The variational projector augmented-wave method for periodic Hamiltonians with Coulomb potentials

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Figure: Silicon

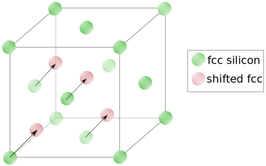


Figure: Silicon unit cell

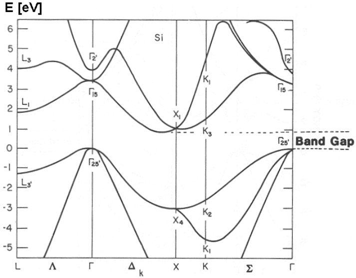


Figure: Silicon band diagram

Periodic Hamiltonian Consider real-valued V_{per} $\mathbb{Z}^3$-periodic function

$$H = -\Delta + V_{\mathrm{per}}, \text{ acting on } L^2(\mathbb{R}^3) \text{ with domain } H^2(\mathbb{R}^3)$$

By Bloch theory

$$\sigma(H) = \bigcup_{\mathbf{q}\in[-\pi,\pi)^3} \sigma(H_{\mathbf{q}}),$$

where $H_{\mathbf{q}}$ is acting on $L^2_{\mathrm{per}}([0,1)^3)$

$$H_{\mathbf{q}} = -|\nabla + i\mathbf{q}|^2 + V_{\mathrm{per}}, \quad \sigma(H_{\mathbf{q}}) = \{E_1 \leq E_2 \leq \cdots \to \infty\}$$

Goal

Solve

$$H_{\mathbf{q}}\psi_k = E_k\psi_k, \quad E_1 \leq E_2 \leq \dots$$

Periodic problem $\Rightarrow$ plane-wave discretization

Advantages

- orthonormal basis
- kinetic operator is diagonal
- Fast Fourier transform
- efficient preconditioner for iterative solvers

Plane-wave convergence rate = regularity of the eigenfunction

Potential $V_{\rm per}$: $V_{\rm per} = V_{\rm coul} + W_{\rm per}$ with $W_{\rm per}$ smooth, $\mathbb{Z}^3$-periodic function,

$$\begin{cases} -\Delta V_{\rm coul} = 4\pi \left(\sum_{\mathbf{T}\in\mathcal{R}} \sum_{I=1}^{N_{at}} Z_I (\delta_{\mathbf{R}_I+\mathbf{T}} - 1) \right) \\ V_{\rm coul} \text{ is } \mathcal{R}\text{-periodic.} \end{cases}$$

Regularity of the eigenfunctions

By Sobolev embedding $H^{3/2+\varepsilon}_{\rm per}([0,1)^3) \hookrightarrow C^0_{\rm per}([0,1)^3)$ for all $\varepsilon > 0$.

$\Rightarrow$ the potential $V_{\rm coul}$ has $H^{1/2-\varepsilon}_{\rm per}([0,1)^3)$ regularity

$\Rightarrow$ by elliptic regularity, an eigenfunction $\psi \in H^{5/2-\varepsilon}_{\rm per}([0,1)^3)$.

Convergence rate

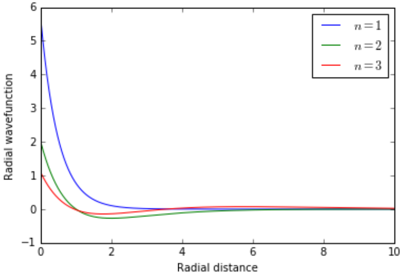
(ψ, E) an eigenpair, $M > 0$ plane-wave cutoff

$$\|\psi - \Pi_M \psi\|_{H^1} \leq \frac{C}{M^{3/2-\varepsilon}} \|\psi\|_{H^{5/2-\varepsilon}} \Rightarrow |E_M - E| \leq \frac{C}{M^{3-\varepsilon}}$$

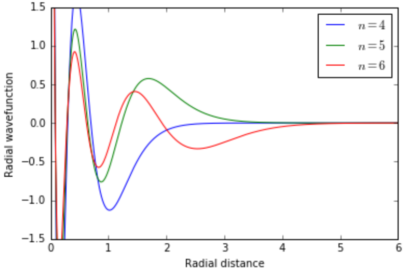
.

Main issues:

- cusp located at each nucleus.
- oscillations close to a nucleus of the valence electrons wave functions.



(a) Core states of the oxygen atom



(b) Valence states of the plutonium atom

⇒ Need a large plane-wave basis to solve accurately the eigenvalue problem

Different approaches to simplify the problem

- Muffin-tin methods: change the basis functions

$$\mathbf{r} \mapsto \begin{cases} \sum_{l,|m|\leq L} \alpha_{lm}\chi_l(|\mathbf{r}|) Y_m^l(\mathbf{r}) & \text{in a ball around each nucleus} \\ e^{i\mathbf{K}\cdot\mathbf{r}} & \text{otherwise} \end{cases}$$

  see Chen, Schneider M2AN (2015)

- Pseudopotentials: regularize the potential
  Instead of solving $(-\Delta + V_{\mathrm{per}})\psi = E\psi$, solve $(-\Delta + \mathcal{V})\widetilde{\psi} = \widetilde{E}\widetilde{\psi}$
  - $\mathcal{V}$ nonlocal, regular operator
  - $\widetilde{E}$ not equal to the original eigenvalue E

  see Cancès, Chakir, Maday M2AN (2012) and Cancès & Mourad, Commun. Math. Sci. (2017)

- PAW/VPAW method

The PAW method (Blöchl 94)

Idea:

- apply an invertible operator $(\mathrm{Id} + T)$ to $H\psi = E\psi$:

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

- expand $\widetilde{\psi}$ in plane-waves
  $\Rightarrow$ hope $\widetilde{\psi}$ is smoother than ψ.

Advantages

- actual wave function easily recovered : $\psi = (\mathrm{Id} + T)\widetilde{\psi}$
- compute the same eigenvalue

How to choose T ?

Remarks on the singularity

- ψ is smooth everywhere except at the positions of the nuclei
- Kato cusp condition: $\overline{\psi}$ spherical average around a singularity at $\mathbf{R}_I$ of charge Z_I:

$$\frac{\partial \overline{\psi}}{\partial r}(0) = -Z_I \psi(\mathbf{R}_I).$$

Universal condition !

Idea

- use atomic eigenfunctions ϕ_i to keep this information,
- want $(\mathrm{Id} + T)$ to map smooth functions $\widetilde{\phi}_i$ to atomic eigenfunctions ϕ_i: :

if $\psi \simeq \sum c_i \phi_i \Rightarrow \widetilde{\psi} = (\mathrm{Id} + T)^{-1}\psi \simeq (\mathrm{Id} + T)^{-1} \sum c_i \phi_i = \sum c_i \widetilde{\phi}_i.$

Construction of T

$$T = \sum_{I=1}^{N_{\mathrm{at}}} T_I,$$

T_I acting locally on each nucleus given by

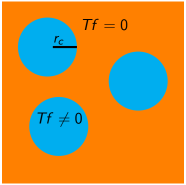


Figure: Unit cell with PAW balls in blue

$$T_I = \sum_{i=1}^{N_{\mathrm{paw}}} (\phi_i - \widetilde{\phi}_i)(\cdot - \mathbf{R}_I)\langle \widetilde{p}_i(\cdot - \mathbf{R}_I), \bullet \rangle$$

- variational PAW (VPAW) method:
  - $N_{\mathrm{paw}} < \infty$
  - keep the Coulomb singular potential
- PAW method:
  - $N_{\mathrm{paw}} = \infty$ and $(\widetilde{\phi}_i)$ basis of $L^2(B_{r_c})$
    Can elegantly rewrite the expression of the PAW Hamiltonian
    $\Rightarrow$ enable to introduce a pseudopotential in a consistent way
  - as $N_{\mathrm{paw}} = \infty$, in practice, need to truncate $\Rightarrow$ introduce an error

PAW/VPAW functions:

- ϕ_i eigenfunctions of an atomic Hamiltonian

$$\left(-\Delta - \frac{Z_I}{|\mathbf{r}|} + \rho_I \star \frac{1}{|\cdot|}\right)\phi_i = \epsilon_i \phi_i$$

- $\widetilde{\phi}_i = \phi_i$ outside a ball B_{r_c}, $\widetilde{\phi}_i$ smooth inside B_{r_c} and matches ϕ_i and some of its derivatives on the sphere $\{|\mathbf{r}| = r_c\}$
- $\widetilde{p}_i$ is smooth, $\mathrm{supp}(\widetilde{p}_i) \subset B_{r_c}$ and is a dual basis to the $\widetilde{\phi}_i$: $\langle \widetilde{p}_i | \widetilde{\phi}_j \rangle = \delta_{ij}$

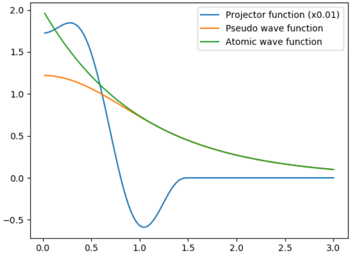


Figure: Plot of some PAW functions for $r_c = 1.5$

By definition:

$$(\mathrm{Id} + T_I)\widetilde{\phi}_i = \widetilde{\phi}_i + \sum_{j=1}^{N_{\mathrm{paw}}} \underbrace{\langle \widetilde{p}_j, \widetilde{\phi}_i \rangle}_{=\delta_{ij}} (\phi_j - \widetilde{\phi}_j) = \phi_i$$

Suppose $\psi = \sum_{j=1}^{N} c_j \phi_j$, for $N \in \mathbb{N}$, then

$$\widetilde{\psi} = (\mathrm{Id} + T)^{-1}\psi = (\mathrm{Id} + T)^{-1} \left(\sum_{j=1}^{N} c_j \phi_j \right) = \sum_{j=1}^{N} c_j \widetilde{\phi}_j$$

$\Rightarrow \widetilde{\psi}$ is smoother than ψ !

VPAW method for 3D linear Hamiltonians

Model Hamiltonian H acting on $L^2_{\rm per}([0,1)^3)$ and domain $H^2_{\rm per}([0,1)^3)$:

$$H = -\Delta + V_{\rm coul} + W_{\rm per},$$

where $W_{\rm per}$ is $\mathbb{Z}^3$-periodic and smooth and $V_{\rm coul}$ is given by

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

How do the eigenfunctions of H behave near a nucleus?

Weighted Sobolev space

Let $k \in \mathbb{N}$ and $\gamma \in \mathbb{R}$. We define the k-th weighted Sobolev space with index γ by:

$$\mathcal{K}^{k,\gamma}([0,1)^3) = \left\{ u \in L^2_{\mathrm{per}}([0,1)^3) : \varrho^{|\alpha|-\gamma} \partial^\alpha u \in L^2_{\mathrm{per}}([0,1)^3) \ \forall \ |\alpha| \leq k \right\},$$

ϱ nonnegative function s.t. $\forall I = 1, \dots, N_{\mathrm{at}}, \ \varrho(\mathbf{R}_I + \mathbf{r}) = |\mathbf{r}|$ for small $\mathbf{r}$.

Weighted Sobolev space with asymptotic type $\sum_{j \in \mathbb{N}} c_j(\hat{\mathbf{r}}) r^j$

$$\mathscr{K}^{k,\gamma}([0,1)^3) = \Bigg\{ u \in \mathcal{K}^{k,\gamma}([0,1)^3) \,\Bigg|\, \forall n \in \mathbb{N}, \, \eta_n \in \mathcal{K}^{k,\gamma+n+1}([0,1)^3),$$

$$\forall x \in [0,1)^3, \ \eta_n(x) = u(x) - \sum_{I=1}^{N_{\mathrm{at}}} \omega(|x - R_I|) \sum_{j=0}^{n} c_j^I(\widehat{x - R_I}) |x - R_I|^j \Bigg\},$$

where $c_j^I \in \mathrm{Span}(Y_{\ell m}, |m| \leq \ell \leq j)$

Theorem (Hunsicker, Nistor, Sofo (2008))

Let ψ be an eigenfunction of H and $\varepsilon > 0$. Then for all $n \in \mathbb{N}$:

$$\psi - \sum_{I=1}^{N_{\mathrm{at}}} \omega(|\mathbf{r} - \mathbf{R}_I|) \sum_{j=0}^{n} c_j^I(\widehat{\mathbf{r} - \mathbf{R}_I})|\mathbf{r} - \mathbf{R}_I|^j \in \mathcal{K}^{\infty, \frac{5}{2}+n-\varepsilon}([0,1)^3)$$

$$\subset H_{\mathrm{per}}^{\frac{5}{2}+n-\varepsilon}([0,1)^3),$$

with ω smooth, nonnegative cut-off function such that $\omega = 1$ near 0 and $\omega = 0$ outside some neighbourhood of 0 and $c_j \in \mathrm{span}(Y_{\ell m}, |m| \leq \ell \leq j)$.

For $n = 1$, for $\mathbf{r}$ sufficiently small,

$$\psi(\mathbf{r}) = \underbrace{\psi(0) + \sum_{m=-1}^{1} c_{1m} r Y_{1m}(\hat{\mathbf{r}})}_{\text{smooth}} + c_{00} r Y_{00}(\hat{\mathbf{r}}) + \underbrace{\eta(\mathbf{r})}_{\in H_{\mathrm{per}}^{\frac{7}{2}-\varepsilon}([0,1)^3)}$$

$$= -Z\psi(0)r + \widetilde{\eta}(\mathbf{r}), \quad \widetilde{\eta} \in H_{\mathrm{per}}^{\frac{7}{2}-\varepsilon}([0,1)^3).$$

The VPAW method

Parameters: r_c radius of PAW balls, N_{paw} number of PAW functions, d smoothness of the pseudo WF.

Atomic WF	$\phi_k(\mathbf{r}) = \phi_k(r)$	Cusp at 0
Pseudo WF	$\widetilde{\phi}(\mathbf{r}) = \widetilde{\phi}_k(r)$	d-th der. jump at $\{r = r_c\}$
Projector function	$\widetilde{p}_k(\mathbf{r}) = \widetilde{p}_k(r)$	Dual basis: $\langle \widetilde{p}_j, \widetilde{\phi}_k \rangle = \delta_{jk}$
VPAW transform	$T = \sum_{i=1}^{N_{\mathrm{paw}}} \langle \widetilde{p}_i, \bullet \rangle (\phi_i - \widetilde{\phi}_i)$	$\psi = (\mathrm{Id} + T)\widetilde{\psi}$

Decomposition of the VPAW wave function $\widetilde{\psi}$ near a nucleus

$$\widetilde{\psi} = \psi - \sum_{i=1}^{N_{\mathrm{paw}}} \langle \widetilde{p}_i, \widetilde{\psi} \rangle (\phi_i - \widetilde{\phi}_i) = -\omega Z \psi(0) r + \eta - \sum_{i=1}^{N_{\mathrm{paw}}} \langle \widetilde{p}_i, \widetilde{\psi} \rangle (\phi_i - \widetilde{\phi}_i)$$

$$= \omega \left(-Z\psi(0) r - \sum_{i=1}^{N_{\mathrm{paw}}} \langle \widetilde{p}_i, \widetilde{\psi} \rangle (\phi_i - \widetilde{\phi}_i) \right) + (1-\omega) \sum_{i=1}^{N_{\mathrm{paw}}} \langle \widetilde{p}_i, \widetilde{\psi} \rangle (\phi_i - \widetilde{\phi}_i) + \eta$$

Let $\widetilde{\psi}_{00}$ be the spherical average of $\widetilde{\psi}$: $\widetilde{\psi}_{00}(r) = \frac{1}{4\pi} \int_{S(0,1)} \widetilde{\psi}(\mathbf{r}) \, \mathrm{d}\hat{\mathbf{r}}$.

Proposition

For any $(c_k)_{1 \leq k \leq N_{\mathrm{paw}}} \in \mathbb{R}^{N_{\mathrm{paw}}}$,

$$\widetilde{\psi}'_{00}(0) = -Z \left(\psi(0) - \sum_{k=1}^{N_{\mathrm{paw}}} c_k \phi_k(0) - A^{-1} \langle \widetilde{\mathbf{p}}, \psi - \sum_{k=1}^{N_{\mathrm{paw}}} c_k \phi_k \rangle \cdot \mathbf{\Phi}(0) \right),$$

where $A = (\langle \widetilde{p}_i, \phi_j \rangle)_{1 \leq i,j \leq N_{\mathrm{paw}}}$, $\widetilde{\mathbf{p}} = (\widetilde{p}_1, \dots, \widetilde{p}_{N_{\mathrm{paw}}})^T$ *and* $\mathbf{\Phi}(0) = (\phi_1(0), \dots, \phi_{N_{\mathrm{paw}}}(0))^T$.

$\Rightarrow$ need to find the best set of coefficients (c_k): we can show

- there exists $(c_k)_{1 \leq k \leq N_{\mathrm{paw}}}$ such that $\|\psi_{00} - \sum_{k=1}^{N_{\mathrm{paw}}} c_k \phi_k\|_{L^2(0,r_c)} \leq C {r_c}^{1/2 + \min(2N_{\mathrm{paw}},5) - \varepsilon}$,
- for any $f \in L^2(B(0,r_c))$, $|A^{-1} \langle \mathbf{p}, f \rangle \cdot \mathbf{\Phi}(0)| \leq \frac{C}{{r_c}^{3/2}} \|f\|_{L^2(B(0,r_c))}$

Cusp reduction

There exists a constant C independent of r_c such that

$$\left|\widetilde{\psi}'_{00}(0)\right| \leq C {r_c}^{\min(2N_{\mathrm{paw}},5)-\varepsilon}$$

Remarks

- decreasing the cut-off radius r_c reduces the cusp
- cannot decrease the cut-off radius too much because of the d-th derivative jump

d-th derivative jump at the PAW sphere

There exists a positive constant C independent of r_c such that

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

VPAW method plane-wave convergence theorem

Theorem (M.D.)

Let E_M be an eigenvalue of the variational approximation of the VPAW eigenvalue problem in a plane-wave basis with wavenumber $|\mathbf{K}| \leq M$, with N_{paw} PAW functions with smoothness $d \geq N_{\mathrm{paw}}$ and cut-off radius r_c. Let E be the corresponding exact eigenvalue. There exists a constant $C > 0$ independent of r_c and M such that for all $\varepsilon > 0$, and for all $\frac{1}{M} < r_c < r_{\mathrm{min}}$:

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

For fixed plane-wave cut-off M, $d = 6$:

$$\text{Optimal } r_c : \; r_c = \frac{1}{M^{\frac{2d-4}{2\min(2N_{\mathrm{paw}},5)+2d-2}}} \Rightarrow E_M - E \leq \frac{C}{M^{\frac{59}{9}}} \text{ for } N_{\mathrm{paw}} = 2$$

For numerical tests:

$$H = -\frac{1}{2}\Delta - \frac{Z}{|\cdot - \frac{\mathbf{R}}{2}|} - \frac{Z}{|\cdot + \frac{\mathbf{R}}{2}|}, \text{ with p.b.c. on } \left[-\frac{L}{2}, \frac{L}{2}\right]^3.$$

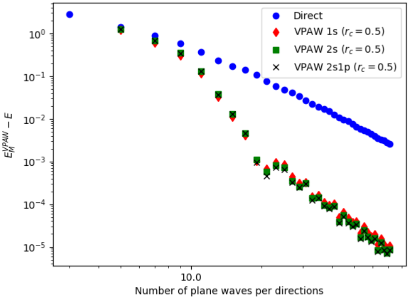


Figure: Error on the lowest eigenvalue against the number of plane-waves per direction ($Z = 3, R = 1, L = 5$)

Thank you for your attention!