ only, "2s" with two PAW functions for $\ell = 0$ and "2s1p" with two PAW functions for $\ell = 0$ and one function for $\ell = 1$, $|m| \leq 1$. The reference value for the lowest eigenvalue is given by the VPAW method for 200 plane waves per direction. Computation of the reference is out of reach by a direct plane-wave

method. Figures 5.4.1 to 5.4.4 are log-log plots of the convergence of the lowest eigenvalue of (5.4.1) with respect to the number of plane-waves per direction for different choices of the PAW parameters.

In Figure 5.4.1, we clearly notice that the VPAW method converges faster than the direct method. The convergence seems marginally faster when increasing the number of PAW functions. However, with our construction, $\widetilde{\mathcal{R}}_{20}$ and $\widetilde{\mathcal{R}}_{21}$ are very close to the functions $\mathcal{R}_{20}$ and $\mathcal{R}_{21}$ which may explain why there is no significant improvement. See Figure 5.4.3, where other PAW functions where used, for which the difference between $\widetilde{\mathcal{R}}_{20}$ and $\mathcal{R}_{20}$ is more pronounced and the VPAW-2s method seems to perform better than the VPAW-1s method. Table 5.4.1 indicates that the asymptotic regime is not reached, however we were unable to compute the lowest eigenvalues for more than 200 plane waves per direction.

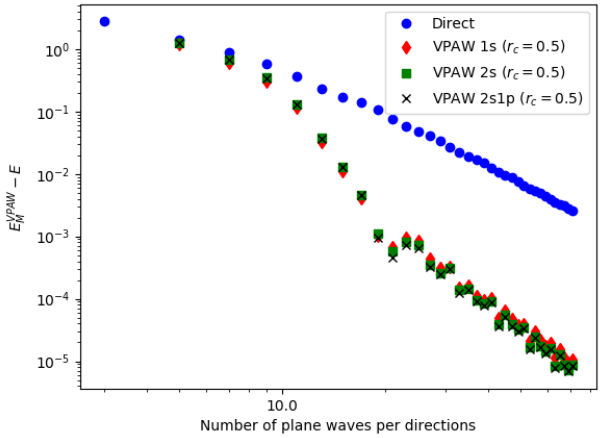


Figure 5.4.1 – Error on the lowest eigenvalue with the VPAW method for different choices of PAW functions.

Methods	Slope
Direct method (for $M \geq 50$)	-2.87
VPAW method (for $M \geq 50$)	-3.80

Table 5.4.1 – Rate of convergence

The size of the VPAW acting region can significantly impact the convergence rate in the pre-asymptotic regime (Figure 5.4.2). This plot suggests that there are different phases in the convergence of the VPAW eigenvalue:

1. for very low plane-wave cut-off, the VPAW acting region is too small to be seen by the Fourier grid, hence no improvement is observed;
2. as the plane-wave cut-off grows, the VPAW eigenvalue converges very fast, since for this regime, the prefactors kill the $\frac{1}{M^3}$ and $\frac{1}{M^4}$ decay;

3. for a larger plane-wave cut-off, the convergence slows down since the prefactor for the $\frac{1}{M^4}$ decay is not negligible anymore.

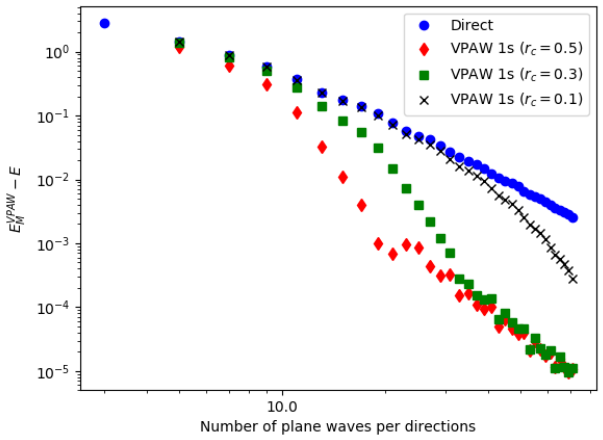


Figure 5.4.2 – Error on the lowest eigenvalue with the VPAW method for different choices of cut-off radius.

In Figure 5.4.3, the Vanderbilt scheme [KF96] for generating the PAW functions was used. The behaviour of the VPAW method for these functions is similar to the VPAW method studied in this paper. This suggests that Theorem 5.6 could be generalized to different families of PAW functions.

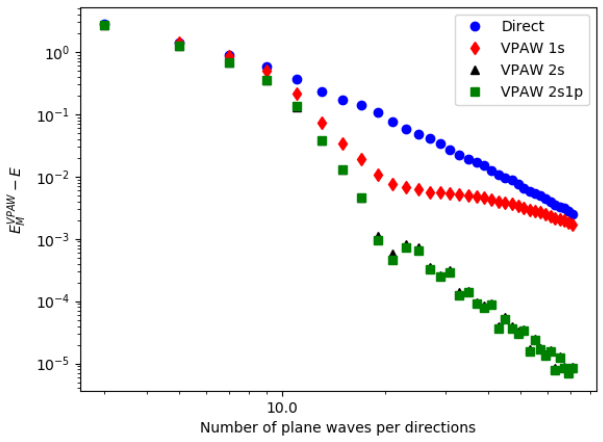


Figure 5.4.3 – Error on the lowest eigenvalue with the VPAW method with Vanderbilt generation scheme.

In Figure 5.4.4, a comparison between the original PAW method and the VPAW method is provided. As expected, the PAW method converges quickly to a value close to the exact eigenvalue. Nevertheless, for very accurate results on the lowest eigenvalue of (5.4.1), the VPAW method seems the method of choice.

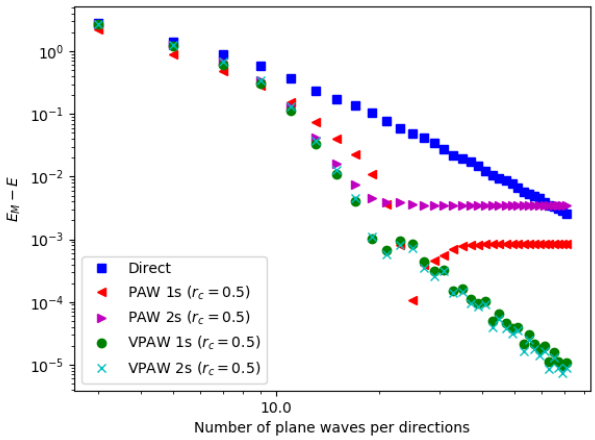


Figure 5.4.4 – Error on the lowest eigenvalue with the PAW and VPAW methods.

5.5 Appendix

We have gathered in this section proofs of some technical lemmas, most of which are simple transpositions of lemmas that can be found in [Dup17, BCD17b].

5.5.1 Results related to the weighted Sobolev space $\mathcal{K}^{\infty,a}(\Gamma)$

Lemma 5.19. *Let $f \in \mathcal{K}^{\infty,a}(\Gamma)$ and $0 < R < 1$. Let $\ell \in \mathbb{N}$ and $m \in \mathbb{N}$ such that $|m| \leq \ell$. Then there exists a constant C independent of f such that*

$$\int_0^R |f_{\ell m}(r)| r^2 \, \mathrm{d}r \leq C R^{a+\frac{3}{2}} \|f\|_{\mathcal{K}^{\infty,a}},$$

and for $a \geq 1$

$$\int_0^R |f_{\ell m}(r)|^2 \, \mathrm{d}r \leq C R^{2a-2} \|f\|_{\mathcal{K}^{\infty,a}}.$$

Proof. Since $Y_{\ell m} \in L^\infty(S(0,1))$, we have

$$\begin{aligned}
\int_0^R |f_{\ell m}(r)| r^2 \, \mathrm{d}r &\leq C \int_{B(0,R)} |f(\mathbf{r})| \, \mathrm{d}\mathbf{r} \\
&\leq C \int_{B(0,R)} r^a r^{-a} |f(\mathbf{r})| \, \mathrm{d}\mathbf{r} \\
&\leq C \left(\int_0^R r^{2a+2} \, \mathrm{d}r \right)^{1/2} \left(\int_{B(0,R)} r^{-2a} |f(\mathbf{r})|^2 \, \mathrm{d}\mathbf{r} \right)^{1/2} \\
&\leq C R^{a+\frac{3}{2}} \|f\|_{\mathcal{K}^{\infty,a}},
\end{aligned}$$

where in the fourth inequality we used the definition of the weighted Sobolev space $\mathcal{K}^{\infty,a}$. The second identity is proved the same way. □

Lemma 5.20. *Let $N \in \mathbb{N}^*$ and η a radial function such that $\eta \in \mathcal{K}^{\infty,5/2+N-\varepsilon}(\Gamma)$, $\varepsilon > 0$. Then for R sufficiently small, we have*

$$\|\eta\|_{L^\infty(0,R)} \leq \|f\|_{\mathcal{K}^{\infty,a}} R^{N+\frac{1}{2}-\varepsilon}.$$

Proof. By definition of the weighted Sobolev space, we have for R sufficiently small,

$$\int_{B(0,R)} |\eta(r)|^2 r^{-5-2N+2\varepsilon}\,\mathrm{d}\mathbf{r} < \infty,$$

hence

$$\int_0^R |\eta(r)|^2 r^{-3-2N+2\varepsilon}\,\mathrm{d}r < \infty,$$

Similarly we have

$$\int_0^R |\eta'(r)|^2 r^{-1-2N+2\varepsilon}\,\mathrm{d}r < \infty.$$

Therefore,

$$\begin{cases} \int_0^R |\eta(r)|^2\,\mathrm{d}r \leq R^{2N+3-2\varepsilon} \int_0^R |\eta(r)|^2 r^{-1-2N+2\varepsilon}\,\mathrm{d}r, \\ \int_0^R |\eta'(r)|^2\,\mathrm{d}r \leq R^{2N+1-2\varepsilon} \int_0^R |\eta'(r)|^2 r^{-1-2N+2\varepsilon}\,\mathrm{d}r. \end{cases}$$

By the Sobolev embedding theorem, we have the result. □

Remark 5.21. *Lemma 5.20 implies that the remainder η_N of the singularity expansion (5.1.20) of radial functions are bounded : $\|\eta_N\|_{L^\infty(0,r_c)} \leq C {r_c}^{N+1}$, where the constant is independent of r_c.*

5.5.2 Validity of the assumptions for the hydrogenoid atom

We show in this subsection that Assumption 5.1 hold in the particular case of the hydrogenoid atom, *i.e.* where in (5.1.6) $W = 0$. The eigenfunctions of the hydrogenoid atom can be written

$$\varphi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}), \quad n \geq \ell + 1,$$

with

$$R_{n\ell}(r) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-Zr/n} \left(\frac{2Zr}{n}\right)^\ell L_{n-\ell-1}^{(2\ell+1)}\left(\frac{2Zr}{n}\right), \tag{5.5.1}$$

where $L_{n-\ell-1}^{(2\ell+1)}$ denotes the generalized Laguerre polynomials.

Lemma 5.22. *Let $R_{n\ell}(r) = L_{n-1}(\frac{2Z}{n}) e^{-\frac{Zr}{n}}$, where $\deg(L_{n-1}) = n-1$. Let $r > 0$ and $\mathcal{R}_k = (R_{1\ell}^{(k)}(r), \ldots, R_{n\ell}^{(k)}(r))^T$ for $0 \leq k \leq n-1$. Then the matrix $(\mathcal{R}_0, \ldots, \mathcal{R}_{n-1})$ is invertible.*

Proof. We have

$$R_{n\ell}^{(k)}(r) = \left(\frac{Z}{n}\right)^k e^{-\frac{Zr}{n}} \sum_{j=0}^k 2^j \binom{k}{j} L_{n-1}^{(j)}\left(\frac{2Zr}{n}\right).$$

Let $\mathcal{P} = \left(L_j^{(k)}(\frac{2Zr}{j+1})\right)_{0\leq j,k\leq n-1}$, $\mathcal{M} = (2^j \binom{k}{j})_{0\leq j,k\leq n-1}$ and $\mathcal{Z} = \left((\frac{Z}{k+1})^j\right)_{0\leq j,k\leq n-1}$. It is easy to check that

$$(\mathcal{R}_0, \ldots, \mathcal{R}_{n-1}) = \mathcal{Z}\ \mathrm{diag}(e^{-Zr}, \ldots, e^{-\frac{Zr}{n}}) \mathcal{P}\mathcal{M}.$$

$\mathcal{P}$ and $\mathcal{M}$ are both triangular with no null entry on the diagonal. $\mathcal{Z}$ is a Vandermonde matrix, hence $(\mathcal{R}_0, \dots, \mathcal{R}_{n-1})$ is invertible. □

5.5.3 Lemmas related to PAW functions

Let P_k, $k \in \mathbb{N}$ the polynomials defined by

$$P_k(t) = \frac{1}{2^k k!}(t^2 - 1)^k. \tag{5.5.2}$$

By definition, these polynomials form a basis of even polynomials and satisfy

$$\begin{cases} P_k^{(j)}(1) = 0, \quad 0 \leq j \leq k-1, \\ P_k^{(k)}(1) = 1. \end{cases}$$

Let P be the vector $(P_0, \dots, P_{d-1})^T$ and $C_{r_c} \in \mathbb{R}^{n \times d}$ be the matrix such that

$$\widetilde{\mathcal{R}}(t) = C_{r_c} P(\tfrac{t}{r_c}). \tag{5.5.3}$$

The following lemma summarizes the main properties of the matrix C_{r_c}.

Lemma 5.23. *Let $C_1 \in \mathbb{R}^{n \times n}$ and $C_2 \in R^{n \times (n-d)}$ be the matrices such that*

$$\widetilde{\mathcal{R}}(r) = \Big(C_1 \;\Big|\; C_2\Big) P(\tfrac{r}{r_c}).$$

Moreover, C_1 is invertible, the norm of $C_1^{-1}C_2$ is uniformly bounded with respect to r_c and

$$C_2^T C_1^{-T} e_0 = \mathcal{O}(r_c).$$

Proof. Let C_{r_c} be the matrix $\Big(C_1 \;\Big|\; C_2\Big)$. Let c_j be the columns of C_{r_c}. By continuity of $\widetilde{\mathcal{R}}$ and of its derivatives at r_c, and by our choice of the polynomials P_k, the columns of C_{r_c} satisfy

$$\forall\, 0 \leq j \leq d-1, \;\; c_j = {r_c}^j \mathcal{R}^{(j)}(r_c) - \sum_{k=0}^{j-1} P_k^{(j)} c_k. \tag{5.5.4}$$

Hence c_k is a linear combination of the vectors ${r_c}^j \mathcal{R}^{(j)}(r_c)$ for $j \leq k$ with coefficients that are *independent* of r_c. It is easy to see that the transformation of $(c_j)_{0 \leq j \leq n-1}$ to $({r_c}^j \mathcal{R}^{(j)}(r_c))_{0 \leq j \leq n-1}$ is invertible. If r_c is sufficiently small, by Assumption 5.1, the family $({r_c}^j \mathcal{R}^{(j)}(r_c))_{0 \leq j \leq n-1}$ is linearly independent, thus we can define $(g_j)_{0 \leq j \leq n-1}$ to be the dual family to $(c_j)_{0 \leq j \leq n-1}$ (*i.e.* $c_j^T g_k = \delta_{jk}$) and we have $\|g_j\| = \mathcal{O}\left(\frac{1}{{r_c}^{n-1}}\right)$. Hence, using the recurrence (5.5.4), it is easy to see that the norm of $C_1^{-1}C_2$ is uniformly bounded with respect to r_c.

To prove $C_2^T C_1^{-T} e_0 = \mathcal{O}(r_c)$, first notice that $C_1^{-T} e_0 = g_1$. Since P_0 is a constant polynomial, for $j \geq 1$, we have

$$c_j = {r_c}^j \mathcal{R}^{(j)}(r_c) - \sum_{k=1}^{j-1} P_k^{(j)} c_k.$$

Thus for $j = n$, we have

$$c_n^T g_0 = {r_c}^n \mathcal{R}^{(n)}(r_c)^T g_0 - \sum_{k=1}^{j-1} P_k^{(j)} c_k^T g_0 = \mathcal{O}(r_c),$$

and by iteration, it is then easy to check that

$$\forall\, n \leq j \leq d-1,\ c_j^T g_0 = \mathcal{O}(r_c).$$

□

Lemma 5.24. *We have*

$$\langle \widetilde{p}\,, f\rangle^T \left(\mathcal{R}(r) - \widetilde{\mathcal{R}}(r)\right) = C_{r_c}^T (C_{r_c} G(P) C_{r_c}^T)^{-1} C_{r_c} \int_0^1 \chi(t) P(t) f_{00}(r_c t) t^2 \,\mathrm{d}t \cdot \left(\begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}(r) - P(\tfrac{r}{r_c}) \right),$$

with P being the vector of the polynomials P_k defined in (5.5.2), C_{r_c} the matrix of coefficients of $\widetilde{\mathcal{R}}$ in the basis (P_k) given in (5.5.3) and $G(P)$ the matrix

$$G(P) = \int_0^1 \chi(t) P(t) P(t)^T t^2 \,\mathrm{d}t.$$

The norm of the matrix $C_{r_c}^T (C_{r_c} G(P) C_{r_c}^T)^{-1} C_{r_c}$ is uniformly bounded as r_c goes to 0 and we have

$$\left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}(r) \right\|_{L^\infty(0,r_c)} \leq C \quad \text{and} \quad \left\| \begin{pmatrix} C_1^{-1} \\ 0 \end{pmatrix} \mathcal{R}'(r) \right\|_{L^\infty(0,r_c)} \leq \frac{C}{r_c}.$$

Proof. Since $G(P)$ is positive-definite, $G(P)^{1/2}$ exists. It is easy to check that the matrix $G(P)^{1/2} C_{r_c}^T (C_{r_c} G(P) C_{r_c}^T)^{-1} C_{r_c} G(P)^{1/2}$ is symmetric and is a projector, hence its norm is independent of r_c.

Writing down the Taylor expansion of $\mathcal{R}$ at r_c, we obtain

$$\begin{aligned} \mathcal{R}(r) &= \sum_{k=0}^{n-1} \frac{(r-r_c)^k}{k!} \mathcal{R}^{(k)}(r_c) + \mathcal{O}((r-r_c)^n) \\ &= \sum_{k=0}^{n-1} \frac{1}{k!} \left(\frac{r}{r_c} - 1 \right)^k {r_c}^k \mathcal{R}^{(k)}(r_c) + \mathcal{O}((r-r_c)^n). \end{aligned}$$

By Lemma 5.23, $\|C_1^{-1} {r_c}^k \mathcal{R}^{(k)}(r_c)\|$ is uniformly bounded as r_c goes to 0, which concludes the proof of the lemma. □

Lemma 5.25. *Let $f \in L^2(\Gamma)$. Let $\ell \geq 0$, $|m| \leq \ell$ be integers. Let n be the number of PAW functions associated to the angular momentum ℓ, m for a cut-off radius r_c. There exists a constant independent of r_c and f such that*

$$|\langle \widetilde{p}\,, f\rangle^T \mathcal{R}(0)| \leq \frac{C}{{r_c}^{3/2}} \|f\|_{L^2(B_{r_c})}.$$

Sketch of the proof. The proof of this lemma is very similar to the proof of Proposition 3.2 in [BCD17b]. We briefly sketch the proof in case $\ell = m = 0$. First, it is easy to show that

$$\langle \widetilde{p}, f \rangle = \int_0^1 \chi(t)(C_{r_c}^{(Q)} G_{r_c})^{-1} C_{r_c}^{(Q)} Q(t) f(r_c t) t^2 \,\mathrm{d}t, \tag{5.5.5}$$

where $Q(t) = (Q_0(t), \dots, Q_{d-1}(t))^T$ is a vector of even polynomials which forms a basis of even polynomials of degree at most $2d-2$,

$$\widetilde{\mathcal{R}}(x) = C_{r_c}^{(Q)} Q(\tfrac{x}{r_c}),$$

with $C_{r_c}^{(Q)} \in \mathbb{R}^{n\times d}$ and

$$G_{r_c} = \int_0^1 \chi(t) Q(t) \mathcal{R}(r_c t)^T t^2 \,\mathrm{d}t \in \mathbb{R}^{d\times n}.$$

By Lemma 5.14, we have that $(\zeta_{2k})_{0\le k\le n-1}$ and $(\zeta_{2k+1})_{0\le k\le n-1}$ defined by the singular expansion of $\mathcal{R}$:

$$\mathcal{R}(t) = \sum_{k=0}^{n-1} \zeta_{2k} t^{2k} + \zeta_{2k+1} t^{2k+1} + \eta_{2n}(t), \tag{5.5.6}$$

satisfy

$$\zeta_{2k} = \sum_{j=0}^{k} \mu_j^{(k)} \mathcal{E}^j \zeta_0 \quad \text{and} \quad \zeta_{2k+1} = \sum_{j=0}^{k} \nu_j^{(k)} \mathcal{E}^j \zeta_0,$$

where $\mu_k^{(k)} \neq 0$ and $\mathcal{E}$ is the diagonal matrix of the eigenvalues $(\epsilon_1, \dots, \epsilon_n)$. By Lemma 5.14, ζ_0 has no null entry. The eigenvalues of the atomic operator (5.1.6) for a fixed ℓ, m are simple, hence $(\mathcal{E}^j \zeta_0)_{0\le j\le n-1}$ is a linearly independent family. Hence, $(\zeta_{2k})_{0\le k\le n-1}$ is a basis of $\mathbb{R}^n$. Let (h_k) be the dual basis to $({r_c}^{2j} \mathcal{E}^j \zeta_0)_{0\le j\le n-1}$, *i.e.* $h_k^T {r_c}^{2j} \mathcal{E}^j \zeta_0 = \delta_{kj}$.

Injecting (5.5.6) in the definition of G_{r_c}, we obtain

$$G_{r_c}^T = \int_0^1 \chi(t) \mathcal{R}(r_c t) Q(t)^T t^2 \,\mathrm{d}t \tag{5.5.7}$$

$$= \int_0^1 \chi(t) \left(\sum_{k=0}^{n-1} {r_c}^{2k} \mathcal{E}^k \zeta_0 \sum_{j=k}^{n-1} \mu_k^{(j)} {r_c}^{2j-2k} t^{2j} + r_c \sum_{k=0}^{n-1} {r_c}^{2k} \mathcal{E}^k \zeta_0 \sum_{j=k}^{n-1} \nu_k^{(j)} {r_c}^{2j-2k} t^{2j+1} + \eta_{2n}(r_c t) \right) Q(t)^T t^2 \,\mathrm{d}t. \tag{5.5.8}$$

By Lemma 5.19, we have

$$\left| \int_0^1 \chi(t) \eta_{2n}(r_c t) Q(t)^T t^2 \,\mathrm{d}t \right| = \frac{1}{r_c^3} \left| \int_0^{r_c} \chi(\tfrac{t}{r_c}) \eta_{2n}(t) Q(\tfrac{t}{r_c})^T t^2 \,\mathrm{d}t \right| \le C {r_c}^{2n}. \tag{5.5.9}$$

Let $(Q_k)_{0\le k\le d-1}$ be the even polynomials such that

$$\int_0^1 \chi(t) t^{2j} Q_k(t) t^2 \,\mathrm{d}t = \delta_{jk}.$$

Such polynomials exist since the Gram matrix $(\int_0^1 \chi(t)t^{2j+2k+2}\,\mathrm{d}t)_{0\le j,k\le n-1}$ is invertible. Let

$$X_j = \int_0^1 \chi(t)t^{2j+1}Q(t)t^2\,\mathrm{d}t,$$

and

$$\mathcal{H} = \begin{pmatrix} h_0^T \\ \vdots \\ h_{n-1}^T \end{pmatrix} \in \mathbb{R}^{n\times n}. \tag{5.5.10}$$

Then denoting by e_k the k-th canonical vector, we have

$$\begin{aligned}\mathcal{H}G_{r_c}^T &= \sum_{k=0}^{n-1}\mu_k^{(k)}e_ke_k^T + \sum_{k=0}^{n-1}\sum_{j=k+1}^{n-1}\mu_k^{(j)}{r_c}^{2j-2k}e_ke_j^T + r_c\sum_{k=0}^{n-1}\nu_k^{(j)}{r_c}^{2j-2k}e_kX_j^T + \mathcal{O}({r_c}^2)\\ &= \sum_{k=0}^{n-1}\mu_k^{(k)}e_ke_k^T + \mathcal{O}(r_c).\end{aligned}$$

Let

$$\mathcal{A} = \sum_{k=0}^{n-1}\mu_k^{(k)}e_ke_k^T \in \mathbb{R}^{n\times n}, \tag{5.5.11}$$

and Π the transition matrix such that

$$C_{r_c}^{(Q)} = C_{r_c}\Pi,$$

where C_{r_c} is defined in (5.5.3). Hence we have

$$\begin{aligned}(C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\mathcal{R}(0) &= (C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\mathcal{H}^{-1}e_0\\ &= (C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c}\mathcal{H}^T)^{-T}e_0\\ &= \Pi^T\begin{pmatrix} I_n \\ M^T+\mathcal{O}(r_c)\end{pmatrix}\left(C^{-1}C_{r_c}\Pi\left(\begin{pmatrix}\mathcal{A}\\0\end{pmatrix}+\mathcal{O}(r_c)\right)\right)^{-T}e_0\\ &= \Pi^T\begin{pmatrix} I_n \\ M^T+\mathcal{O}(r_c)\end{pmatrix}\left(\left(\begin{array}{c|c} I_n & M+\mathcal{O}(r_c)\end{array}\right)\Pi\left(\begin{pmatrix}\mathcal{A}\\0\end{pmatrix}+\mathcal{O}(r_c)\right)\right)^{-T}e_0,\end{aligned}$$

where we used Lemma 5.23 in the third and fourth inequality. Decomposing Π into four blocks

$$\Pi = \begin{pmatrix}\Pi_1 & \Pi_2\\ \Pi_3 & \Pi_4\end{pmatrix}, \quad \text{with } \Pi_1 \in \mathbb{R}^{n\times n},$$

we obtain

$$\begin{aligned}(C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\mathcal{R}(0) &= \left(\begin{pmatrix}\Pi_1^T+\Pi_3^T M^T\\ \Pi_2^T+\Pi_4^T M^T\end{pmatrix}+\mathcal{O}(r_c)\right)(\Pi_1\mathcal{A}+M\Pi_3\mathcal{A}+\mathcal{O}(r_c))\,e_0\\ &= \begin{pmatrix}\mathcal{A}^{-1}\\ (\Pi_2^T+\Pi_4^T M^T)(\Pi_1+M\Pi_3)^{-1}\end{pmatrix}e_0+\mathcal{O}(r_c).\end{aligned}$$

Hence $\|(C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\mathcal{R}(0)\|$ is uniformly bounded as r_c goes to 0. Thus, there exists a constant C independent of r_c and f such that :

$$\begin{aligned}\left|\langle\widetilde{p},f\rangle^T\mathcal{R}(0)\right| &\leq C\int_0^1|f(r_ct)|t^2\,\mathrm{d}t\\ &\leq \frac{C}{{r_c}^{3/2}}\|f\|_{L^2_{\mathrm{per}}}.\end{aligned}$$

□

We can now prove Lemma 5.16.

Proof of Lemma 5.16. We start with the proof of the estimate of $\left[\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T\widetilde{\mathcal{R}}^{(d)}\right]_{r_c}$. We have using (5.5.5) and (5.5.3)

$$\left[\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T\widetilde{\mathcal{R}}^{(d)}\right]_{r_c} = \left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T(\mathcal{R}^{(d)}(r_c)-\widetilde{\mathcal{R}}^{(d)}(r_c)) \tag{5.5.12}$$

$$= \frac{1}{{r_c}^d}\int_0^1\chi(t)\psi_{00}(r_ct)Q(t)t^2\,\mathrm{d}t\cdot(C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\left({r_c}^d\mathcal{R}^{(d)}(r_c)-C_{r_c}P^{(d)}(1)\right). \tag{5.5.13}$$

First, we prove that

$$(C_{r_c}^{(Q)})^T(C_{r_c}^{(Q)}G_{r_c})^{-T}\left({r_c}^d\mathcal{R}^{(d)}(r_c)-C_{r_c}P^{(d)}(1)\right) = \begin{pmatrix}0\\ *\end{pmatrix}+\mathcal{O}(r_c), \tag{5.5.14}$$

then

$$\int_0^1\chi(t)\psi_{00}(r_ct)Q(t)t^2\,\mathrm{d}t = \psi(0)e_0+\mathcal{O}(r_c). \tag{5.5.15}$$

If both statements are true, then it is easy to deduce that there exists a constant C independent of r_c such that

$$\left|\left[\left\langle\widetilde{p},\widetilde{\psi}\right\rangle^T\widetilde{\mathcal{R}}^{(d)}\right]_{r_c}\right| \leq \frac{C}{{r_c}^{d-1}}.$$

Step 1 (proof of (5.5.14)) By (5.3.22), we have for $0 \leq j \leq 2n-1$ even

$$r_c{}^j \mathcal{R}^{(j)}(r_c) = \sum_{k=j/2}^{n-1} \zeta_{2k} \frac{(2k)!}{(2k-j)!} r_c{}^{2k} + \zeta_{2k+1} \frac{(2k+1)!}{(2k+1-j)!} r_c{}^{2k+1} + \mathcal{O}(r_c{}^{2n})$$
$$= \sum_{k=j/2}^{n-1} \sum_{\ell=0}^{k} \mu_\ell^{(k)} r_c{}^{2\ell} \mathcal{E}^\ell \zeta_0 \frac{(2k)!}{(2k-j)!} r_c{}^{2k-2\ell} + r_c \sum_{k=j/2}^{n-1} \sum_{\ell=0}^{k} \nu_\ell^{(k)} r_c{}^{2\ell} \mathcal{E}^\ell \zeta_0 \frac{(2k+1)!}{(2k+1-j)!} r_c{}^{2k-2\ell} + \mathcal{O}(r_c{}^{2n}),$$

where we applied Lemma 5.20 to estimate the remainder of the singular expansion. By noticing that $\mathcal{H} r_c{}^{2j} \mathcal{E}^j \zeta_0 = e_j$ with $\mathcal{H}$ defined in (5.5.10), we have

$$(C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} r_c{}^j \mathcal{E}^j \zeta_0 = \begin{pmatrix} \mathcal{A}^{-1} \\ * \end{pmatrix} e_j + \mathcal{O}(r_c).$$

Using $\|(C_{r_c}^{(Q)})(C_{r_c}^{(Q)} G_{r_c})^{-1}\| = \mathcal{O}\left(\frac{1}{r_c{}^{2n-2}}\right)$, we thus get

$$(C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} r_c{}^j \mathcal{R}^{(j)}(r_c) = \begin{pmatrix} I_n \\ * \end{pmatrix} \sum_{k=j/2}^{n-1} e_k + \mathcal{O}(r_c). \tag{5.5.16}$$

For $0 \leq j \leq 2n-1$ odd, we have

$$r_c{}^j \mathcal{R}^{(j)}(r_c) = r_c{}^j \zeta_j + \sum_{k=\frac{j+1}{2}}^{n-1} \zeta_{2k} \frac{(2k)!}{(2k-j)!} r_c{}^{2k} + \zeta_{2k+1} \frac{(2k+1)!}{(2k+1-j)!} r_c{}^{2k+1} + \mathcal{O}(r_c{}^{2n}),$$

similarly to the even case, we thus obtain

$$(C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} r_c{}^j \mathcal{R}^{(j)}(r_c) = \begin{pmatrix} \mathcal{A}^{-1} \\ * \end{pmatrix} \sum_{k=\frac{j+1}{2}}^{n-1} \nu_k^{(k)} e_k + \mathcal{O}(r_c). \tag{5.5.17}$$

For $j \geq 2n$, using $\|(C_{r_c}^{(Q)})(C_{r_c}^{(Q)} G_{r_c})^{-1}\| = \mathcal{O}\left(\frac{1}{r_c{}^{2n-2}}\right)$, then

$$(C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} r_c{}^j \mathcal{R}^{(j)}(r_c) = \mathcal{O}(r_c). \tag{5.5.18}$$

From (5.5.16) (when $d \leq 2n-1$ and d is even), (5.5.17) (when $d \leq 2n-1$ and d is odd) or (5.5.18) (when $d \geq 2n$), we have

$$(C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} r_c{}^d \mathcal{R}^{(d)}(r_c) = \begin{pmatrix} 0 \\ * \end{pmatrix} + \mathcal{O}(r_c).$$

It remains to prove the same statement for the other part. By definition of the polynomials P_k

(5.5.2), we have

$$P^{(d)}(1) = (\underbrace{0, \dots, 0}_{\lfloor \frac{d}{2} \rfloor}, *, \dots, *)^T,$$

so $C_{r_c} P^{(d)}(1)$ is a linear combination of the last $\lceil \frac{d}{2} \rceil$ columns of C_{r_c}. However, by Lemma 5.23, we know that except the first column of C_{r_c}, the columns of C_{r_c} do not depend on $\mathcal{R}(r_c)$ and by (5.5.16) and (5.5.17), for $j \geq 1$,

$$e_0^T (C_{r_c}^{(Q)})^T (C_{r_c}^{(Q)} G_{r_c})^{-T} {r_c}^j \mathcal{R}^{(j)}(r_c) = \mathcal{O}(r_c),$$

which finishes the proof of the first step.

Step 2 (proof of (5.5.15)) Since $\psi \in H^2_{\text{per}}(\Gamma)$, by the Sobolev embedding theorem, ψ is continuous, hence $\psi(0)$ is finite. Thus

$$\begin{aligned}\int_0^1 \chi(t)\psi_{00}(r_c t) Q(t) t^2 \, \mathrm{d}t &= \int_0^1 \chi(t) \left(\psi(0) + \int_0^{r_c t} \psi'_{00}(u) \, \mathrm{d}u \right) Q(t) t^2 \, \mathrm{d}t \\ &= \psi(0) e_0 + \int_0^1 \chi(t) \int_0^{r_c t} \psi'_{00}(u) \, \mathrm{d}u \, Q(t) t^2 \, \mathrm{d}t,\end{aligned}$$

by definition of the polynomials Q_k.

We have (C denotes a constant independent of r_c)

$$\begin{aligned}\left| \int_0^1 \chi(t) \int_0^{r_c t} \psi'_{00}(u) \, \mathrm{d}u \; Q(t) t^2 \, \mathrm{d}t \right| &\leq \left(\int_0^1 \chi(t)^2 Q(t)^2 t^4 \, \mathrm{d}t \int_0^1 \left(\int_0^{r_c t} \psi'_{00}(u) \, \mathrm{d}u \right)^2 \mathrm{d}t \right)^{1/2} \\ &\leq C r_c \left(\int_0^1 \left(\frac{1}{u} \psi'_{00} \right)^2 u^2 \, \mathrm{d}u \right)^{1/2}.\end{aligned}$$

Using a Hardy inequality [Eva10] (Theorem 7, p. 298), we get

$$\left| \int_0^1 \chi(t) \int_0^{r_c t} \psi'_{00}(u) \, \mathrm{d}u \; Q(t) t^2 \, \mathrm{d}t \right| \leq C r_c \|\psi\|_{H^1_{\text{per}}},$$

which ends the proof of (5.5.15).

The proof of the bound on $\left\langle \widetilde{p}, \widetilde{\psi} \right\rangle^T (\mathcal{R}^{(k)} - \widetilde{\mathcal{R}}^{(k)})$ is a simple extension of the proof of (5.5.14). □

APPENDIX A

THE FROZEN CORE APPROXIMATION

In this appendix, we give the proof of the results stated in Section 1.2.2 in Chapter 1. The computations are very similar with those for the Hartree-Fock theory. A detailed exposition of the Hartree-Fock theory can be found in [CLBM06].

We are interested in the minimal energy of the N-body Schrödinger operator

$$E_0^N = \inf_{\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3), \|\Psi\|=1} \left\langle \Psi | H^N | \Psi \right\rangle, \tag{A.1}$$

where

$$H^N = \frac{1}{2}\sum_{i=1}^N \Delta_i - \sum_{i=1}^N \sum_{I=1}^{N_{\text{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{A.2}$$

Let $n_c < N$ and $n_v = N - n_c$. Let $\phi_1, \ldots, \phi_{n_c}$ in $H^1(\mathbb{R}^3)$. The wave functions $(\phi_i)_{1\leq i\leq n_c}$ are called core wave functions and are supposed mutually orthogonal ($\int_{\mathbb{R}^3} \phi\phi_j = \delta_{ij}$). We introduce the core electron density

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{n_c} |\phi_i(\mathbf{r})|^2.$$

To reduce the dimension of the minimization problem, in the same fashion as the Hartree-Fock method, the test functions Ψ are reduced to

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = C \sum_{\sigma\in\mathcal{S}_N} (-1)^\sigma \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \ldots, \mathbf{r}_{\sigma(N)}), \tag{A.3}$$

where C is a normalization factor and $\Phi_v \in \bigwedge_{i=1}^{n_v} L^2(\mathbb{R}^3)$ is normalized and orthogonal to the core wave functions

$$\forall \mathbf{r}_2, \ldots, \mathbf{r}_{n_v} \in \mathbb{R}^3, \quad \int_{\mathbb{R}^3} \Phi_v(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}) \phi_i(\mathbf{r})\, \mathrm{d}\mathbf{r} = 0.$$

Let V^{FC} be the set of such functions:

$$V^{\mathrm{FC}} = \Bigg\{ \Psi \text{ is given by (A.3)}, \|\Psi\| = 1, \int_{\mathbb{R}^{3n_v}} |\Phi_v|^2 = 1, \int_{\mathbb{R}^3} \Phi_v(\mathbf{r}, \cdot)\phi_i(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0, \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \Bigg\}. \quad \text{(A.4)}$$

We denote by $\mathcal{E}^{\mathrm{FC}}$ the frozen core energy functional

$$\mathcal{E}^{\mathrm{FC}}(\Psi) = \left\langle \Psi | H^N | \Psi \right\rangle, \quad \Psi \in V^{\mathrm{FC}}. \quad \text{(A.5)}$$

In the following, in an abuse of notation, for $f, g \in L^2(\mathbb{R}^d)$, $\langle f|g\rangle$ denotes the L^2 scalar product in $L^2(\mathbb{R}^d)$.

Proposition A.1. *Let Ψ given by (A.3). Then the normalization constant C is equal to*

$$C = \sqrt{N!\,n_v!}.$$

Proof. We have

$$\langle \Psi\,, \Psi \rangle = C^2 \sum_{\sigma\in\mathcal{S}_N} \sum_{\sigma'\in\mathcal{S}_N} (-1)^{\sigma+\sigma'} \Bigg\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1}, \ldots, \mathbf{r}_{\sigma(N)}), \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)}) \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \ldots, \mathbf{r}_{\sigma'(N)}) \Bigg\rangle \quad \text{(A.6)}$$

By the orthogonality assumption on the core wave functions $(\phi_i)_{1\le i\le n_c}$, the scalar products are equal to 0 if the permutations σ and σ' are not equal on $[\![1, n_c]\!]$. If $\sigma = \sigma'$ on $[\![1, n_c]\!]$, we have:

$$\begin{aligned} &\Bigg\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)})\, \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \ldots, \mathbf{r}_{\sigma(N)}), \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)}) \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \ldots, \mathbf{r}_{\sigma'(N)}) \Bigg\rangle \\ &\qquad = \left\langle \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \ldots, \mathbf{r}_{\sigma(N)}), \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \ldots, \mathbf{r}_{\sigma'(N)}) \right\rangle \\ &\qquad = (-1)^{\sigma-\sigma'}, \end{aligned}$$

because Φ_v is antisymmetric and normalized.

Now we simply have to count how many permutations σ and σ' in (A.6) yield non zero terms. σ and σ' simply have to be equal on $[\![1, n_c]\!]$. Hence, there are $N!$ possible choices for σ and with the previous requirement $n_v!$ possible choices for σ'. Thus

$$C^2 = N!\,n_v!.$$

□

As in the Hartree-Fock theory, it is possible to rewrite the energy functional $\mathcal{E}^{\mathrm{FC}}$.

Theorem A.2. *If Ψ belongs to V^{FC} then*

$$\mathcal{E}^{\mathrm{FC}}(\Psi) = \mathcal{E}_{CORE}(\phi_1, \ldots, \phi_{n_c}) + \mathcal{E}_v^{\mathrm{FC}}(\phi_1, \ldots, \phi_{n_c}, \Phi_v),$$

where the core energy $\mathcal{E}_{CORE}$ is

$$\mathcal{E}_{CORE}(\phi_1, \ldots, \phi_{n_c}) = \sum_{i=1}^{n_c} \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 - \int_{\mathbb{R}^3} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \rho_c(\mathbf{r})\, \mathrm{d}\mathbf{r} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left| \sum_{j=1}^{n_c} \phi_j(\mathbf{r})\phi_j(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'.$$

and the valence energy functional $\mathcal{E}_v^{\mathrm{FC}}$ is

$$\begin{aligned}
\mathcal{E}_v^{\mathrm{FC}}(\phi_1, \ldots, \phi_{n_c}, \Phi_v) &= \frac{1}{2} \int_{\mathbb{R}^{3n_v}} |\nabla \Phi_v|^2 - \sum_{i=1}^{n_v} \int_{\mathbb{R}^{3n_v}} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} |\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v})|^2\, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{n_v} \\
&+ \sum_{1 \le i < j \le n_v} \int_{\mathbb{R}^{3n_v}} \frac{|\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v})|^2}{|\mathbf{r}_i - \mathbf{r}_j|}\, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{n_v} + \sum_{i=1}^{n_v} \int_{\mathbb{R}^{3n_v+3}} \frac{\rho_c(\mathbf{r}_0)|\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v})|^2}{|\mathbf{r}_0 - \mathbf{r}_i|}\, \mathrm{d}\mathbf{r}_0 \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{n_v} \\
&- \sum_{i=1}^{n_c} \sum_{j=1}^{n_v} \int_{\mathbb{R}^{3n_v+3}} \frac{\phi_i(\mathbf{r}_0)\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_N)\phi_i(\mathbf{r}_1)\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{j-1}, \mathbf{r}_0, \mathbf{r}_{j+1}, \ldots, \mathbf{r}_{n_v})}{|\mathbf{r}_0 - \mathbf{r}_j|}\, \mathrm{d}\mathbf{r}_0 \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{n_v}.
\end{aligned}$$

The proof of this theorem is divided into several lemmas.

Lemma A.3. *Let $\Psi \in V^{\mathrm{FC}}$. Then*

$$\left\langle \Psi \middle| -\frac{1}{2} \sum_{i=1}^{N} \Delta_i \middle| \Psi \right\rangle = \frac{1}{2} \sum_{i=1}^{n_c} \|\nabla \phi_i\|^2_{L^2(\mathbb{R}^3)} + \frac{1}{2} \int_{\mathbb{R}^{3n_v}} |\nabla \Phi_v|^2,$$

and

$$\left\langle \Psi \middle| - \sum_{i=1}^{N} \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \middle| \Psi \right\rangle = \int_{\mathbb{R}^3} - \sum_{I=1}^{N_{\mathrm{at}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \rho_c(\mathbf{r})\, \mathrm{d}\mathbf{r} - \sum_{i=1}^{n_v} \sum_{I=1}^{N_{\mathrm{at}}} \int_{\mathbb{R}^{3n_v}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} |\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v})|^2\, \mathrm{d}\mathbf{r}_1 \ldots \mathbf{r}_{n_v}.$$

Proof. We only prove the first assertion of this lemma since the proof of the second identity is similar.

We have

$$\left\langle \Psi | -\frac{1}{2}\sum_{i=1}^{N}\Delta_i|\Psi \right\rangle = \frac{1}{N!n_v!}\sum_{\sigma\in\mathcal{S}_N}\sum_{\sigma'\in\mathcal{S}_N}(-1)^{\sigma+\sigma'}\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma(i)})\Phi_v(\mathbf{r}_{\sigma(n_c+1)},\dots,\mathbf{r}_{\sigma(N)})| \right.$$
$$\left. -\frac{1}{2}\sum_{i=1}^{N}\Delta_i|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)},\dots,\mathbf{r}_{\sigma'(N)})\right\rangle. \quad \text{(A.7)}$$

The idea of the proof consists in counting the non-zero terms in the double sum over σ and σ' in (A.7). First, we can rewrite it as

$$\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma(i)})\ \Phi_v(\mathbf{r}_{\sigma(n_c+1)},\dots,\mathbf{r}_{\sigma(N)})| -\frac{1}{2}\sum_{i=1}^{N}\Delta_{\sigma(i)}|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)},\dots,\mathbf{r}_{\sigma'(N)})\right\rangle$$
$$= \left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1},\dots,\mathbf{r}_N)| -\frac{1}{2}\sum_{i=1}^{N}\Delta_i|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\tau(i)})\Phi_v(\mathbf{r}_{\tau(n_c+1)},\dots,\mathbf{r}_{\tau(N)})\right\rangle,$$

where $\tau=\sigma'\sigma^{-1}$.

If $\tau(i)\neq i$ for some $i=1,\dots,n_c$, by orthogonality of the core wave functions $(\phi_i)_{1\leq i\leq n_c}$ and the valence wave function Φ_v, the scalar product is equal to 0. Otherwise, we have

$$\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma(i)})\ \Phi_v(\mathbf{r}_{\sigma(n_c+1)},\dots,\mathbf{r}_{\sigma(N)})| -\frac{1}{2}\sum_{i=1}^{N}\Delta_i|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)},\dots,\mathbf{r}_{\sigma'(N)})\right\rangle$$
$$= \left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1},\dots,\mathbf{r}_N)| -\frac{1}{2}\sum_{i=1}^{N}\Delta_i|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{\tau(n_c+1)},\dots,\mathbf{r}_{\tau(N)})\right\rangle$$
$$= \sum_{j=1}^{N}\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1},\dots,\mathbf{r}_N)| -\frac{1}{2}\Delta_j|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{\tau(n_c+1)},\dots,\mathbf{r}_{\tau(N)})\right\rangle$$
$$= (-1)^{\sigma'-\sigma}\frac{1}{2}\sum_{j=1}^{n_c}\|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)} + (-1)^{\sigma'-\sigma}\frac{1}{2}\int_{\mathbb{R}^{3n_v}}|\nabla\Phi_v|^2,$$

where we have used that $\Phi_v(\mathbf{r}_{\tau(n_c+1)},\dots,\mathbf{r}_{\tau(N)})=(-1)^\tau\Phi_v(\mathbf{r}_{n_c+1},\dots,\mathbf{r}_N)$ and $(-1)^\tau=(-1)^{\sigma'-\sigma}$.

It remains to count the number of permutations yielding non-zero terms in (A.7): there are $N!$ permutations σ. σ' should be equal to σ on $[\![1,n_c]\!]$, hence there are $n_v!$ of them. □

We now turn to the two-body interactions.

Lemma A.4. *Let $\Psi \in V^{\mathrm{FC}}$. Then*

$$\left\langle \Psi \middle| \sum_{1\le i<j\le N} \frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \middle| \Psi \right\rangle = \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' - \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\left|\sum_{i=1}^{n_c}\phi_i(\mathbf{r})\phi_i(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$
$$+ \sum_{1\le i<j\le n_v}\int_{\mathbb{R}^{3n_v}} \frac{|\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\,\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v} + \sum_{i=1}^{n_v}\int_{\mathbb{R}^{3n_v+3}} \frac{\rho_c(\mathbf{r}_0)|\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{n_v})|^2}{|\mathbf{r}_0-\mathbf{r}_i|}\,\mathrm{d}\mathbf{r}_0\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v}$$
$$- \sum_{i=1}^{n_c}\sum_{j=1}^{n_v}\int_{\mathbb{R}^{3n_v+3}} \frac{\phi_i(\mathbf{r}_0)\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_N)\phi_i(\mathbf{r}_1)\Phi_v(\mathbf{r}_1,\dots,\mathbf{r}_{j-1},\mathbf{r}_0,\mathbf{r}_{j+1},\dots,\mathbf{r}_{n_v})}{|\mathbf{r}_0-\mathbf{r}_j|}\,\mathrm{d}\mathbf{r}_0\mathrm{d}\mathbf{r}_1\dots\mathrm{d}\mathbf{r}_{n_v},$$

where ρ_c is the core electronic density

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{n_c}|\phi_i(\mathbf{r})|^2.$$

Proof. The two-body interaction potential can be written

$$\sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} = \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

We have

$$\left\langle \Psi \middle| \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\middle|\Psi\right\rangle = \frac{1}{N!n_v!}\sum_{\sigma\in\mathcal{S}_N}\sum_{\sigma'\in\mathcal{S}_N}(-1)^{\sigma+\sigma'}\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma(i)})\Phi_v(\mathbf{r}_{\sigma(n_c+1)},\dots,\mathbf{r}_{\sigma(N)})\right|$$
$$\left.\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\left|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)},\dots,\mathbf{r}_{\sigma'(N)})\right\rangle\right. . \quad \text{(A.8)}$$

We count and compute the non-zero terms appearing in (A.8). This depends on the number of transpositions in $[\![1,n_c]\!]$.

First, we have

$$\left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma(i)})\Phi_v(\mathbf{r}_{\sigma(n_c+1)},\dots,\mathbf{r}_{\sigma(N)})\middle|\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\middle|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)},\dots,\mathbf{r}_{\sigma'(N)})\right\rangle$$
$$= \left\langle \prod_{i=1}^{n_c}\phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1},\dots,\mathbf{r}_N)\middle|\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\middle|\prod_{i=1}^{n_c}\phi_i(\mathbf{r}_{\tau(i)})\Phi_v(\mathbf{r}_{\tau(n_c+1)},\dots,\mathbf{r}_{\tau(N)})\right\rangle, \quad \text{(A.9)}$$

where $\tau = \sigma'\sigma^{-1}$.

If $\tau(i) = i$ on $[\![1, n_c]\!]$, then

$$\begin{aligned}
&\left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)})\Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \dots, \mathbf{r}_{\sigma(N)}) | \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)})\Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \dots, \mathbf{r}_{\sigma'(N)}) \right\rangle \\
&\quad = \frac{(-1)^\tau}{2} \left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_i) | \sum_{\substack{i,j=1 \\ i\neq j}}^{n_c} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_i) \right\rangle \\
&\qquad + (-1)^\tau \left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) | \sum_{\substack{1\leq i\leq n_c \\ n_c+1\leq j\leq N}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) \right\rangle \\
&\qquad + \frac{(-1)^\tau}{2} \left\langle \Phi_v | \sum_{\substack{i,j=n_c+1 \\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Phi_v \right\rangle \\
&\quad = \frac{(-1)^\tau}{2} \sum_{1\leq i\neq j\leq n_c} \left\langle \phi_i(\mathbf{r}_i)\phi_j(\mathbf{r}_j) | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \phi_i(\mathbf{r}_i)\phi_j(\mathbf{r}_j) \right\rangle \\
&\qquad + (-1)^\tau \sum_{\substack{1\leq i\leq n_c \\ n_c+1\leq j\leq N}} \left\langle \phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \phi_i(\mathbf{r}_i)\Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) \right\rangle \\
&\qquad + \frac{(-1)^\tau}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{n_v} \int_{\mathbb{R}^{3n_v}} \frac{|\Phi_v(\mathbf{r}_1, \dots, \mathbf{r}_{n_v})|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, \mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_{n_v} \\
&\quad = \frac{(-1)^\tau}{2} \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\sum_{1\leq i\neq j\leq n_c} |\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&\qquad + (-1)^\tau \sum_{j=1}^{n_v} \int_{\mathbb{R}^{3n_v+3}} \frac{\sum_{i=1}^{n_c} |\phi_i(\mathbf{r}_0)|^2 |\Phi_v(\mathbf{r}_1, \dots, \mathbf{r}_{n_v})|^2}{|\mathbf{r}_0 - \mathbf{r}_i|} \, \mathrm{d}\mathbf{r}_0 \dots \mathrm{d}\mathbf{r}_{n_v} \qquad \text{(A.10)} \\
&\qquad + \sum_{\substack{i,j=1 \\ i\neq j}}^{n_v} \frac{(-1)^\tau}{2} \int_{\mathbb{R}^{3n_v}} \frac{|\Phi_v(\mathbf{r}_1, \dots, \mathbf{r}_{n_v})|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, \mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_{n_v}.
\end{aligned}$$

There $N!$ possible choices for σ and $n_v!$ permutations such that $\sigma = \sigma'$ on $[\![1, n_c]\!]$.

If in (A.9), there is exactly one integer $k \in [\![1, n_c]\!]$ such that $\tau(k) \neq k$, then $\tau(k) \in [\![n_c + 1, N]\!]$.

We denote by $m = \tau(k)$.

$$\left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \dots, \mathbf{r}_{\sigma(N)}) | \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)}) \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \dots, \mathbf{r}_{\sigma'(N)}) \right\rangle$$

$$= \left\langle \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i) \phi_k(\mathbf{r}_k) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) | \right.$$

$$\left. \frac{1}{2} \sum_{\substack{a,b=1 \\ a \neq b}}^{N} \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} | \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i) \phi_k(\mathbf{r}_m) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_{\tau(N)}) \right\rangle.$$

Then, we have

$$\left\langle \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i) \phi_k(\mathbf{r}_k) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) | \frac{1}{2} \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} | \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i) \phi_k(\mathbf{r}_m) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_{\tau(N)}) \right\rangle = 0,$$

- if both a and b are not equal to k because $\int_{\mathbb{R}^3} \phi_k(\mathbf{r}_k) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_{\tau(N)}) \ \mathrm{d}\mathbf{r}_k = 0$,
- or if $a = k$ and $b \in [\![1, n_c]\!]$, because $\int_{\mathbb{R}^3} \phi_k(\mathbf{r}_m) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_m, \dots, \mathbf{r}_{\tau(N)}) \ \mathrm{d}\mathbf{r}_m = 0$.

Thus

$$\left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)}) \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \dots, \mathbf{r}_{\sigma(N)}) | \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)}) \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \dots, \mathbf{r}_{\sigma'(N)}) \right\rangle$$

$$= \left\langle \phi_k(\mathbf{r}_k) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) | \sum_{j=n_c+1}^{N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|} | \phi_k(\mathbf{r}_m) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_{\tau(N)}) \right\rangle$$

$$= (-1)^{\tau-1} \left\langle \phi_k(\mathbf{r}_k) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_N) | \sum_{j=n_c+1}^{N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|} | \phi_k(\mathbf{r}_m) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_N) \right\rangle$$

$$= (-1)^{\tau-1} \sum_{j=1}^{n_v} \int_{\mathbb{R}^{3n_v}} \frac{\phi_k(\mathbf{r}_0) \Phi_v(\mathbf{r}_1, \dots, \mathbf{r}_{n_v}) \phi_k(\mathbf{r}_1) \Phi_v(\mathbf{r}_0, \mathbf{r}_2, \dots, \mathbf{r}_{n_v})}{|\mathbf{r}_0 - \mathbf{r}_j|} \mathrm{d}\mathbf{r}_0 \dots \mathrm{d}\mathbf{r}_{n_v}. \tag{A.11}$$

It remains to count the number of such terms appearing in (A.8). There are $N!$ choices possible for σ. For a fixed $k \in [\![1, n_c]\!]$, there are $n_v!$ permutations such that $\sigma'(k) \neq \sigma(k)$ and $\sigma'(i) = \sigma(i)$ for $i \in [\![1, n_c]\!]$, $i \neq k$.

If in (A.9), there are exactly two integers $(k, l) \in [\![1, n_c]\!]^2$ such that $\tau(k) \neq k$ and $\tau(l) \neq l$. If $\tau(k) \neq l$, then $\tau(k) \in [\![n_c + 1, N]\!]$ and the integral

$$\left\langle \phi_k(\mathbf{r}_k) \phi_l(\mathbf{r}_l) \Phi_v(\mathbf{r}_{n_c+1}, \dots, \mathbf{r}_{\tau(k)}, \dots, \mathbf{r}_N) | \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} | \phi_k(\mathbf{r}_{\tau(k)}) \phi_l(\mathbf{r}_{\tau(l)}) \Phi_v(\mathbf{r}_{\tau(n_c+1)}, \dots, \mathbf{r}_k, \dots, \mathbf{r}_{\tau(N)}) \right\rangle = 0,$$

for any $1 \leq a \neq b \leq N$.

Hence $1 \leq \tau(k), \tau(l) \leq n_c$ and so $\tau(k) = l$ and $\tau(l) = k$. Finally we obtain

$$\left\langle \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma(i)})\ \Phi_v(\mathbf{r}_{\sigma(n_c+1)}, \ldots, \mathbf{r}_{\sigma(N)}) | \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \prod_{i=1}^{n_c} \phi_i(\mathbf{r}_{\sigma'(i)}) \Phi_v(\mathbf{r}_{\sigma'(n_c+1)}, \ldots, \mathbf{r}_{\sigma'(N)}) \right\rangle$$
$$= \frac{(-1)^{\tau-1}}{2} \left\langle \phi_k(\mathbf{r}_k)\phi_l(\mathbf{r}_l) | \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} | \phi_k(\mathbf{r}_l)\phi_l(\mathbf{r}_k) \right\rangle. \tag{A.12}$$

There $N!$ possible choices for σ and for each $(k, l) \in [\![1, n_c]\!]^2, k \neq l$, there are $n_v!$ permutations σ' such that $\sigma(k) = \sigma'(l)$ and $\sigma(l) = \sigma'(k)$.

If there are more permutations in τ in (A.9), using the orthogonality of $(\phi_i)_{1 \leq i \leq n_c}$ and Φ_v, for any $1 \leq a \neq b \leq N$ we have

$$\left\langle \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i)\phi_k(\mathbf{r}_k)\Phi_v(\mathbf{r}_{n_c+1}, \ldots, \mathbf{r}_N) | \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} | \prod_{i=1, i\neq k}^{n_c} \phi_i(\mathbf{r}_i)\phi_k(\mathbf{r}_m)\Phi_v(\mathbf{r}_{\tau(n_c+1)}, \ldots, \mathbf{r}_k, \ldots, \mathbf{r}_{\tau(N)}) \right\rangle = 0.$$

By inserting (A.10), (A.11) and (A.12) in (A.8) and noticing that

$$\sum_{1 \leq i \neq j \leq n_c} |\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2 - \sum_{1 \leq i \neq j \leq n_c} \phi_i(\mathbf{r})\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\phi_j(\mathbf{r}')$$
$$= \sum_{i,j=1}^{n_c} |\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2 - \sum_{i,j=1}^{n_c} \phi_i(\mathbf{r})\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\phi_j(\mathbf{r}')$$
$$= \rho_c(\mathbf{r})\rho_c(\mathbf{r}') - \left| \sum_{i=1}^{n_c} \phi_i(\mathbf{r})\phi_i(\mathbf{r}') \right|^2,$$

we finish the proof of the lemma. □

In the frozen core approximation, the core orbitals $(\phi_i)_{1 \leq i \leq n_c}$ are fixed and the minimization is carried over the valence wave function Φ_v. The minimization problem thus becomes

$$E_v^{\mathrm{FC}} = \min_{\Phi_v \in V_{\mathrm{fc}}} \mathcal{E}_v^{\mathrm{FC}}(\phi_1, \ldots, \phi_c, \Phi_v), \tag{A.13}$$

where V_{fc} is

$$V_{\mathrm{fc}} = \left\{ \Phi_v \in \bigwedge_{i=1}^{n_v} L^2(\mathbb{R}^3),\ \|\Phi_v\|_{L^2(\mathbb{R}^{3n_v})} = 1,\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}_1)\Phi_v(\mathbf{r}_1, \ldots, \mathbf{r}_{n_v})\, \mathrm{d}\mathbf{r}_1 = 0,\ \forall\, 1 \leq i \leq n_c \right\}.$$

Theorem A.5. *Let $(\phi_i)_{1 \leq i \leq n_c} \in H^1(\mathbb{R}^3)$ and suppose the minimization problem (A.13) has a minimizer Φ_v. Then Φ_v satisfies the Euler-Lagrange equation*

$$H_v \Phi_v = E_v^{\mathrm{FC}} \Phi_v,$$

with

$$H_v = \sum_{j=1}^{n_v} \left(-\frac{1}{2}\Delta_j - \sum_{I=1}^{N_{\text{at}}} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|} + J_c(j) - K_c(j) \right) + \sum_{1 \le i < j \le n_v} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

$J_c(j)$ is the Coulomb operator with the core electrons

$$J_c(j)\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}) = \sum_{i=1}^{n_c} \int_{\mathbb{R}^3} \frac{|\phi_i(\mathbf{r}')|^2}{|\mathbf{r}_j - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \; \Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}),$$

and $K_c(j)$ the exchange operator with the core electrons

$$K_c(j)\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n_v}) = \sum_{i=1}^{n_c} \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}')\Phi_v(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{j-1}, \mathbf{r}', \mathbf{r}_{j+1}, \ldots, \mathbf{r}_{n_v})}{|\mathbf{r}_j - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \phi_i(\mathbf{r}_j).$$

Proof. The Euler-Lagrange equations are easily deduced from the minimization problem (A.13). □

APPENDIX B

FUNDAMENTAL FORMULA OF THE PAW METHOD

In this appendix, a proof of the formula for the PAW Hamiltonian (see Chapter 1):

$$(\mathrm{Id}+T)^* H (\mathrm{Id}+T)\widetilde{\psi} = H + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\langle \phi_i^I \, , H\phi_j^I \rangle - \left\langle \widetilde{\phi}_i^I \, , H\widetilde{\phi}_j^I \right\rangle \right) \langle \widetilde{p}_j^I, \cdot \rangle,$$

is given.

Recall that $T = \sum\limits_{I=1}^{N_{\mathrm{at}}} T_I$ where

$$T_I = \sum_{i=1}^{\infty} (\phi_i^I - \widetilde{\phi}_i^I) \langle \widetilde{p}_i^I, \cdot \rangle.$$

For each $I = 1, \ldots, N_{\mathrm{at}}$, the functions $(\phi_i^I)_{i\geq 1}, (\widetilde{\phi}_i^I)_{i\geq 1}$ and $(\widetilde{p}_i^I)_{i\geq 1}$ are such that:

1. outside $B(\mathbf{R}_I, r_c)$, $\widetilde{\phi}_i^I = \phi_i^I$ and $\widetilde{\phi}_i^I - \phi_i^I$ is C^1 at $S(\mathbf{R}_I, r_c)$;
2. $(\widetilde{\phi}_i^I)_{i\geq 1}$, $(\widetilde{p}_i)_{i\geq 1}$ are Riesz basis of $H^1(\mathbf{R}_I, r_c)$, *i.e.* for any $f \in H^1(B(\mathbf{R}_I, r_c))$:

$$f = \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, \widetilde{\phi}_i^I.$$

3. for all $i \geq 1$, $\widetilde{p}_i^I$ is supported in $B(\mathbf{R}_I, r_c)$.

Moreover the balls $B(\mathbf{R}_I, r_c)$, $I = 1, \ldots, N_{\mathrm{at}}$ are pairwise disjoint.

Proposition B.1. *Let $H = -\frac{1}{2}\Delta + V$ where V is a smooth, bounded multiplicative operator. Then*

$$(\mathrm{Id}+T)^* H (\mathrm{Id}+T)\widetilde{\psi} = H + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \widetilde{p}_i^I \left(\langle \phi_i^I \, , H\phi_j^I \rangle - \left\langle \widetilde{\phi}_i^I \, , H\widetilde{\phi}_j^I \right\rangle \right) \langle \widetilde{p}_j^I, \cdot \rangle,$$

Proof. We have

$$\begin{aligned}(\mathrm{Id}+T)^*H(\mathrm{Id}+T) =& H + T^*H + HT + T^*HT \\ =& H + \sum_{I=1}^{N_{\mathrm{at}}}(T_I^*H + HT_I) + \sum_{I,J=1}^{N_{\mathrm{at}}} T_I^*HT_J.\end{aligned}$$

Let $f, g \in H^1(\mathbb{R}^3)$. We have

$$\langle f\,, T_I^*HT_Jg\rangle = \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I\,, f\rangle\,(\phi_i^I - \widetilde{\phi}_i^I)\,, \sum_{i=1}^{\infty} \langle \widetilde{p}_i^J\,, g\rangle\, H(\phi_i^J - \widetilde{\phi}_i^J)\right\rangle.$$

The functions $\phi_i^I - \widetilde{\phi}_i^I$ and $\phi_i^J - \widetilde{\phi}_i^J$ are C^1 at the sphere $S(\mathbf{R}_I, r_c)$. Moreover they are supported respectively in $B(\mathbf{R}_I, r_c)$ and $B(\mathbf{R}_J, r_c)$ which are disjoint. Hence $\langle f\,, T_I^*HT_Jg\rangle = 0$. Thus

$$\begin{aligned}\langle f\,, (\mathrm{Id}+T)^*H(\mathrm{Id}+T)g\rangle &= \left\langle f + \sum_{I=1}^{N_{\mathrm{at}}} T_If\,, Hg + \sum_{I=1}^{N_{\mathrm{at}}} HT_Ig\right\rangle \\ &= \langle f\,, Hg\rangle + \sum_{I=1}^{N_{\mathrm{at}}}\left\langle \sum_{i=1}^{\infty}\langle \widetilde{p}_i^I\,, f\rangle\,(\phi_i^I - \widetilde{\phi}_i^I)\,, Hg\right\rangle \\ &\quad + \sum_{I=1}^{N_{\mathrm{at}}}\left\langle f\,, H\sum_{i=1}^{\infty}\langle \widetilde{p}_i^I\,, g\rangle\,(\phi_i^I - \widetilde{\phi}_i^I)\right\rangle \\ &\quad + \sum_{I=1}^{N_{\mathrm{at}}}\left\langle \sum_{i=1}^{\infty}\langle \widetilde{p}_i^I\,, f\rangle\,(\phi_i^I - \widetilde{\phi}_i^I)\,, \sum_{i=1}^{\infty}\langle \widetilde{p}_i^I\,, g\rangle\, H(\phi_i^I - \widetilde{\phi}_i^I)\right\rangle.\end{aligned}$$

Since $\phi_i^I - \widetilde{\phi}_i^I$ are supported in $B(\mathbf{R}_I, r_c)$, the integrals appearing above can be restricted to $B(\mathbf{R}_I, r_c)$. We denote by

$$\langle f\,, Hg\rangle_{I,r_c} = \int_{B(\mathbf{R}_I, r_c)} \frac{1}{2}\nabla f\cdot\nabla g + Vfg.$$

The integrals are restricted to the balls $B(\mathbf{R}_I, r_c)$, hence we can use that $f = \sum_{i=1}^{\infty}\langle \widetilde{p}_i^I\,, f\rangle\,\widetilde{\phi}_i^I$ and

$g = \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, \widetilde{\phi}_i^I$ in $B(\mathbf{R}_I, r_c)$. Thus, we have

$$\begin{aligned}
\langle f \, , (\mathrm{Id}+T)^* H (\mathrm{Id}+T) g \rangle &= \langle f \, , Hg \rangle + \sum_{I=1}^{N_{\mathrm{at}}} \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, \widetilde{\phi}_i^I \, , H \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, (\phi_i^I - \widetilde{\phi}_i^I) \right\rangle_{I,r_c} \\
&\quad + \sum_{I=1}^{N_{\mathrm{at}}} \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, (\phi_i^I - \widetilde{\phi}_i^I) \, , H \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, \widetilde{\phi}_i^I \right\rangle_{I,r_c} \\
&\quad + \sum_{I=1}^{N_{\mathrm{at}}} \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, (\phi_i^I - \widetilde{\phi}_i^I) \, , \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, H (\phi_i^I - \widetilde{\phi}_i^I) \right\rangle_{I,r_c} \\
&= \langle f \, , Hg \rangle + \sum_{I=1}^{N_{\mathrm{at}}} \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, \widetilde{\phi}_i^I \, , H \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, (\phi_i^I - \widetilde{\phi}_i^I) \right\rangle_{I,r_c} \\
&\quad + \sum_{I=1}^{N_{\mathrm{at}}} \left\langle \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , f \rangle \, (\phi_i^I - \widetilde{\phi}_i^I) \, , \sum_{i=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \, H \phi_i^I \right\rangle_{I,r_c} \\
&= \langle f \, , Hg \rangle + \sum_{I=1}^{N_{\mathrm{at}}} \sum_{i,j=1}^{\infty} \langle \widetilde{p}_i^I \, , g \rangle \left(\langle \phi_i^I \, , H \phi_j^I \rangle_{I,r_c} - \left\langle \widetilde{\phi}_i^I \, , H \widetilde{\phi}_j^I \right\rangle_{I,r_c} \right) \langle \widetilde{p}_j \, , f \rangle \, .
\end{aligned}$$

□

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Abstract

Cette thèse est consacrée à l'étude de la méthode PAW (projector augmented-wave) et d'une de ses modifications, baptisée méthode PAW variationnelle (VPAW), pour le calcul de l'état fondamental d'Hamiltoniens en géométrie périodique. Ces méthodes visent à améliorer la vitesse de convergence des méthodes d'ondes planes (ou méthodes de Fourier) en appliquant une transformation inversible au problème aux valeurs propres initial agissant au voisinage de chaque site atomique. Cette transformation permet de capter une partie des difficultés dues aux singularités coulombiennes. La méthode VPAW est analysée pour un opérateur de Schrödinger unidimensionnel avec des potentiels de Dirac. Les fonctions propres de ce modèle comprennent des sauts de dérivées similaires aux cusps électroniques. Le saut de dérivée des fonctions propres du problème aux valeurs propres issu de la méthode VPAW est réduit de façon importante. Cela entraîne une accélération de convergence en ondes planes du calcul des valeurs propres corroborée par une étude numérique. Une étude de la méthode VPAW est conduite pour des Hamiltoniens 3D périodiques avec des singularités coulombiennes, parvenant à des conclusions similaires. Pour la méthode PAW, la transformation inversible comporte des sommes infinies qui sont tronquées en pratique. Ceci introduit une erreur, qui est rarement quantifiée en pratique. Elle est analysée dans le cas de l'opérateur de Schrödinger unidimensionnel avec des potentiels de Dirac. Des bornes sur la plus basse valeur propre en fonction des paramètres PAW sont prouvées conformes aux tests numériques.

Keywords: quantum chemistry, eigenvalue problems, plane-waves discretization, projector augmented-wave method

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Abstract

This thesis is devoted to the study of the PAW method (projector augmented-wave) and of a variant called the variational PAW method (VPAW). These methods aim to accelerate the convergence of plane-wave methods in electronic structure calculations. They rely on an invertible transformation applied to the eigenvalue problem, which acts in a neighborhood of each atomic site. The transformation captures some difficulties caused by the Coulomb singularities. The VPAW method is applied to a periodic one-dimensional Schrödinger operator with Dirac potentials and analyzed in this setting. Eigenfunctions of this model have derivative jumps similar to the electronic cusps. The derivative jumps of eigenfunctions of the VPAW eigenvalue problem are significantly reduced. Hence, a smaller plane-wave cut-off is required for a given accuracy level. The study of the VPAW method is also carried out for 3D periodic Hamiltonians with Coulomb singularities yielding similar results. In the PAW method, the invertible transformation has infinite sums that are truncated in practice. The induced error is analyzed in the case of the periodic one-dimensional Schrödinger operator with Dirac potentials. Error bounds on the lowest eigenvalue are proved depending on the PAW parameters.

Keywords: quantum chemistry, eigenvalue problems, plane-waves discretization, projector augmented-wave method

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