Contents lists available at ScienceDirect

C. R. Acad. Sci. Paris, Ser. I

www.sciencedirect.com

Partial differential equations/Numerical analysis

Variational projector augmented-wave method

La méthode VPAW

Xavier Blanc [a], Éric Cancès [b], Mi-Song Dupuy [a]

[a] *Université Paris-Diderot, Sorbonne Paris Cité, Laboratoire Jacques-Louis-Lions, UMR 7598, UPMC, CNRS, 75205 Paris, France*
[b] *CERMICS, École des ponts and Inria Paris, 6 & 8, avenue Blaise-Pascal, 77455 Marne-la-Vallée, France*

A R T I C L E   I N F O

A B S T R A C T

In Kohn–Sham electronic structure computations, wave functions have singularities at nuclear positions. Because of these singularities, plane wave expansions give a poor approximation of the eigenfunctions. The PAW (projector augmented-wave) method circumvents this issue by replacing the original eigenvalue problem by a new one with the same eigenvalues, but smoother eigenvectors. Here a slightly different method, called VPAW (variational PAW), is proposed and analyzed. This new method allows for a better convergence with respect to the number of plane waves. Some numerical results on an idealized case corroborate this efficiency.

© 2017 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

R É S U M É

Dans les calculs de structure électronique de type Kohn–Sham, les fonctions d'ondes présentent des singularités aux positions des noyaux. Ces singularités empêchent une bonne approximation de la fonction par des ondes planes. La méthode PAW (*projector augmented-wave*) vise à contourner cette difficulté en remplaçant le problème aux valeurs propres d'origine par un autre ayant les mêmes valeurs propres, mais des vecteurs propres plus réguliers. Nous proposons et analysons une implémentation différente de cette méthode, baptisée VPAW (*variational PAW*). Elle permet d'obtenir une meilleure convergence en nombre d'ondes planes. Quelques résultats numériques sur un cas idéalisé confirment son efficacité.

© 2017 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

0. Introduction

Electronic structure calculations for solid-state physics and materials science are usually performed using the Kohn–Sham (KS) model in a periodic supercell, together with plane wave (*i.e.* Fourier spectral) discretization method. The KS Hamiltonian is a Schrödinger operator with Coulomb singularities at the nuclei. Therefore, the occupied KS orbitals, referred to as wave functions in the following, exhibit cusps. This universal behavior was first explained mathematically by Kato ([7], see also

[4,5]). This considerably impedes the rate of convergence of a plane wave expansion. Pseudopotentials or the projector augmented-wave (PAW) [3] method must be used. The latter method consists in building an invertible operator that carries the cusp behavior information. A key ingredient in the analysis proposed by Blöchl in [3] is that this operator is constructed using a complete basis. The wave function is thus transformed into a pseudo-wave function that is smoother and can be efficiently expanded in plane waves. In practice, the aforementioned complete basis is truncated, introducing a numerical error, which is rarely analyzed. Nevertheless, because of its efficiency to produce accurate results, the PAW method has become a very popular tool and has been implemented in widely distributed plane-wave molecular codes (AbInit [11], VASP [8]).

The purpose of this note is to present a modification of the PAW method for which we can provide, for a 1D toy model, accurate theoretical estimates in excellent agreement with numerical tests. This method is variational and seems to be more accurate than the usual PAW method. We first briefly present the variational PAW (VPAW) method applied to KS equations in Section 1. Detailed expositions of the original PAW method can be found in [1,6,10]. In Section 2, 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 that is similar to the electronic wave function cusp. Furthermore, the eigenvalues and eigenfunctions are known analytically, so it is possible to compute exactly the error of the numerical method.

1. PAW vs VPAW methods

1.1. General setting

In order to simplify the formalism, we describe the PAW and VPAW methods for finite molecular systems in $\mathbb{R}^3$. The periodic setting will be presented in [2]. The KS equations are (here, N_{at} is the number of atoms, n the number of electrons, Z_I, R_I the charge and position of the I-th nucleus):

$$H\psi_k = E_k\psi_k, \quad E_1 \leq E_2 \leq E_3 \leq \ldots, \quad \int_{\mathbb{R}^3} \psi_k\psi_l = \delta_{kl},$$

with

$$H = -\frac{1}{2}\Delta - \sum_{I=1}^{N_{\text{at}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \left(\rho \star \frac{1}{|\cdot|}\right)(\mathbf{r}) + V_{\text{xc}}[\rho](\mathbf{r}), \quad \rho(\mathbf{r}) = \sum_{k=1}^{n} |\psi_k(\mathbf{r})|^2,$$

where ρ is the ground-state electronic density and V_{xc} the exchange-correlation potential.

Following the idea of the PAW method, an invertible transformation $(\text{Id} + T)$ is applied to the eigenvalue problem, where T is the sum of operators T_I acting locally around each nucleus. To build the operator T_I, the atomic KS eigenvalue problem is solved:

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

with

$$H_I = -\frac{1}{2}\Delta - \frac{Z_I}{|\mathbf{r}|} + \left(\rho_I \star \frac{1}{|\cdot|}\right)(\mathbf{r}) + V_{\text{xc}}[\rho_I](\mathbf{r}), \quad \rho_I(\mathbf{r}) = \sum_{k=1}^{Z_I} \left|\phi_k^I(\mathbf{r})\right|^2.$$

The pseudo wave functions $(\widetilde{\phi}_k^I)_{1 \leq k \leq N_I}$, with $N_I \leq Z_I$, are defined such that:

(i) for $|\mathbf{r}| \geq r_c$, $\widetilde{\phi}_k^I(\mathbf{r}) = \phi_k^I(\mathbf{r})$;
(ii) for $|\mathbf{r}| < r_c$, $\widetilde{\phi}_k^I$ is smooth and matches ϕ_k^I and several of its derivatives on the sphere $\{|\mathbf{r}| = r_c\}$.

The parameter r_c is called the cut-off radius and is chosen such that balls of radius r_c at two different nuclei do not intersect. Finally, we define the projector functions $(\tilde{p}_k^I)_{1 \leq k \leq N_I}$:

(i) the projector functions are supported in $B(0, r_c)$,
(ii) they form a dual family to the pseudo wave functions: $\langle \tilde{p}_k^I, \widetilde{\phi}_{k'}^I \rangle = \delta_{kk'}$.

The operator T_I is then defined by:

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

By our choice of the pseudo wave functions $\widetilde{\phi}_k^I$ and of the projectors $\tilde{p}_k^I$, T_I acts locally in the ball $B(\mathbf{R}_I, r_c)$.

The VPAW equations to solve are then:

$$\widetilde{H}\tilde{\psi} = E\widetilde{S}\tilde{\psi},$$

where $\widetilde{H} = (\mathrm{Id} + T)^* H (\mathrm{Id} + T)$, $\widetilde{S} = (\mathrm{Id} + T)^*(\mathrm{Id} + T)$ and $T = \sum_I T_I$. Thus, if $(\mathrm{Id} + T)$ is invertible, it is easy to recover the eigenfunctions of H by the formula $\psi = (\mathrm{Id} + T)\tilde{\psi}$, and the eigenvalues are identical. By construction, $(\mathrm{Id} + T_I)\tilde{\phi}_k^I = \phi_k^I$. So, if locally around each nucleus, the functions ψ "behave" like the atomic wave functions ϕ_k^I, we can hope that the cusp behavior of ψ is captured by the operator T. Thus $\tilde{\psi}$ is smoother than ψ and the plane-wave expansion of $\tilde{\psi}$ converges faster than the expansion of ψ.

The classical PAW equations solved in materials science codes are different. As in [3], the construction of T_I involves "complete" infinite sets of functions ϕ_k^I, $\tilde{\phi}_k^I$ and $\tilde{p}_k^I$, which yields the following PAW equations:

$$H^{\mathrm{PAW}}\tilde{\psi} = E\,S^{\mathrm{PAW}}\tilde{\psi},$$

with (S^{PAW} is obtained by replacing H by Id in the equation below):

$$H^{\mathrm{PAW}} = (\mathrm{Id} + T^*)H(\mathrm{Id} + T) = H + \sum_{I=1}^{N_{\mathrm{at}}}\sum_{i,j=1}^{\infty} \tilde{p}_i^I(\cdot - \mathbf{R}_I)$$
$$\left(\left\langle \phi_i^I(\cdot - \mathbf{R}_I), H\phi_j^I(\cdot - \mathbf{R}_I)\right\rangle - \left\langle \tilde{\phi}_i^I(\cdot - \mathbf{R}_I), H\tilde{\phi}_j^I(\cdot - \mathbf{R}_I)\right\rangle\right)\left\langle \tilde{p}_j^I(\cdot - \mathbf{R}_I), \bullet\right\rangle.$$

The double sums on i, j appearing in the operators H^{PAW} and S^{PAW} are then truncated and the so-obtained generalized eigenvalue problem is solved. Thus the identity $\psi = (\mathrm{Id} + T)\tilde{\psi}$ does not hold anymore and the eigenvalues of the truncated problem are different from the exact ones. In contrast, in VPAW, one uses a finite number of wave functions ϕ_i^I right from the beginning, avoiding truncation errors.

Remark 1. A further modification is used in practice. The expression of H^{PAW} is

$$H^{\mathrm{PAW}} = H_{\mathrm{ps}} + \sum_{I=1}^{N_{\mathrm{at}}}\sum_{i,j=1}^{N_I} \tilde{p}_i^I(\cdot - \mathbf{R}_I)\left(\left\langle \phi_i^I(\cdot - \mathbf{R}_I), H\phi_j^I(\cdot - \mathbf{R}_I)\right\rangle - \left\langle \tilde{\phi}_i^I(\cdot - \mathbf{R}_I), H_{\mathrm{ps}}\tilde{\phi}_j^I(\cdot - \mathbf{R}_I)\right\rangle\right)\left\langle \tilde{p}_j^I(\cdot - \mathbf{R}_I), \bullet\right\rangle,$$

where in H_{ps} the Coulomb potential is replaced by a smoother pseudopotential. In Fig. 1, the PAW simulations are done with this modification.

1.2. Computational complexity

A detailed analysis of the computational cost of the PAW method can be found in [9]: 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 $\widetilde{H}\tilde{\psi}$ and $\widetilde{S}\tilde{\psi}$ where $\tilde{\psi}$ is expanded in M plane waves. We will only focus on $\widetilde{H}\tilde{\psi}$ as the analysis $\widetilde{S}\tilde{\psi}$ is very similar. Let us split $\widetilde{H}$ into four terms:

$$\widetilde{H}\tilde{\psi} = H\tilde{\psi} + P D_H P^{\mathrm{T}}\tilde{\psi} + H\left(\Phi - \widetilde{\Phi}\right)P^{\mathrm{T}}\tilde{\psi} + P H\left(\Phi - \widetilde{\Phi}\right)^{\mathrm{T}}\tilde{\psi},$$

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 $H(\phi_i - \tilde{\phi}_i)$, and D_H is the $N \times N$ matrix $\langle \phi_i - \tilde{\phi}_i, H(\phi_j - \tilde{\phi}_j)\rangle$. Thus, the total numerical cost is of order $\mathcal{O}(MN + M\log M)$, which is the same as for the PAW method.

Notice that D_H depends self-consistently on $\tilde{\psi}$ so it has to be updated at each self-consistent iteration. This also applies to the matrix $H(\Phi - \widetilde{\Phi})$. This matrix 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 intermediate in the computation of $\tilde{\psi}$, which is well approximated by plane waves. Hence it is not clear whether a poor approximation of this term should imply a poor approximation of $\tilde{\psi}$.

2. The VPAW method for a one-dimensional model

2.1. A 1D periodic Schrödinger equation with double Dirac potential

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

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

where $0 < a < 1$, $Z_0, Z_a > 0$. The solutions to $H\psi_k = E_k\psi_k$ are known explicitly (see [2] for the details). Depending on the sign of E_k, the wave functions ψ_k are either a combination of plane waves or of real exponentials on each interval $[0, a]$ and $[a, 1]$, whose coefficients may be computed using the continuity and derivative jumps at 0 and a: $\psi'(0_+) - \psi'(0_-) = -Z_0\psi(0)$ and $\psi'(a_+) - \psi'(a_-) = -Z_a\psi(a)$.

2.2. The VPAW method

The core of the VPAW method is to solve the generalized eigenvalue problem:

$$(\mathrm{Id} + T)^* H (\mathrm{Id} + T)\tilde{\psi} = E(\mathrm{Id} + T)^*(\mathrm{Id} + T)\tilde{\psi}, \tag{3}$$

where $\mathrm{Id} + T$ is an invertible operator. Thus the sought eigenvalues are identical and it is straightforward to recover the actual eigenfunctions

$$\psi = (\mathrm{Id} + T)\tilde{\psi}. \tag{4}$$

T is the sum of two local operators T_0 and T_a acting near the atomic sites. To define T_0, we fix an integer $N_0 = N_a = \frac{N}{2}$ and a radius $0 < r_c < \min(\frac{a}{2}, \frac{1-a}{2})$ so that T_0 and T_a act on non-overlapping regions.

Let H_0 be the 1D-Schrödinger operator on $L^2_{\mathrm{per}}(0, 1)$ with form domain $H^1_{\mathrm{per}}(0, 1)$ defined by:

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

Each eigenfunction of this operator is either even or odd. The odd eigenfunctions are in fact $x \mapsto \sin(2\pi kx)$, $k \in \mathbb{N}^*$, which are smooth and do not need to be included in the VPAW treatment. In contrast, the even ones have a derivative jump at each $m \in \mathbb{Z}$. To construct T_0, we will only select the even eigenfunctions and denote them by ϕ_i. We define the pseudo wave functions $(\widetilde{\phi}_i)_{1 \leq i \leq N_0} \in (L^2_{\mathrm{per}}(0, 1))^{N_0}$ as follows:

(i) for $r_c \leq x \leq 1 - r_c$, $\widetilde{\phi}_i(x) = \phi_i(x)$;
(ii) for $|x| \leq r_c$, $\widetilde{\phi}_i$ is an even polynomial of degree $2d - 2$, $d \geq N_0$;
(iii) $\widetilde{\phi}_i$ is of class C^{d-1} at $\pm r_c$ i.e. $\widetilde{\phi}_i^{(k)}(\pm r_c) = \phi_i^{(k)}(\pm r_c)$ for $0 \leq k \leq d - 1$.

The projector functions $(\tilde{p}_i)_{1 \leq i \leq N_0}$ are obtained by an orthogonalization procedure on the functions $p_i(t) = \rho_{r_c}(t)\widetilde{\phi}_i(t)$, where ρ_{r_c} is a 1-periodic cut-off function with support in $\bigcup_{k\in\mathbb{Z}}[k - r_c, k + r_c]$, in order to satisfy the duality condition: $\langle \tilde{p}_i, \widetilde{\phi}_j \rangle := \int_0^1 \tilde{p}_i(x)\widetilde{\phi}_j(x)\,\mathrm{d}x = \delta_{ij}$. The matrix $(\langle p_i, \widetilde{\phi}_j \rangle)$ is the Gram matrix of the functions $\widetilde{\phi}_j$ for the weight ρ_{r_c} so the orthogonalization is possible if the family $(\widetilde{\phi}_i)_{1 \leq i \leq N_0}$ is free – thus necessarily $d \geq N_0$. The functions $\tilde{p}_i$ are obtained by inverting this Gram matrix.

The operators T_0 and T_a are then defined according to the formulas given in (1). In the VPAW method, the generalized eigenvalue problem (3) is solved by expanding $\tilde{\psi}$ in plane waves.

2.3. Main results

We know from (4) that

$$\tilde{\psi} = \psi - \sum_{i=1}^{N_0}(\phi_i - \tilde{\phi}_i)\langle \tilde{p}_i, \tilde{\psi} \rangle - \sum_{i=1}^{N_a}(\phi_i^a - \tilde{\phi}_i^a)\langle \tilde{p}_i^a, \tilde{\psi} \rangle.$$

So $\tilde{\psi}$ is a piecewise smooth function with singularities at points of $\mathbb{Z}$, $\mathbb{Z} \pm r_c$, $\mathbb{Z} + a$ and $\mathbb{Z} + a \pm r_c$. Since $\tilde{\psi}$ is smooth at any other point, these singularities drive the decay of the Fourier expansion. Thus to study the Fourier convergence rate, it suffices to study the dependency of the different singularities with respect to $N_0 = N_a$, d and r_c. Proofs of the following estimates will be given in [2].

Proposition 2.1 (derivative jumps at 0). There exists $C > 0$ independent of r_c such that

$$\forall 0 \leq j \leq N_0 - 1, \left|\left[\tilde{\psi}^{(2j+1)}\right]_0\right| \leq Cr_c^{2N_0-2j} \text{ and } \forall j \geq N_0 \left|\left[\tilde{\psi}^{(2j+1)}\right]_0\right| \leq C.$$

Proposition 2.2 (d-th derivative jump at r_c). There exists $C > 0$ independent of r_c such that

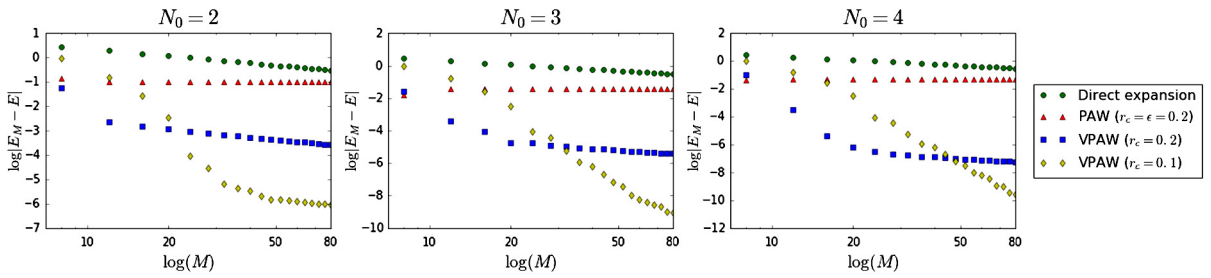$$\left|\left[\tilde{\psi}^{(d)}\right]_{r_c}\right| \leq \frac{C}{r_c^{d-1}}.$$

Fig. 1. Comparison of the PAW and VPAW methods ($d = 6$).
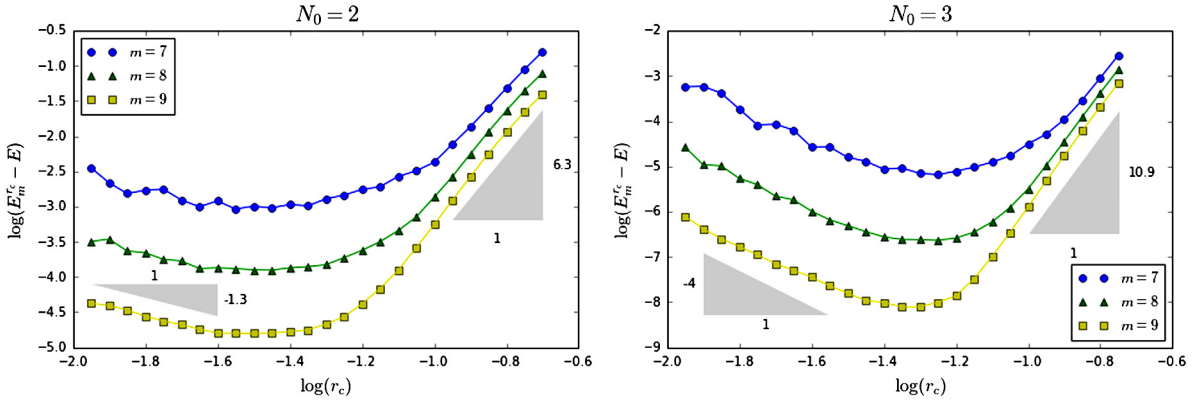

Fig. 2. Error on the 10th eigenvalue for different values of $M = 2^m$ ($d = N_0$).

Then, using classical estimates on eigenvalue approximations, we have the following theorems.

Theorem 2.3 (estimates on the Fourier coefficients). *Let $\widehat{\tilde{\psi}}_m$ be the m-th Fourier coefficient of $\tilde{\psi}$. There exists $C > 0$ independent of r_c and m such that*

$$\left| \widehat{\tilde{\psi}}_m \right| \leq C \left(\frac{r_c^{2N_0}}{m^2} + \frac{1}{r_c^{d-1}m^{d+1}} \right).$$

Theorem 2.4 (estimates on the eigenvalues). *Let E_M be an eigenvalue of the variational approximation* (3) *in a basis of M plane waves and E the corresponding exact eigenvalue. Then there exists a constant C independent of r_c and M such that*

$$0 < E_M - E \leq C \left(\frac{r_c^{4N_0}}{M} + \frac{1}{r_c^{2d-2}} \frac{1}{M^{2d-1}} \right). \tag{5}$$

The first term has the same decay in M as the brute force discretization of the problem with the original potential. However, the prefactor $r_c^{4N_0}$ can be made small by using a small cut-off radius r_c and/or a large N_0. Doing so, we introduce another error term that decays as M^{1-2d}, with a prefactor of order r_c^{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.

2.4. Numerical tests

All numerical simulations are carried out with $Z_0 = Z_a = 10$ and $a = 0.4$. For the PAW simulations, the Dirac potentials are replaced by a smooth mollifier $\chi_\epsilon \geq 0$ supported in $\bigcup_{k \in \mathbb{Z}}[k - \epsilon, k + \epsilon]$ such that the mass of χ_ϵ in $[-\epsilon, \epsilon]$ is one.

In Fig. 1, E is the lowest eigenvalue of the 1D-Schrödinger operator H. The PAW method quickly converges to a wrong eigenvalue. It is interesting to notice that, asymptotically, the VPAW convergence is of order $\mathcal{O}\left(\frac{1}{M}\right)$, but that, for small enough values of M and r_c, the second term in the RHS of (5) dominates.

In Fig. 2, the gaps between the slopes are close to the estimates given in Theorem 2.4 (around $0.3 \simeq \log(2)$ between the decreasing lines in both graphs and between the increasing lines, respectively $0.9 \simeq 3\log(2)$ for $N_0 = 2$ and $1.5 \simeq 5\log(2)$ for $N_0 = 3$). The slopes are also in good agreement with the theoretical estimates. More evidence will be provided in [2].

References

[1] C. Audouze, F. Jollet, M. Torrent, X. Gonze, Projector augmented-wave approach to density-functional perturbation theory, Phys. Rev. B 73 (23) (2006) 235101.
[2] X. Blanc, E. Cancès, M.-S. Dupuy, in preparation.
[3] P.E. Blochl, Projector augmented-wave method, Phys. Rev. B 50 (24) (1994) 17953–17979.
[4] S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, T.Ø. Sørensen, Sharp regularity results for coulombic many-electron wave functions, Commun. Math. Phys. 255 (2005) 183–227.
[5] E. Hunsicker, V. Nistor, J.O. Sofo, Analysis of periodic Schrödinger operators: regularity and approximation of eigenfunctions, J. Math. Phys. 49 (8) (2008) 083501.
[6] F. Jollet, M. Torrent, N. Holzwarth, Generation of projector augmented-wave atomic data: a 71 element validated table in the XML format, Comput. Phys. Commun. 185 (4) (2014) 1246–1254.
[7] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, Commun. Pure Appl. Math. 10 (2) (1957) 151–177.
[8] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (3) (1999) 1758–1775.
[9] A. Levitt, M. Torrent, Parallel eigensolvers in plane-wave density functional theory, Comput. Phys. Commun. 187 (2015) 98–105.
[10] C. Rostgaard, The projector augmented-wave method, arXiv preprint arXiv:0910.1921, 2009.
[11] M. Torrent, F. Jollet, F. Bottin, G. Zérah, X. Gonze, Implementation of the projector augmented-wave method in the ABINIT code: application to the study of iron under pressure, Comput. Mater. Sci. 42 (2) (2008) 337–351.