Lecture on First-principles Computations (12): The Ultrasoft Pseudopotential and the Projector Augmented Wave (PAW) Methods

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Recall: Norm-conserving separable pseudopotential operators

Norm-conserving pseudopotential are intrinsically semilocal (SL)

$$\hat{V}_{SL} = V_{local}(r) + \sum_{lm} |Y_{lm}\rangle\, \delta V_l(r) \langle Y_{lm}|$$

Computationally inefficient!

Reference atomic pseudofunction

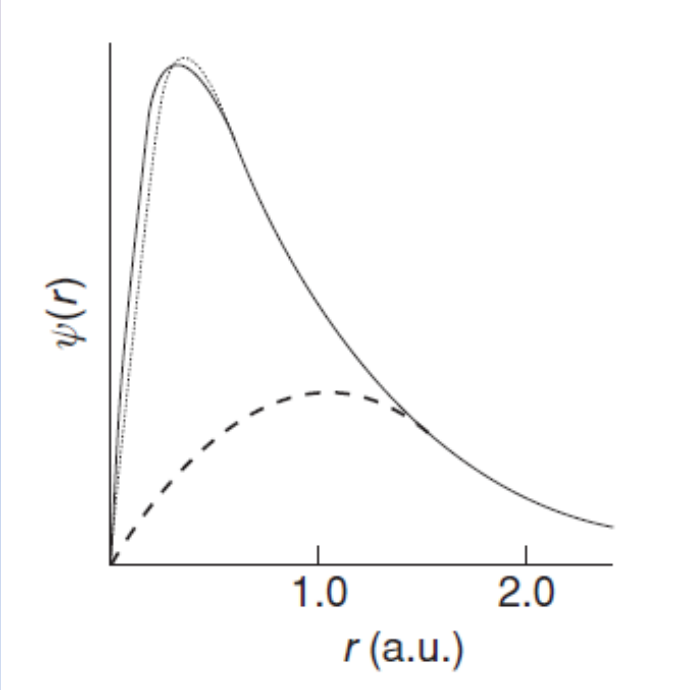
→ Nonlocal (NL) separable potential

$$\hat{V}_{\mathrm{NL}} = V_{local}(r) + \sum_{lm} \frac{\left|\psi^{\mathrm{PS}}_{lm}\delta V_l\right\rangle \left\langle \delta V_l \psi^{\mathrm{PS}}_{lm}\right|}{\langle \psi^{\mathrm{PS}}_{lm} \mid \delta V_l \mid \psi^{\mathrm{PS}}_{lm}\rangle}$$

$$\langle \psi_i \mid \delta\hat{V}_{\mathrm{NL}} \mid \psi_j\rangle = \sum_{lm} \frac{\langle \psi_i \mid \psi^{\mathrm{PS}}_{lm}\delta V_l\rangle\langle \delta V_l \psi^{\mathrm{PS}}_{lm} \mid \psi_j\rangle}{\langle \psi^{\mathrm{PS}}_{lm} \mid \delta V_l \mid \psi^{\mathrm{PS}}_{lm}\rangle}$$

Kleinman & Bylander (1982)

Problems with norm-conserving pseudopotentials



Norm-conserving pseudopotentials are still too "hard" for valence states at the beginning of an atomic shell: 2*p*, 3*d*, ...

Direct construction of non-local pseudopotential operator

$$\hat{H}^{\mathrm{PS}}\tilde{\psi}_{lm} = \epsilon_s \tilde{\psi}_{lm}$$

D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

$$\hat{H}^{\mathrm{PS}} = -\frac{1}{2m}\nabla^2 + V_{local} + \delta\hat{V}_{NL}$$

$$\chi_{lm}(\boldsymbol{r}) = \left[\epsilon_s - \left(-\frac{1}{2}\nabla^2 + V_{loal}(r)\right)\right]\tilde{\psi}_{lm}(\boldsymbol{r}) = [\delta\hat{V}_{NL}\tilde{\psi}_{lm}](\boldsymbol{r})$$

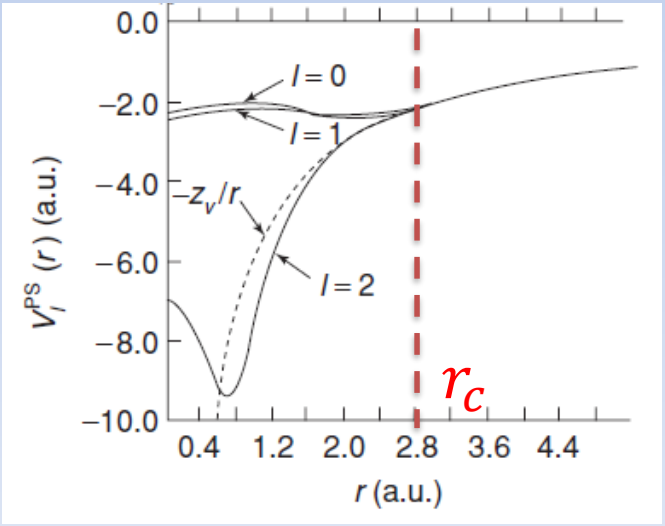
($\chi_{lm}(\mathbf{r})$ is restricted within r_c)

$$\Rightarrow \quad \delta\hat{V}_{NL} = \sum_{lm} \frac{|\chi_{lm}\rangle\langle\chi_{lm}|}{\langle\chi_{lm} \mid \tilde{\psi}_{lm}\rangle}$$

For more than one reference energy *s*, with given *l,m*

$$B_{s,s'} = \langle\tilde{\psi}_s \mid \chi_{s'}\rangle, \qquad \beta_s = \sum_{s'} B^{-1}_{s,s'}\chi_{s'}$$

$$\Rightarrow \quad \delta\hat{V}_{NL} = \sum_{lm}\left[\sum_{s,s'} B_{s,s'}|\beta_s\rangle\langle\beta_{s'}|\right]_{lm}$$



Vanderbilt Ultrasoft(US) pseudopotential

For a given angular momentum channel l, m

$$\left(-\frac{1}{2}\nabla^2 + V_{loal}\right)\left|\tilde{\psi}_s\right\rangle + \sum_{s',s''} B_{s',s''}\left|\beta_{s'}\right\rangle\langle\beta_{s''}\left|\tilde{\psi}_s\right\rangle = \epsilon_s\left|\tilde{\psi}_s\right\rangle$$

$$\Delta Q_{s,s'} = \int_0^{R_c} dr\, \Delta Q_{s,s'}(r)$$

$$\Delta Q_{s,s'}(r) = r^2\psi_s^*(r)\psi_{s'}(r) - r^2\tilde{\psi}_s^*(r)\tilde{\psi}_{s'}(r)$$

$$\delta\hat{V}_{\mathrm{NL}}^{\mathrm{US}} = \sum_{s,s'} D_{s,s'}\left|\beta_s\right\rangle\langle\beta_{s'}\right|$$

$$D_{s.s'} = B_{s,s'} + \epsilon_{s'}\Delta Q_{s,s'}, \qquad \hat{S} = \hat{\mathbf{1}} + \sum_{s,s'} \Delta Q_{s,s'}\left|\beta_s\right\rangle\langle\beta_{s'}\right|$$

(Generalized eigenvalue problem)

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{local}} + \delta\hat{V}_{\mathrm{NL}}^{\mathrm{US}}\right)\tilde{\psi}_s = \epsilon_s\hat{S}\tilde{\psi}_s$$

D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

Density and energy in the untrasoft pseudopotential framework.

Orthonormality relation: $\langle \tilde{\psi}_i \mid \hat{S} \mid \tilde{\psi}_{i'} \rangle = \delta_{i,i'}$

$$n_v(\mathbf{r}) = \sum_{i}^{occ} \mid \tilde{\psi}_i(\mathbf{r}) \mid^2 + \sum_{s,s'} \rho_{s,s'} \Delta Q_{s,s'}(\mathbf{r})$$

$$\rho_{s,s'} = \sum_{i}^{occ} \langle \tilde{\psi}_i \mid \beta_s \rangle \langle \beta_s{}' \mid \tilde{\psi}_i \rangle$$

$$E_0[n_v] = \sum_{i}^{occ} \left\langle \tilde{\psi}_i(\mathbf{r}) \right| -\frac{1}{2}\nabla^2 + V_{local}^{ion} + \sum_{s,s'} D_{s,s'}^{ion} \left| \beta_s \right\rangle \left\langle \beta_{s'} \right| \tilde{\psi}_i(\mathbf{r}) \rangle$$

$$+ E_{Hartree}[n_v] + E_{xc}[n_v]$$

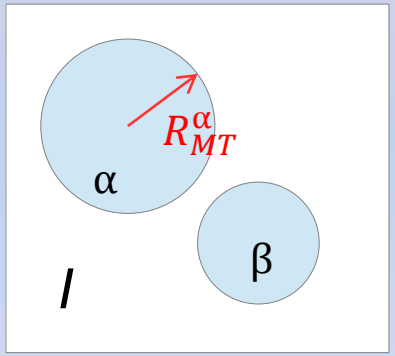
In practice $\Delta Q_{s,s'}(r)$ is pseudized and allows for treatment on a regular grid.

Recall: Linearized augmented plane wave

$$\chi_{\mathbf{k+G}}^{\mathrm{LAPW}}(\boldsymbol{r}) = \begin{cases} e^{i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{r}}, & \boldsymbol{r} \in I \\ \sum_L \left(A_{L\alpha}(\mathbf{k}+\mathbf{G})u_{l\alpha}(r,E_l) + B_{L\alpha}(\mathbf{k}+\mathbf{G})\dot{u}_{l\alpha}(r,E_l)\right) Y_L(\hat{\mathbf{r}}_{\boldsymbol{\alpha}}), & \boldsymbol{r} \in MT_\alpha \end{cases}$$

$$L = (lm)$$

$$\left[\frac{1}{2\mathrm{m}}\left(\frac{-d^2}{dr^2} + \frac{l(l+1)}{r^2}\right) + V_s(r) - E_l\right] r u_{l\alpha}(r,E_l) = 0$$



The concept of the projector augmented wave (PAW) method

OPW → Phillips-Kleinman pseudopotential :

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \tilde{\psi}_{n\boldsymbol{k}}(\boldsymbol{r}) - \sum_j \langle u_j \mid \tilde{\psi}_{n\boldsymbol{k}} \rangle \, u_j(\boldsymbol{r})$$

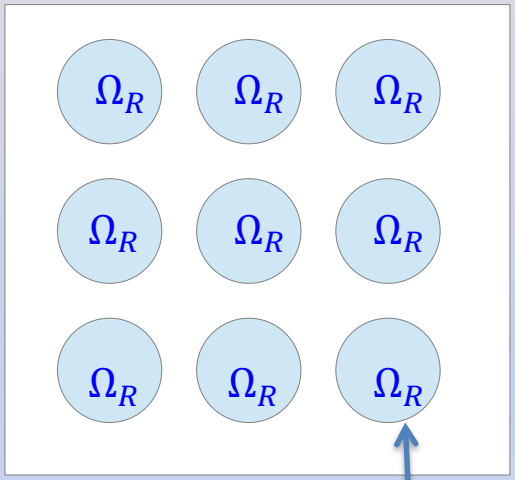
In general, we can write

$$|\psi\rangle = T\left|\tilde{\psi}\right\rangle$$

$$\langle A \rangle = \langle \psi \mid A \mid \psi \rangle = \langle \tilde{\psi} \mid T^\dagger A T \mid \tilde{\psi} \rangle$$

$$= \langle \tilde{\psi} \mid \tilde{A} \mid \tilde{\psi} \rangle$$

$$\tilde{A} = T^\dagger A T$$



A particular choice of T

$$T = 1 + \sum_{\boldsymbol{R}} T_R$$

T_R acts only within Ω_R around the atoms.

The transformation operator in the PAW method

P. Blöchl, Phys. Rev. B ***50****,17953 (1994)*

Within each Ω_R,

PS partial waves

$$|\phi_i\rangle = (1 + T_{\boldsymbol{R}})\,|\tilde{\phi}_i\rangle$$

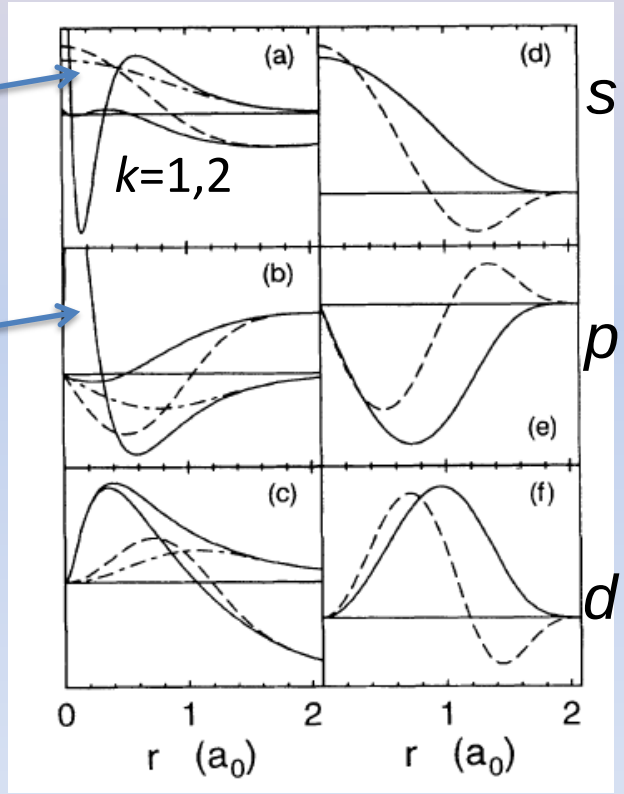
i=***R****, l, m, κ*

AE partial waves

$$|\psi> = \sum_i |\phi_i\rangle\, c_i \text{ within } \Omega_{\mathbf{R}}$$

$$|\tilde{\psi}> = \sum_i |\tilde{\phi}_i\rangle\, c_i \text{ within } \Omega_{\mathbf{R}}$$

Mn



The projector functions

$$|\psi> = |\tilde{\psi}> - \sum_i |\tilde{\phi}_i> c_i + \sum_i |\phi_i> c_i$$

Requiring T to be linear =>

$$c_j = \langle \tilde{p}_j \mid \tilde{\psi} \rangle$$

Projector functions

Within Ω_R $\quad \sum_i |\tilde{\phi}_i><\tilde{p}_i| = 1$

$$\langle \tilde{p}_i \mid \tilde{\phi}_j \rangle = \delta_{ij}$$

$$T = 1 + \sum_i \left(|\phi_i> - |\tilde{\phi}_i>\right) <\tilde{p}_i|$$

$\tilde{p}_i$ is the dual basis of $\tilde{\phi}_j$.

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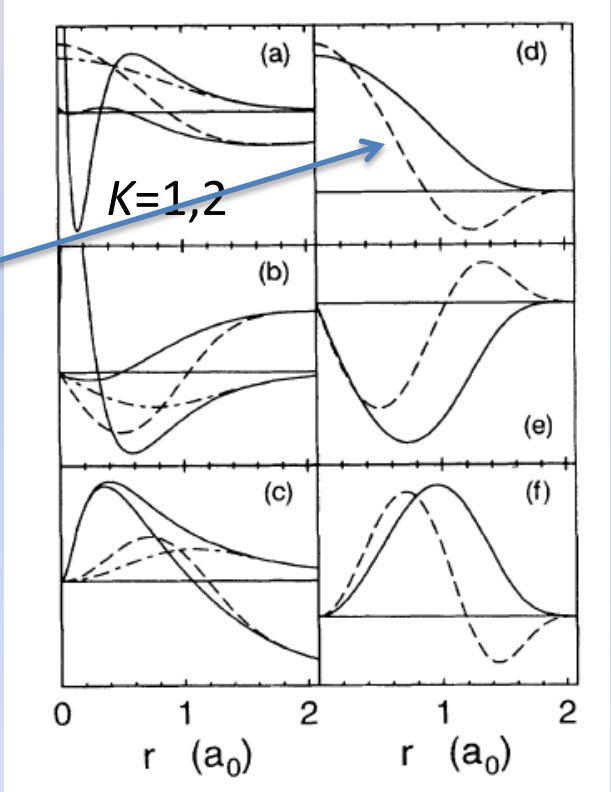


PAW: from PS wavefunction to all-electron (AE) wave function

One can restore the AE wave function from the PS wave function:

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle \tilde{p}_i|\tilde{\psi}\rangle$$

AE partial waves: $\phi_i(\boldsymbol{r}) = \phi_{ls}(|\,\boldsymbol{r}-\boldsymbol{R}\,|)Y_{lm}\left(\widehat{\boldsymbol{r}-\boldsymbol{R}}\right)$

Solution of the atomic Schrödinger equation for a set of energies

PS partial waves: $\tilde{\phi}_i(\mathbf{r}) = \tilde{\phi}_{ls}(|\,\boldsymbol{r}-\boldsymbol{R}\,|)Y_{lm}\left(\widehat{\boldsymbol{r}-\boldsymbol{R}}\right)$

Projector functions: $\langle \tilde{p}_i \mid \tilde{\phi}_j \rangle = \delta_{ij}$, localized within Ω_R

The core functions

$$|\psi^c> = |\tilde{\psi}^c> + |\phi^c> - |\tilde{\phi}^c>$$

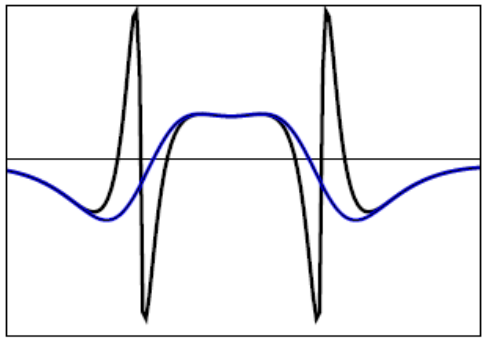
$$|\psi^c> = |\phi^c>$$

$$|\tilde{\psi}^c> = |\tilde{\phi}^c>$$

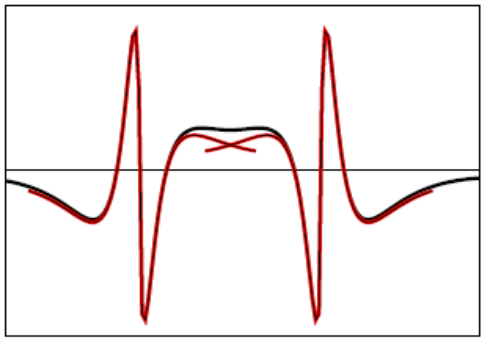
$c_i = 1$, no projector function is needed!

$|\phi^c>$ is imported from isolated atom calculations =>
frozen-core approximation

Example p-σ orbital of Cl_2

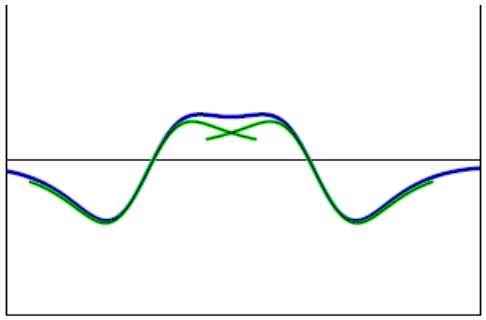


$|\Psi\rangle, |\tilde{\Psi}\rangle$

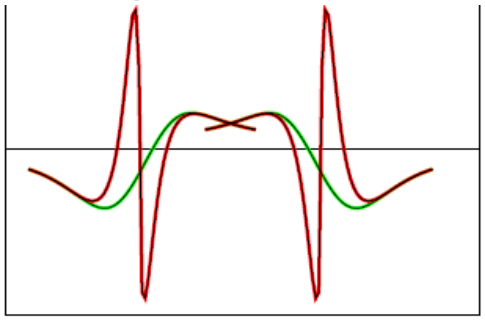


$|\Psi\rangle, |\Psi^1\rangle$

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{p}_i|\tilde{\Psi}\rangle$$

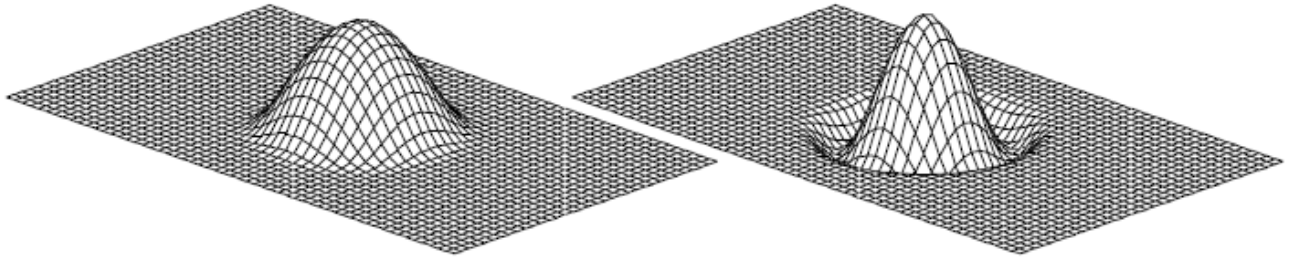


$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$

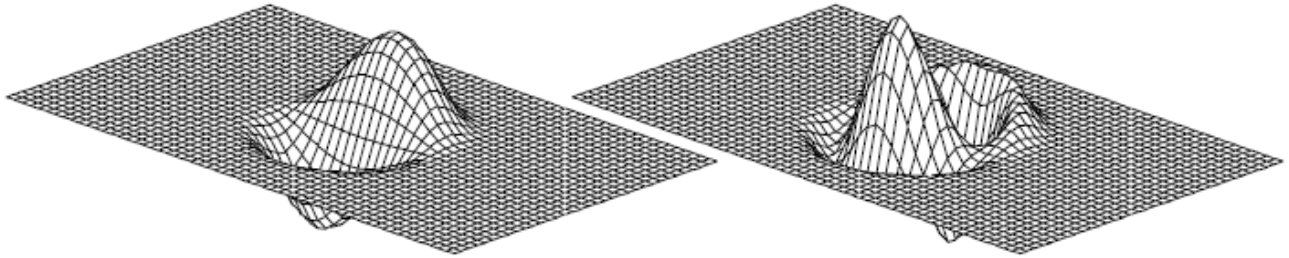


$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

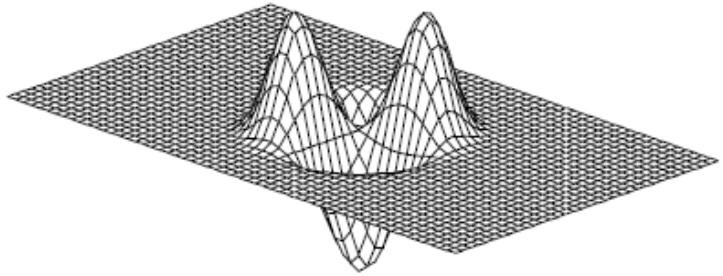
s-type projector functions



p-type projector functions



d-type projector function



The operators in the PAW method

$$\tilde{\mathrm{A}} = \mathrm{T}^{\dagger}\mathrm{A}\mathrm{T} = \mathrm{A} + \sum_{\mathrm{ij}} |\tilde{p}_i\rangle\left(\langle\phi_i \mid A \mid \phi_j\rangle - \langle\tilde{\phi}_i \mid A \mid \tilde{\phi}_j\rangle\right)\langle\tilde{p}_j|$$

$$\langle A\rangle = \sum_n \langle\psi_n \mid A \mid \psi_n\rangle = \sum_n \langle\tilde{\psi}_n \mid \tilde{A} \mid \tilde{\psi}_n\rangle$$

$$= \sum_{n\in v} \langle\tilde{\psi}_n \mid A \mid \tilde{\psi}_n\rangle + \sum_{ij} \rho_{ij}\left(\langle\phi_i \mid A \mid \phi_j\rangle - \langle\tilde{\phi}_i \mid A \mid \tilde{\phi}_j\rangle\right)$$

$$+ \sum_{n\in c} \langle\psi_n^c \mid A \mid \psi_n^c\rangle$$

$$\rho_{ij} = \sum_{n\in v} \langle\tilde{p}_i \mid \tilde{\psi}_n\rangle\langle\tilde{\psi}_n \mid \tilde{p}_j\rangle$$

Charge Density

$$n(\boldsymbol{r}) = \tilde{n}(\boldsymbol{r}) + n^1(\boldsymbol{r}) - \tilde{n}^1(\boldsymbol{r})$$

Occupation number

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \mid \tilde{\psi}_n(\mathbf{r}) \mid^2$$

$$n^1(\mathbf{r}) = \sum_{n,ij} f_n \, \rho_{ij} \phi_i(\mathbf{r}) \phi_j(\mathbf{r})$$

$$\tilde{n}^{\mathbf{1}}(\boldsymbol{r}) = \sum_{n,ij} f_n \, \rho_{ij} \tilde{\phi}_i^*(\mathbf{r}) \tilde{\phi}_{\boldsymbol{j}}(\mathbf{r})$$

The total energy

$$E = \tilde{E} + E^1 - \tilde{E}^1$$

Arbitrary potential localized in the augmentation region

$$\tilde{E} = \sum_n f_n \langle \tilde{\psi}_n \mid -\frac{1}{2\mathrm{m}} \nabla^2 \mid \tilde{\psi}_n \rangle + \int d^3 r \tilde{n} \bar{v}$$

$$+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{(\tilde{n} + \Delta n)(\tilde{n} + \Delta n)}{\mid \mathbf{r} - \mathbf{r}' \mid} + \int d^3 r \tilde{n} \epsilon_{xc}(\tilde{n})$$

Compensating charge

$$E^1 = \sum_{n,ij} f_n \rho_{ij} \langle \phi_i \mid -\frac{1}{2\mathrm{m}} \nabla^2 \mid \phi_j \rangle$$

$$+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{(n^1 + n^Z)(n^1 + n^Z)}{\mid \mathbf{r} - \mathbf{r}' \mid} + \int d^3 r n^1 \epsilon_{xc}(n^1)$$

Nuclear charge

$$\tilde{E}^1 = \sum_{n,ij} f_n \rho_{ij} \langle \tilde{\phi}_i \mid -\frac{1}{2\mathrm{m}} \nabla^2 \mid \tilde{\phi}_j \rangle + \int d^3 r \tilde{n}^1 \bar{v}$$

$$+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{(\tilde{n}^1 + \Delta n)(\tilde{n}^1 + \Delta n)}{\mid \mathbf{r} - \mathbf{r}' \mid} + \int d^3 r \tilde{n}^1 \epsilon_{xc}(\tilde{n}^1)$$

Feathers of the PAW method

- All-electron density and wave functions are accessible with a pseudopotential computational effort.
- Frozen-core approximation (can be overcome)
- Plane-wave convergence comparable to ultrasoft pseudopotentials
- Compared to the LAPW method, PAW offers a more general way of “augmentation” (projector functions)

Literature

Phys. Rev. B ***50****, 17953 (1994)*

Projector augmented-wave method

P. E. Blöchl
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland
(Received 13 June 1994; revised manuscript received 22 August 1994)

An approach for electronic structure calculations is described that generalizes both the pseudopotential method and the linear augmented-plane-wave (LAPW) method in a natural way. The method allows high-quality first-principles molecular-dynamics calculations to be performed using the original fictitious Lagrangian approach of Car and Parrinello. Like the LAPW method it can be used to treat first-row and transition-metal elements with affordable effort and provides access to the full wave function. The augmentation procedure is generalized in that partial-wave expansions are not determined by the value and the derivative of the envelope function at some muffin-tin radius, but rather by the overlap with localized projector functions. The pseudopotential approach based on generalized separable pseudopotentials can be regained by a simple approximation.

Literature

*Phys. Rev. B **59**, 1758 (1999)*

G. Kresse
Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10/136, A-1040 Wien, Austria

D. Joubert
Physics Department, University of the Witwatersrand, P.O. Wits 2050, Johannesburg, South Africa
(Received 6 July 1998)

The formal relationship between ultrasoft (US) Vanderbilt-type pseudopotentials and Blöchl's projector augmented wave (PAW) method is derived. It is shown that the total energy functional for US pseudopotentials can be obtained by linearization of two terms in a slightly modified PAW total energy functional. The Hamilton operator, the forces, and the stress tensor are derived for this modified PAW functional. A simple way to implement the PAW method in existing plane-wave codes supporting US pseudopotentials is pointed out. In addition, critical tests are presented to compare the accuracy and efficiency of the PAW and the US pseudopotential method with relaxed core all electron methods. These tests include small molecules (H_2, H_2O, Li_2, N_2, F_2, BF_3, SiF_4) and several bulk systems (diamond, Si, V, Li, Ca, CaF_2, Fe, Co, Ni). Particular attention is paid to the bulk properties and magnetic energies of Fe, Co, and Ni.
[S0163-1829(98)00848-0]

Computer code (www.vasp.at)