Essence of the Projector Augmented Wave (PAW) Method used in QMAS

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Outline of Lecture

1. Pseudo-Potentials and Projectors 1) & 2)
2. Transformation Theory: Wave Functions, Expectation Values and Charge Density Distribution 3) & 4)
3. Formulation of Total Energy: Kinetic Energy, Exchange-Correlation Energy, Hartree Energy and Compensation Charge 3) & 4)
4. Hamiltonian, Kohn-Sham Equation, and Atomic Forces 4)
5. Representation by Plane-Wave Basis Set
6. Stress Tensor by Nielsen-Matrin Scheme 5)
7. Efficient Scheme to Obtain Ground-State Electronic Structure

1) P.E. Blöchl, PRB 41 (1990) 5414,
2) D. Vanderbilt, PRB 41 (1990) 7892,
3) P.E. Blöchl, PRB 50 (1994) 17953,
4) G. Kresse and D. Joubert, PRB59 (1999) 1758,
5) O.H. Nielsen and R.M. Martin, PRB 32 (1985) 3780

Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Features of Projector Augmented Wave (PAW) Method

1. The PAW scheme was developed by combining ideas from pseudo-potential and all-electron FLAPW methods.
2. Accuracy corresponding to that of the FLAPW method within frozen core approximation is attained. True valence wave functions with true nodes near nuclei are obtained. Thus magnetic and optical properties are accurately dealt with.
3. Efficiency in plane-wave basis computations like USPP (Ultrasoft PP). Smooth pseudo wave functions are dealt with in actual SCF computations, where usual iterative algorithms can be utilized combined with FFT techniques. Atomic forces and stress tensors are easily obtained by solved wave functions and SCF potentials. Thus large-scale supercell computations can be performed.
4. Transferability of pseudo-potentials and projectors of each species is guaranteed as USPP, and the expectation values like charge density and total energy are given by transformation theory. Physical quantities inside the augmentation regions near nuclei are given via replacing the PS partial-wave expression by the AE partial-wave expression, computed on radial grid mesh, while those in the interstitial regions are given by usual pseudo-wave functions, computed on usual FFT mesh.

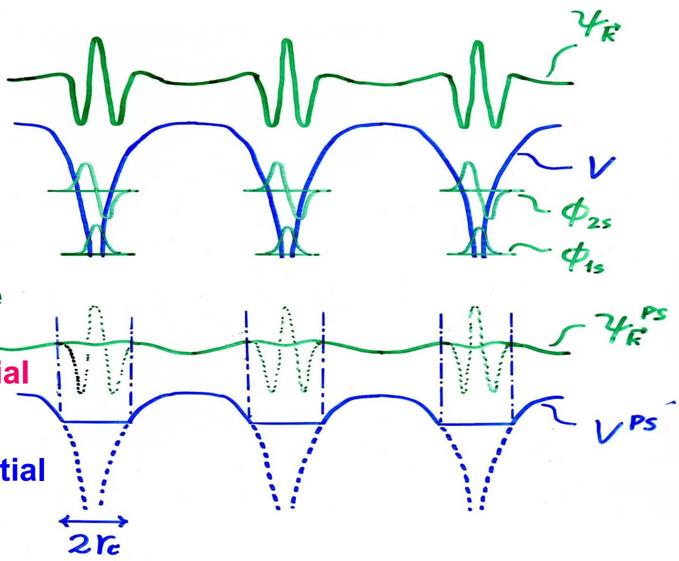
Wave Functions in Projector Augmented Wave (PAW) and Usual Pseudopotential Schemes

Valence Wave Functions in PAW Scheme

Core Wave Functions

Pseudo-Wave Functions in Pseudo-Potential Scheme

Pseudo-Potential



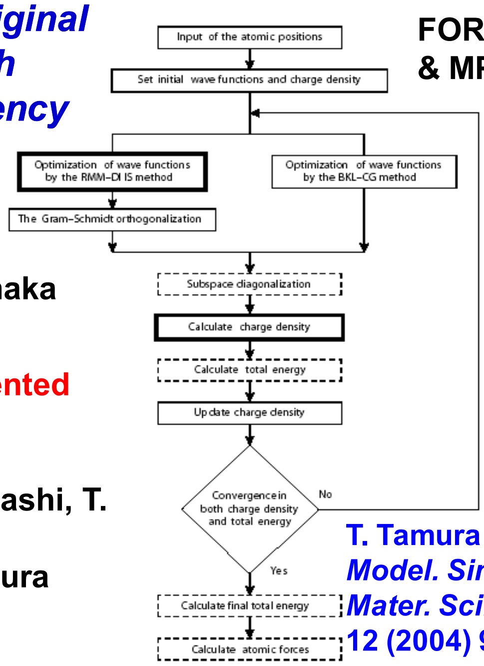
Development of Original Ab Initio Codes with High Parallel Efficiency

FORTRAN & MPI

Norm-Conserving PP Version "KAMIKAZE"

by M. Kohyama, S. Tanaka and T. Tamura (2001-)

PAW (Projector Augmented Wave) Version "QMAS (Qauntum MAterials Simulator)" by S. Ishibashi, T. Tamura, S. Tanaka, M. Kohyama and K. Terakura (2004-)



T. Tamura *et al., Model. Simul. Mater. Sci. Eng.* 12 (2004) 945

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Norm-Conserving Pseudo-Potential

$$(-\tfrac{1}{2}\Delta+\mathrm{v}_{\mathrm{AE}})\Psi_l(\vec{r})=\varepsilon_l\Psi_l(\vec{r}) \qquad \Psi_l(\vec{r})=\Phi_l(r)Y_{lm}(\hat{\Omega})$$

All-Electron (AE) Atomic KS Eq.

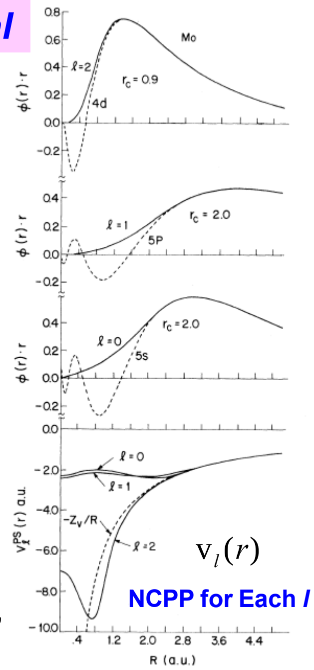
$$(-\tfrac{1}{2}\Delta+\mathrm{v}_l)\tilde{\Psi}_l(\vec{r})=\varepsilon_l\tilde{\Psi}_l(\vec{r}) \qquad \tilde{\Psi}_l(\vec{r})=\tilde{\Phi}_l(r)Y_{lm}(\hat{\Omega})$$

$$\tilde{\Phi}_l(r)=\Phi_l(r)\quad for\ \ r\ge r_c$$

$$\int_0^{r_c}|\tilde{\Phi}_l|^2 r^2dr=\int_0^{r_c}|\Phi_l|^2 r^2dr$$

$$\varepsilon=\varepsilon_l : correct\ energy$$

Construction of V_l so as to Generate Pseudo Atomic Wave Functions to Satisfy *the Norm-Conserving Conditions*



NCPP in Usual Semilocal Form

$$\mathrm{V}_{\mathrm{ps}}=\sum_l \mathrm{v}_l(r)\hat{P}_l=\mathrm{v}_{local}(r)+\sum_l\Delta\mathrm{v}_l(r)\hat{P}_l$$

$$\hat{P}_l=\sum_m|Y_{lm}(\hat{\Omega})><Y_{lm}(\hat{\Omega})|$$ Angular-Momentum Projection Operator

$$\Delta\mathrm{v}_l(r)=\mathrm{v}_l(r)-\mathrm{v}_{local}(r)$$

$\mathrm{v}_l(r)$ NCPP for Each *l*

Non-local PP, Zero for $r>r_c$

D.R. Hamann *et al.*, PRL43(1979)1494

Pseudo-Potentials (PP) & Projectors

Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

NCPP in Usual Semilocal Form

$$\mathrm{V}_{\mathrm{ps}}=\sum_l \mathrm{v}_l(r)\hat{P}_l=\mathrm{v}_{local}(r)+\sum_l\Delta\mathrm{v}_l(r)\hat{P}_l$$

$$\hat{P}_l=\sum_m|Y_{lm}(\hat{\Omega})><Y_{lm}(\hat{\Omega})|$$ Angular-Momentum Projection Operator

$\mathrm{v}_l(r)$ NCPP for Each *l* from Atomic Calculations

$$\Delta\mathrm{v}_l(r)=\mathrm{v}_l(r)-\mathrm{v}_{local}(r)$$

Non-local PP, Zero for $r>r_c$

v_{local} *Screened* Local PP

Kleinman-Bylander (KB) Separable Form of NCPP

$$\mathrm{V}_{\mathrm{ps}}=\mathrm{v}_{local}(r)+\sum_{lm}|Y_{lm}>\Delta\mathrm{v}_l(r)<Y_{lm}|$$

Kleinman & Bylander, PRL48(1982)1425

$$\approx\mathrm{v}_{local}(r)+\sum_{lm}|\Delta\mathrm{v}_l\tilde{\Phi}_lY_{lm}>(1/C_l)<\Delta\mathrm{v}_l\tilde{\Phi}_lY_{lm}|=\mathrm{V}_{\mathrm{ps}}^{\mathrm{KB}}$$

$$C_l=<\tilde{\Phi}_lY_{lm}|\Delta\mathrm{v}_l|\tilde{\Phi}_lY_{lm}>$$

Proof Inside the Atomic Region, the Pseudo Wave Function is Approximately Expressed as

$$\tilde{\Psi}(\vec{r})=\sum_{lm}A_{lm}\tilde{\Phi}_l(r)Y_{lm}(\hat{\Omega})$$

$\tilde{\Phi}_l(r)Y_{lm}(\hat{\Omega})$ Pseudo Atomic Wave Function for v_l

Thus

$$\mathrm{V}_{\mathrm{ps}}\tilde{\Psi}(\vec{r})=\mathrm{v}_{local}\tilde{\Psi}+\sum_{lm}A_{lm}\Delta\mathrm{v}_l(r)\tilde{\Phi}_l(r)Y_{lm}(\hat{\Omega})=\mathrm{V}_{\mathrm{ps}}^{\mathrm{KB}}\tilde{\Psi}(\vec{r})$$

Pseudo-Potentials (PP) & Projectors
Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

Generalized PP by PS Partial Waves with Selected Energy and Solved within r_c

AE Atomic KS Eq.

$$\{\phi_i\} \quad \phi_i = \Phi_l(r) Y_{lm}(\check{E})$$

$$(-\tfrac{1}{2}\Delta + v_{AE})\phi_i = \varepsilon_i \phi_i$$

AE Partial Waves Defined within r_c

Unbounded States can be Dealt with

$$\{\tilde{\phi}_i\} \quad \tilde{\phi}_i = \tilde{\Phi}_l(r) Y_{lm}(\check{E}) \quad (-\tfrac{1}{2}\Delta + v_{local} + v_i)\tilde{\phi}_i = \varepsilon_i \tilde{\phi}_i$$

Smooth PS Partial Waves without Nodes Defined within r_c

$$\tilde{\Phi}_l(r) = \Phi_l(r); \quad r \geq r_c$$

Smooth Connection between AE and PS Radial Functions

$$v_i = \Delta v_l = v_l - v_{local}$$

$$v_i \tilde{\phi}_i = \{\varepsilon_i - (-\tfrac{1}{2}\Delta + v_{local})\}\tilde{\phi}_i \qquad v_i \tilde{\phi}_i = v_i \tilde{\Phi}_l Y_{lm}$$

Role as Projector

$$V_{ps}^{KB} = v_{local}(r) + \sum_i | v_i \tilde{\phi}_i > (1/ < \tilde{\phi}_i \mid v_i \tilde{\phi}_i >) < v_i \tilde{\phi}_i |$$

Single Projector for Each *l* Hamann, PRB 40(1989) 2980

Pseudo-Potentials (PP) & Projectors
Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

Generalized Separable PP proposed by Blöchl

Blöchl, PRB 41(1990)5414

$$\{\phi_i\} \quad i = (l, \tau, m), \tau = 1,2$$

Multiple Projectors for Each l

$$\{\tilde{\phi}_i\} \quad \tilde{\phi}_i = \tilde{\Phi}_{l,\tau}(r) Y_{lm}(\check{E})$$

$$(-\tfrac{1}{2}\Delta + v_{local} + v_i)\tilde{\phi}_i = \varepsilon_i \tilde{\phi}_i$$

AE Partial and PS Partial Waves Defined within r_c

$$v_i \tilde{\phi}_i = \{\varepsilon_i - (-\tfrac{1}{2}\Delta + v_{local})\}\tilde{\phi}_i \qquad v_i = \Delta v_{l,\tau} = v_{l,\tau} - v_{local}$$

No Need to Determine V_i

$$v_i \tilde{\phi}_i = v_i \tilde{\Phi}_{l,\tau} Y_{lm} = \tilde{\chi}_i \qquad B_{ij} = < \tilde{\phi}_i \mid \tilde{\chi}_j >$$

Integration within r_c

$$\{\tilde{p}_i\} \quad \tilde{p}_i = \sum_j [B^{-1}]_{ji} \tilde{\chi}_j \qquad \tilde{\chi}_i = \sum_j [B]_{ji} \tilde{p}_j$$

Gram-Schmidt type Orthogonalization is also Possible

Dual $< \tilde{p}_i \mid \tilde{\phi}_j > = < \tilde{\phi}_i \mid \tilde{p}_j > = \delta_{ij}$

Construction of the Projector Dual to the Partial Waves

Completeness $\sum_i |\tilde{p}_i\rangle\langle\tilde{\phi}_i| = \sum_i |\tilde{\phi}_i\rangle\langle\tilde{p}_i| = 1$

$$V_{ps} = v_{local}(r) + \sum_{ij} |\tilde{p}_i > B_{ij} < \tilde{p}_j |$$

Generalized Separable PP

$$(-\tfrac{1}{2}\Delta + v_{local}(r) + \sum_{ij} |\tilde{p}_i > B_{ij} < \tilde{p}_j |)\tilde{\Psi} = \varepsilon \tilde{\Psi}$$

Pseudo-Potentials (PP) & Projectors

Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

$\{\phi_i\}\ \{\tilde{\phi}_i\}\ \{\tilde{p}_i\}$ **AE Partial Waves, PS Partial Waves and Projectors**

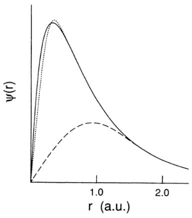
$$(-\tfrac{1}{2}\Delta + \mathrm{v}_{local} + \mathrm{v}_i)\tilde{\phi}_i = \varepsilon_i\tilde{\phi}_i$$

$$\mathrm{v}_i\tilde{\phi}_i = \{\varepsilon_i - (-\tfrac{1}{2}\Delta + \mathrm{v}_{local})\}\tilde{\phi}_i = \tilde{\chi}_i$$

$$B_{ij} = <\tilde{\phi}_i|\tilde{\chi}_j> \quad \tilde{p}_i = \sum_j [B^{-1}]_{ji}\tilde{\chi}_j \quad <\tilde{p}_i|\tilde{\phi}_j> = \delta_{ij}$$

$$(-\tfrac{1}{2}\Delta + \mathrm{v}_{local}(r) + \sum_{ij}|\tilde{p}_i > B_{ij} < \tilde{p}_j|)\tilde{\Psi} = \varepsilon\tilde{\Psi}$$

Generalized Separable NCPP: Set of Local PP and Projectors for Each Atom



Relaxation of the Norm-Conserving Condition ⇒ USPP by Vanderbilt

$$q_{ij} = <\phi_i|\phi_j> - <\tilde{\phi}_i|\tilde{\phi}_j> \qquad q_{ij} \neq 0$$

Integration within r_c

Vanderbilt, PRB41 (1990)7892

$$S = 1 + \sum_{ij} q_{ij}|\tilde{p}_i><\tilde{p}_j| \quad <\tilde{\Psi}|S|\tilde{\Psi}> = 1 \quad H\tilde{\Psi} = \varepsilon S\tilde{\Psi}$$

Generalized Eigenvalue Problem Including S

$$\{-\tfrac{1}{2}\Delta + \mathrm{v}_{local}(r) + \sum_{ij}(B_{ij} + \varepsilon_j q_{ij})|\tilde{p}_i><\tilde{p}_j|\}\tilde{\phi}_l = \varepsilon(1 + \sum_{ij} q_{ij}|\tilde{p}_i><\tilde{p}_j|)\tilde{\phi}_l$$

Eq. for Atomic Pseudo Wave Functions

Pseudo-Potentials (PP) & Projectors

Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

Transferability of NCPP: Scattering properties are reproduced with the Norm-Conserving Condition

$$2\pi\left[(r\varphi)^2\frac{d}{d\epsilon}\frac{d}{dr}\ln\varphi\right]_R = 4\pi\int_0^R \varphi^2 r^2\,dr.$$

Logarithmic derivative of the radial WF is accurate around ε_l

USPP: Violation of the Norm-Conserving Condition, Compensation Charge Recovers the Transferability

$$0 = \left(\frac{d}{d\varepsilon}\langle\phi_\varepsilon|T + V_{\mathrm{loc}} + V_{\mathrm{NL}} - \varepsilon S|\phi_\varepsilon\rangle_R\right)_{\varepsilon=\varepsilon_i}$$

Logarithmic derivative is accurate around ε_1 and ε_2

that

Q_{ii}: Compensation Charge

$$-\frac{1}{2}u_i^2\frac{d}{d\varepsilon}\frac{d}{dr}\ln u_\varepsilon(r)\Big|_R = \langle\phi_i|\phi_i\rangle_R + Q_{ii} = \langle\psi_i|\psi_i\rangle_R$$

Multiple Projectors for Each *l* Increase the Accuracy

Pseudo-Potentials (PP) & Projectors

Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

USPP & PAW: Common Set of Local PP, AE & PS Partials, and Projectors

$\{\phi_i\} \Rightarrow \{\tilde{\phi}_i\},\ \mathrm{v}_{local} \Rightarrow \{\tilde{p}_i\}$

$i=(l,\tau,m), \tau=1,2$

v_{local} : *Screened Local PP*

$\tilde{\phi}_i = \tilde{\Phi}_{l,\tau}(r) Y_{lm}(\hat{r})$

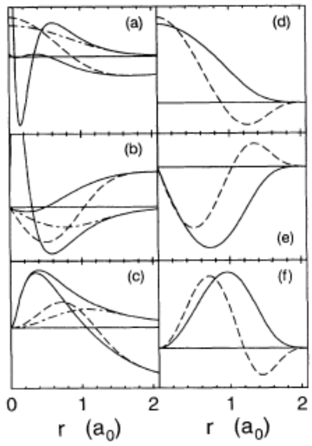
$\mathrm{v}_i \tilde{\phi}_i = \tilde{\chi}_i = \{\varepsilon_i - (-\frac{1}{2}\Delta + \mathrm{v}_{local})\}\tilde{\phi}_i$

$B_{ij} =< \tilde{\phi}_i | \tilde{\chi}_j >$ $\quad$ $\tilde{p}_i = \sum_j [B^{-1}]_{ji} \tilde{\chi}_j$

$\tilde{p}_i = \tilde{P}_{l,\tau}(r) Y_{lm}(\hat{r})$

$< \tilde{p}_i | \tilde{\phi}_j > = < \tilde{\phi}_i | \tilde{p}_j > = \delta_{ij}$

Gram-Schmidt type orthogonalization is also possible



Example of AE & PS Partial Waves and Projectors for Mn

Left: $\{\phi_i\}$ $\{\tilde{\phi}_i\}$

Right: $\tilde{p}_i = \tilde{P}_{l,\tau}(r) Y_{lm}(\hat{r})$

Blöchl, PRB 50 (1994) 17953

Pseudo-Potentials (PP) & Projectors

Norm-Conserving PP, KB-Separable PP, Generalized PP, Generalized Separable PP, and Ultrasoft (Vanderbilt) PP

USPP & PAW: Set of Local PP and Projectors for Each Atom & Generalized Eigenvalue Problem Including S

AE Partial Waves, PS Partial Waves, Projectors and Local PP

$\{\phi_i\} \Rightarrow \{\tilde{\phi}_i\},\ \mathrm{v}_{local} \Rightarrow \{\tilde{p}_i\}$ $\quad$ $i=(l,\tau,m), \tau=1,2$ $\quad$ $\tilde{\phi}_i = \tilde{\Phi}_{l,\tau}(r) Y_{lm}(\hat{r})$

$(-\frac{1}{2}\Delta + \mathrm{v}_{local} + \mathrm{v}_i)\tilde{\phi}_i = \varepsilon_i \tilde{\phi}_i$ $\quad$ $\mathrm{v}_i \tilde{\phi}_i = \tilde{\chi}_i = \{\varepsilon_i - (-\frac{1}{2}\Delta + \mathrm{v}_{local})\}\tilde{\phi}_i$ $\quad$ v_{local} : *Screened Local PP*

$B_{ij} =< \tilde{\phi}_i | \tilde{\chi}_j >$ $\quad$ $\tilde{p}_i = \sum_j [B^{-1}]_{ji} \tilde{\chi}_j$ $\quad$ $\tilde{p}_i = \tilde{P}_{l,\tau}(r) Y_{lm}(\hat{r})$

Gram-Schmidt type orthogonalization is also possible

$< \tilde{p}_i | \tilde{\phi}_j > = < \tilde{\phi}_i | \tilde{p}_j > = \delta_{ij}$

$\sum_i |\tilde{p}_i\rangle\langle\tilde{\phi}_i| = \sum_i |\tilde{\phi}_i\rangle\langle\tilde{p}_i| = 1$

$q_{ij} =< \phi_i | \phi_j > - < \tilde{\phi}_i | \tilde{\phi}_j >$ $\quad$ $S = 1 + \sum_{ij} q_{ij} | \tilde{p}_i >< \tilde{p}_j |$

$< \tilde{\Psi} | S | \tilde{\Psi} > = 1$

$H\tilde{\Psi} = \varepsilon S \tilde{\Psi}$

$$\{-\frac{1}{2}\Delta + \mathrm{v}_{local}(r) + \sum_{ij}(B_{ij} + \varepsilon_j q_{ij}) |\tilde{p}_i >< \tilde{p}_j |\}\tilde{\phi}_l = \varepsilon(1 + \sum_{ij} q_{ij} |\tilde{p}_i >< \tilde{p}_j |)\tilde{\phi}_l$$

Equation for Scattering Property of an Atom, Non-SCF, Screened

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Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Transformation Theory

AE and PS Partial Waves & Projectors within Radius r_c at Each Atomic Site

$$\{\phi_i\}\ \{\tilde{\phi}_i\}\ \{\tilde{p}_i\}\quad \langle \tilde{p}_i | \tilde{\phi}_i \rangle = \delta_{ij} \quad \tilde{\phi}_i(\vec{r}) = \frac{\phi_{n_i l_i}(r)}{r} Y_{l_i m_i}(\hat{r}) \quad i = (\vec{R}+\vec{t}_a, l, \tau, m), \tau = 1,2$$

AE Valence Wave Function from PS Valence Wave Function by the Projection

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

$\Psi_n(\vec{r})$ **Bulk AE Wave Function** $\tilde{\Psi}_n(\vec{r})$ **Bulk PS Wave Function**

***n*: Index of Eigen State**

Transformation Operator *T*

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

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

Sum of i : All the Projectors for Each Atomic Site

Transformation Theory of Expectation Value <A>

$$\langle A \rangle = \sum_n^{\text{occ}} f_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_{(i,j)} \rho_{ij} \left(\langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \right)$$

$$\rho_{ij} = \sum_n^{\text{occ}} f_n \langle \tilde{\Psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_n \rangle$$

Sum of (i, j): All the Projector Pairs for Each Atomic Site

Projector Function

Transformation Theory

Proof of the Transformation Theory

Operator T $\quad |\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle\tilde{p}_i|\tilde{\Psi}_n\rangle = T|\tilde{\Psi}_n\rangle \quad T = 1 + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle\tilde{p}_i|$

Expectation Value <A> $\quad \langle A\rangle = \sum_n f_n \langle\Psi_n|A|\Psi_n\rangle = \sum_n f_n \langle T\tilde{\Psi}_n|A|T\tilde{\Psi}_n\rangle = \sum_n f_n \langle\tilde{\Psi}_n|T^* A T|\tilde{\Psi}_n\rangle$

$$T^* A T = \left\{1 + \sum_i |\tilde{p}_i\rangle\left(\langle\phi_i| - \langle\tilde{\phi}_i|\right)\right\} A \left\{1 + \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle\right)\langle\tilde{p}_j|\right\}$$

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

$$+ \sum_{i,j} |\tilde{p}_i\rangle\left(\langle\phi_i|A|\phi_j\rangle + \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle - \langle\phi_i|A|\tilde{\phi}_j\rangle - \langle\tilde{\phi}_i|A|\phi_j\rangle\right)\langle\tilde{p}_j|$$

Insert this in the 2nd and 3rd terms

$$\sum_i |\tilde{p}_i\rangle\langle\tilde{\phi}_i| = \sum_i |\tilde{\phi}_i\rangle\langle\tilde{p}_i| = 1$$

Approximate Completeness

$$T^* A T = A + \sum_{i,j} |\tilde{p}_i\rangle\left(\langle\phi_i|A|\tilde{\phi}_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)\langle\tilde{p}_j|$$

$$+ \sum_{i,j} |\tilde{p}_i\rangle\left(\langle\tilde{\phi}_i|A|\phi_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)\langle\tilde{p}_j|$$

$$+ \sum_{i,j} |\tilde{p}_i\rangle\left(\langle\phi_i|A|\phi_j\rangle + \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle - \langle\phi_i|A|\tilde{\phi}_j\rangle - \langle\tilde{\phi}_i|A|\phi_j\rangle\right)\langle\tilde{p}_j|$$

$$= A + \sum_{i,j} |\tilde{p}_i\rangle\left(\langle\phi_i|A|\phi_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)\langle\tilde{p}_j|$$

Projector Function

$$\rho_{ij} = \sum_n^{\mathrm{occ}} f_n \langle\tilde{\Psi}_n|\tilde{p}_i\rangle\langle\tilde{p}_j|\tilde{\Psi}_n\rangle$$

Final Form

$$\langle A\rangle = \sum_n^{\mathrm{occ}} f_n \langle\tilde{\Psi}_n|A|\tilde{\Psi}_n\rangle + \sum_{(i,j)} \rho_{ij}\left(\langle\phi_i|A|\phi_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)$$

Transformation Theory

Total Valence Charge Density Distribution from Transformation Theory

$$\langle A\rangle = \sum_n^{\mathrm{occ}} f_n \langle\tilde{\Psi}_n|A|\tilde{\Psi}_n\rangle + \sum_{(i,j)} \rho_{ij}\left(\langle\phi_i|A|\phi_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)$$

$$n(\vec{r}) = \tilde{n}(\vec{r}) + n^1(\vec{r}) - \tilde{n}^1(\vec{r}) \qquad A = |\vec{r}\rangle\langle\vec{r}|$$

$$\tilde{n}(\vec{r}) = \sum_n f_n \langle\tilde{\Psi}_n|\vec{r}\rangle\langle\vec{r}|\tilde{\Psi}_n\rangle$$

Throughout the Cell

$$n^1(\vec{r}) = \sum_n f_n \left\langle\tilde{\Psi}_n\middle|\sum_{(i,j)}|\tilde{p}_i\right\rangle\langle\tilde{\phi}_i|\vec{r}\rangle\langle\vec{r}|\tilde{\phi}_j\rangle\langle\tilde{p}_j|\tilde{\Psi}_n\rangle$$

$$= \sum_{(i,j)} \rho_{ij}\langle\phi_i|\vec{r}\rangle\langle\vec{r}|\phi_j\rangle$$

$$= \sum_{(i,j)} \rho_{ij}\phi_i^*(\vec{r})\phi_j(\vec{r})$$

$$\tilde{n}_1(\vec{r}) = \sum_n f_n \left\langle\tilde{\Psi}_n\middle|\sum_{(i,j)}|\tilde{p}_i\right\rangle\langle\tilde{\phi}_i|\vec{r}\rangle\langle\vec{r}|\tilde{\phi}_j\rangle\langle\tilde{p}_j|\tilde{\Psi}_n\rangle$$

$$= \sum_{(i,j)} \rho_{ij}\tilde{\phi}_i^*(\vec{r})\tilde{\phi}_j(\vec{r})$$

$$n^1(\vec{r}),\ \tilde{n}^1(\vec{r})$$

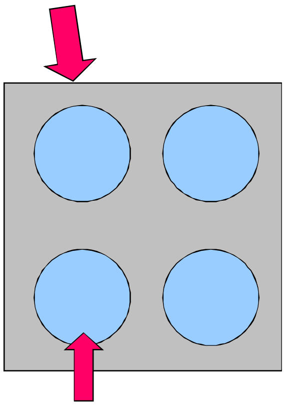
Inside the Augmented Sphere at Each Atomic Site

$$\rho_{ij} = \sum_n f_n \langle\tilde{\Psi}_n|\tilde{p}_i\rangle\langle\tilde{p}_j|\tilde{\Psi}_n\rangle$$

Projector Function

Whole Space including Atomic Regions

$$\left|\tilde{\Psi}_n\right\rangle, \sum_n^{occ} f_n \left\langle \tilde{\Psi}_n \,|\, A \,|\, \tilde{\Psi}_n \right\rangle,\ \tilde{n}(\vec{r}),\ \tilde{E}$$



Atomic Sphere

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

$$\left\langle A \right\rangle = \sum_n^{occ} f_n \left\langle \tilde{\Psi}_n \middle| A \middle| \tilde{\Psi}_n \right\rangle + \sum_{(i,j)} \rho_{ij} \left(\left\langle \phi_i \middle| A \middle| \phi_j \right\rangle - \left\langle \tilde{\phi}_i \middle| A \middle| \tilde{\phi}_j \right\rangle \right)$$

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

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

$$\sum_i \left(\left|\phi_i\right\rangle - \left|\tilde{\phi}_i\right\rangle\right)\left\langle \tilde{p}_i \,|\, \tilde{\Psi}_n \right\rangle,\ \sum_{(i,j)} \rho_{ij} \left(\left\langle \phi_i \middle| A \middle| \phi_j \right\rangle - \left\langle \tilde{\phi}_i \middle| A \middle| \tilde{\phi}_j \right\rangle \right),\ n^1 - \tilde{n}^1,\ E^1 - \tilde{E}^1$$

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1. **Pseudo-Potentials and Projectors** 1) & 2)
2. **Transformation Theory: Wave Functions, Expectation Values and Charge Density Distribution** 3) & 4)
3. **Formulation of Total Energy: Kinetic Energy, Exchange-Correlation Energy, Hartree Energy and Compensation Charge** 3) & 4)
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Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Formulation of Total Energy by Transformation Theory

$$E_{tot}=\sum_n f_n\langle\Psi_n|-\tfrac{1}{2}\Delta|\Psi_n\rangle+E_H[n+n_z]+E_{xc}[n]$$

Total Energy by True AE Wave Functions and True Charges

f_n : occupancy, Ψ_n : True Wave Function

n : electronic charge density, n_z : point charge density of nuclei

Transformation Theory

$$\langle A\rangle=\sum_n^{\mathrm{occ}} f_n\langle\tilde{\Psi}_n|A|\tilde{\Psi}_n\rangle+\sum_{(i,j)}\rho_{ij}\left(\langle\phi_i|A|\phi_j\rangle-\langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle\right)$$

Final Expression

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

Kinetic Energy

$$A=-\tfrac{1}{2}\Delta$$

$E^1_{kin},\ \tilde{E}^1_{kin}$ **Inside the Atomic Sphere**

$$E_{kin}=\tilde{E}_{kin}+E^1_{kin}-\tilde{E}^1_{kin}$$

$$E^1_{kin}=\sum_{(i,j)}\rho_{ij}\langle\phi_i|-\tfrac{1}{2}\Delta|\phi_j\rangle$$

$$\tilde{E}_{kin}=\sum_n f_n\langle\tilde{\Psi}_n|-\tfrac{1}{2}\Delta|\tilde{\Psi}_n\rangle\qquad \tilde{E}^1_{kin}=\sum_{(i,j)}\rho_{ij}\langle\tilde{\phi}_i|-\tfrac{1}{2}\Delta|\tilde{\phi}_j\rangle$$

Formulation of Total Energy: Hartree Energy

$$n_{zc}=n_z+n_c$$

$$\int_{\Omega r} n_{zc}(\vec{r})d^3\vec{r}=\int_{\Omega r}\tilde{n}_{zc}(\vec{r})d^3\vec{r}$$

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

$$n(\vec{r})\cong\tilde{n}(\vec{r})+\hat{n}(\vec{r})$$

n_{zc} : *Nuclear and Core Charge Density*

$\tilde{n}_{zc}$: *Pseudized Nuclear & Core Charge Density*

$n(\vec{r})$: *True Valence Charge Density*

$\hat{n}(\vec{r})$: *Compensation Charge Density*

$\hat{n}(\vec{r})$ & $n^1(\vec{r})-\tilde{n}^1(\vec{r})$: *Same Multipole Moments*

Bulk Region **Atomic Sphere**

$$\begin{aligned}n_T&=n(\vec{r})+n_{zc}(\vec{r})\\&=\underbrace{\left(\tilde{n}(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_{zc}(\vec{r})\right)}_{\tilde{n}_T}+\underbrace{\left(n^1+n_{zc}\right)}_{n^1_T}-\underbrace{\left(\tilde{n}^1(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_{zc}(\vec{r})\right)}_{\tilde{n}^1_T}\end{aligned}$$

$$\tilde{n}_T=\tilde{n}(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_{zc}(\vec{r})$$

$$n^1_T=n^1(\vec{r})+n_{zc}(\vec{r})$$

$$\tilde{n}^1_T=\tilde{n}^1(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_{zc}(\vec{r})$$

n_{zc} vs $\tilde{n}_{zc}$: *Same Moment*

$\hat{n}$ vs $n^1-\tilde{n}^1$: *Same Multipole Moments*

$n^1_T=n^1+n_{zc}$ vs $\tilde{n}^1_T=\tilde{n}^1+\hat{n}+\tilde{n}_{zc}$

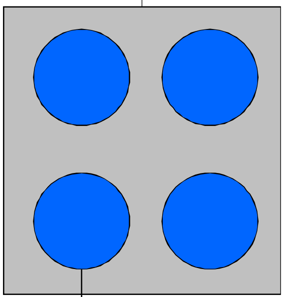
: *Same Multipole Moments*

$n^1_T-\tilde{n}^1_T$: *No Moments outside Atomic Sphere*

$\tilde{n}_T$

Whole Space including Atomic Regions

$$n_T = n + n_{zc} = \tilde{n}_T + n_T^1 - \tilde{n}_T^1$$



$$\tilde{n}_T = \tilde{n} + \hat{n} + \tilde{n}_{zc}$$

$$n_T^1 = n^1 + n_{zc}$$

$$\tilde{n}_T^1 = \tilde{n}^1 + \hat{n} + \tilde{n}_{zc}$$

$\tilde{n}_T^1$ vs n_T^1 : *Same Mulpipole Moments*

$v_H[\tilde{n}_{zc}]$: *Unscreened Local Pseudopotential*

$n_T^1 - \tilde{n}_T^1$

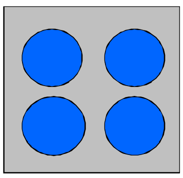
Atomic Sphere

Formulation of Total Energy: Hartree Energy

$$E_H = \frac{1}{2}(n_T)(n_T)$$
$$= \frac{1}{2}(\tilde{n}_T + n_T^1 - \tilde{n}_T^1)(\tilde{n}_T + n_T^1 - \tilde{n}_T^1)$$
$$= \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) + (n_T^1 - \tilde{n}_T^1)(\tilde{n}_T) + \frac{1}{2}(n_T^1 - \tilde{n}_T^1)(n_T^1 - \tilde{n}_T^1)$$
$$\approx \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) + \overline{(n_T^1 - \tilde{n}_T^1)(\tilde{n}_T^1)} + \frac{1}{2}\overline{(n_T^1 - \tilde{n}_T^1)(n_T^1 - \tilde{n}_T^1)}$$
$$= \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) + \frac{1}{2}\overline{(n_T^1)(n_T^1)} - \frac{1}{2}\overline{(\tilde{n}_T^1)(\tilde{n}_T^1)}$$

$$\frac{1}{2}(n_T)(n_T) \leftarrow \frac{1}{2}\iint \frac{n_T(\vec{r})n_T(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'d\vec{r}$$

Electrostatic Interactions Among All the Electrons and Nuclei



Bar Means Integration inside Atomic Sphere

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

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

Proof

$n_T^1 - \tilde{n}_T^1$: *No Moments outside Atomic Sphere*

$\tilde{n}_T \approx \tilde{n}_T^1$, *due to* $\tilde{n} \approx \tilde{n}^1$ *inside Atomic Sphere*

Final Three Terms Correspond to the Hartree Energy in Each Energy Term

Formulation of Total Energy: ***Hartree Energy and Exchange-Correlation Energy***

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

$$\frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) = \frac{1}{2}(\tilde{n}+\hat{n}+\tilde{n}_{zc})(\tilde{n}+\hat{n}+\tilde{n}_{zc})$$

$$= \frac{1}{2}(\tilde{n}+\hat{n})(\tilde{n}+\hat{n}) + (\tilde{n}_{zc})(\tilde{n}+\hat{n}) + \frac{1}{2}(\tilde{n}_{zc})(\tilde{n}_{zc})$$

$$= \frac{1}{2}(\tilde{n}+\hat{n})(\tilde{n}+\hat{n}) + (\tilde{n}_{zc})(\tilde{n}+\hat{n}) + \frac{1}{2}\overline{(\tilde{n}_{zc})(\tilde{n}_{zc})} + U(\vec{R}, Z_{ion})$$

Electrostatic Interactions among PS Valence Charges, among Ions and between PS Charges and Ions (Local PP).

***U*: Ion-Ion Electrostatic Term**

$$\frac{1}{2}\overline{(n_T^1)(n_T^1)} = \frac{1}{2}\overline{(n^1)(n^1)} + \overline{(n_{zc})(n^1)} + \frac{1}{2}\overline{(n_{zc})(n_{zc})}$$

Interactions among True Valence Charges and between True Valence Charge and Nuclear & Core Charges inside Atomic Sphere

$$-\frac{1}{2}\overline{(\tilde{n}_T^1)(\tilde{n}_T^1)} = -\frac{1}{2}\overline{(\tilde{n}^1+\hat{n}+\tilde{n}_{zc})(\tilde{n}^1+\hat{n}+\tilde{n}_{zc})}$$

$$= -\frac{1}{2}\overline{(\tilde{n}^1+\hat{n})(\tilde{n}^1+\hat{n})} - \overline{(\tilde{n}_{zc})(\tilde{n}^1+\hat{n})} - \frac{1}{2}\overline{(\tilde{n}_{zc})(\tilde{n}_{zc})}$$

Interactions among PS Charges and between PS Charges and Ions (Local PP) inside Atomic Sphere

$$n(\vec{r}) + n_c(\vec{r}) = (\tilde{n}+\hat{n}+\tilde{n}_c) + (n^1+n_c) - (\tilde{n}+\hat{n}+\tilde{n}_c)$$

True Electronic Charge

Exchange-Correlation Energy

$$E_{xc}[n+n_c] \approx E_{xc}[\tilde{n}+\hat{n}+\tilde{n}_c] + E_{xc}\overline{[n^1+n_c]} - E_{xc}\overline{[\tilde{n}^1+\hat{n}+\tilde{n}_c]}$$

n_c : *Core Charge Density* $\tilde{n}_c$: *Partial Core Charge*

Louie et al. PRB26(1982)1738

Formulation of Total Energy: ***Final Form***

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

$$\tilde{E} = \sum_n f_n \langle \tilde{\Psi}_n | -\tfrac{1}{2}\Delta | \tilde{\Psi}_n \rangle + E_{xc}[\tilde{n}+\hat{n}+\tilde{n}_c] + E_H[\tilde{n}+\hat{n}]$$

$$+ \int v_H[\tilde{n}_{zc}](\tilde{n}+\hat{n})d\vec{r} + U(\vec{R}, Z_{ion})$$

Integration throughout the System

$$E^1 = \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\tfrac{1}{2}\Delta | \phi_j \rangle + E_{xc}\overline{[n^1+n_c]}$$

$$+ E_H\overline{[n^1]} + \int_{\Omega r} v_H[n_{zc}]n^1 d\vec{r}$$

Integration inside Each Atomic Sphere

$$\tilde{E}^1 = \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\tfrac{1}{2}\Delta | \tilde{\phi}_j \rangle + E_{xc}\overline{[\tilde{n}^1+\hat{n}+\tilde{n}_c]}$$

$$+ E_H\overline{[\tilde{n}^1+\hat{n}]} + \int_{\Omega r} v_H[\tilde{n}_{zc}](\tilde{n}^1+\hat{n})d\vec{r}$$

$$E_H[n] = \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' d\vec{r}$$

U : *Electrostatic Interaction among Ions*

$v_H[\tilde{n}_{zc}]$: *Unscreened Local Pseudopotential*

$v_H[n_{zc}]$: *True Electrostatic Potential by Nuclear and Core Electrons*

$\tilde{E}$: *Energy for Pseudo Valence Wave Functions and Charges obtained for Supercell or Crystal*

E^1 & $\tilde{E}^1$: *Sum for Each Atomic Site*

Formulation of Total Energy: Compensation Charge $\hat{n}(\vec{r})$

True Charge Density

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

$$n(\vec{r}) = \tilde{n}(\vec{r}) + \hat{n}(\vec{r})$$

Used Instead of True Density

$\hat{n}(\vec{r})$ is constructed so as to have the same multipole moments with $n^1(\vec{r}) - \tilde{n}^1(\vec{r})$ at each atomic site and with enough smoothness for FFT

$$n^1 - \tilde{n}^1 = \sum_{(i,j)} \rho_{ij} \left(\phi_i^*(\vec{r})\phi_j(\vec{r}) - \tilde{\phi}_i^*(\vec{r})\tilde{\phi}_j(\vec{r}) \right) = \sum_{(i,j)} \rho_{ij} Q_{ij}(\vec{r})$$

L-th Moment of Q_{ij}

$$Q_{ij}(\vec{r}) = \phi_i^*(\vec{r})\phi_j(\vec{r}) - \tilde{\phi}_i^*(\vec{r})\tilde{\phi}_j(\vec{r})$$

$$q_{ij}^L = \int_{\Omega r} Q_{ij}(\vec{r}) \left| \vec{r} - \vec{R} \right|^l Y_L^*(r - R) d\vec{r}^3$$

$$= \int_0^{r_{rad}} Q_{ij}^{rad}(r) r^{l+2} dr G_{l_i m_i, l_j m_j}^{lm}$$

$Q_{ij}^{rad}(r)$: *Radial Part of* $Q_{ij}(\vec{r})$

$G_{l_i m_i, l_j m_j}^{lm}$: *Gaunt Coefficient*

$$\hat{Q}_{ij}^L(\vec{r}) = q_{ij}^L \times g_l\left(\left| \vec{r} - \vec{R} \right| \right) Y_L(r - R) \qquad L = (l, m)$$

$$\int_0^{r_{\mathrm{comp}}} g_l(r) r^{l+2} dr = 1$$

$$\hat{n}(\vec{r}) = \sum_{(i,j)} \rho_{ij} \sum_L \hat{Q}_{ij}^L(\vec{r})$$

Final Expression
Only ρ_{ij} is Updated

g_l: Compensation Function for Smoothing

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Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Hamiltonian and Kohn-Sham Equation

Ortho-Normatilty Condition among Pseudo Wave Functions and Overlap Operator *S*

$$\langle \tilde{\Psi}_n | S | \tilde{\Psi}_m \rangle = \delta_{nm} \qquad \boxed{S[\{\vec{R}\}] = 1 + \sum_{(i,j)} |\tilde{p}_i\rangle q_{ij} \langle \tilde{p}_j|} \qquad q_{ij} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle = \sqrt{4\pi} q_{ij}^0$$

Hamilton Operator *H* from the PAW Total Energy

$$\frac{dE_{tot}}{d\tilde{\rho}} = \frac{\partial E_{tot}}{\partial \tilde{\rho}} + \int \frac{\delta E_{tot}}{\delta \tilde{n}(\vec{r})} \times \underbrace{\frac{\partial \tilde{n}(\vec{r})}{\partial \tilde{\rho}}}_{|\vec{r}\rangle\langle\vec{r}|} d\vec{r} + \sum_{(i,j)} \frac{\partial E_{tot}}{\partial \rho_{ij}} \underbrace{\frac{\partial \rho_{ij}}{\partial \tilde{\rho}}}_{|\tilde{p}_i\rangle\langle\tilde{p}_j|}$$

$$\boxed{H = -\tfrac{1}{2}\Delta + \tilde{\upsilon}_{\text{eff}}(\vec{r}) + \sum_{(i,j)} |\tilde{p}_i\rangle \left(\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1 \right) \langle \tilde{p}_j|}$$

$$\tilde{\upsilon}_{\text{eff}}(\vec{r}) = \upsilon_H[\tilde{n}_{zc} + \tilde{n} + \hat{n}] + \upsilon_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c]$$

Bulk Screened Local Pseudo-Potential

$$\upsilon_{\text{eff}}^{\ 1} = \upsilon_H[n_{zc} + n^1] + \upsilon_{xc}[n^1 + n_c]$$

Screened Potential by True Valence Charge inside Each Atomic Sphere

$$\tilde{\upsilon}_{\text{eff}}^{\ 1} = \upsilon_H[\tilde{n}_{zc} + \tilde{n}^1 + \hat{n}] + \upsilon_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]$$

Screened Local Atomic Pseudo-Potential inside Each Atomic Sphere

$$\hat{D}_{ij} = \sum_L \int \tilde{\upsilon}_{\text{eff}}(\vec{r}) \hat{Q}_{ij}^L(\vec{r}) d\vec{r}^{\,3}$$

Bulk

$$D_{ij}^1 = \langle \phi_i | -\tfrac{1}{2}\Delta + \upsilon_{\text{eff}}^{\ 1} | \phi_j \rangle$$

$$\tilde{D}_{ij}^1 = \langle \tilde{\phi}_i | -\tfrac{1}{2}\Delta + \tilde{\upsilon}_{\text{eff}}^{\ 1} | \tilde{\phi}_j \rangle + \sum_L \int_{\Omega r} \tilde{\upsilon}_{\text{eff}}^{\ 1}(\vec{r}) \hat{Q}_{ij}^L(\vec{r}) d\vec{r}^{\,3}$$

Each Atomic Site

Kohn-Sham Equation

$$\boxed{H\tilde{\Psi}_n = \varepsilon S \tilde{\Psi}_n}$$

$$\tilde{E} = \sum_n f_n \langle \tilde{\Psi}_n | -\frac{1}{2}\Delta | \tilde{\Psi}_n \rangle + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + E_H[\tilde{n} + \hat{n}]^{\text{註 25}}$$
$$+ \int \upsilon_H[\tilde{n}_{zc}](\tilde{n} + \hat{n}) d\vec{r}^{3} + U(\vec{R}, Z_{\text{ion}}) \tag{1.20}$$

$$\tilde{E}^1 = \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2}\Delta | \tilde{\phi}_j \rangle + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]}$$
$$+ \overline{E_H[\tilde{n}^1 + \hat{n}]} + \int_{\Omega_r} \upsilon_H[\tilde{n}_{zc}](\tilde{n}^1 + \hat{n}) d^3\vec{r}^{\text{ 註 26}} \tag{1.21}$$

$$E^1 = \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2}\Delta | \phi_j \rangle + \overline{E_{xc}[n^1 + n_c]}$$
$$+ \overline{E_H[n^1]} + \int_{\Omega_r} \upsilon_H[n_{zc}] n^1 d^3\vec{r} \tag{1.22}$$

PAW Note V.1.6

▶ $\tilde{\rho} = \sum_n f_n |\tilde{\Psi}_n\rangle\langle\tilde{\Psi}_n|$: Pseudodensity Operator.

ハミルトニアン

Total Energy の$\tilde{\rho}$での変分 $\Rightarrow$ $\frac{dE}{d\tilde{\rho}} = \boldsymbol{H}$

$$\frac{dE}{d\tilde{\rho}} = \frac{\partial E}{\partial\tilde{\rho}} + \int \frac{\delta E}{\delta\tilde{n}(\vec{r})} \times \underbrace{\frac{\partial\tilde{n}(\vec{r})}{\partial\tilde{\rho}}}_{|\vec{r}\rangle\langle\vec{r}|} d\vec{r} + \sum_{(i,j)} \frac{\partial E}{\partial\rho_{ij}} \underbrace{\frac{\partial\rho_{ij}}{\partial\tilde{\rho}}}_{|\tilde{p}_i\rangle\langle\tilde{p}_j|} \tag{1.33}$$

$E = \tilde{E} + E^1 - \tilde{E}^1$ 内の ① $|\tilde{\Psi}_n\rangle$ での変分, ② $\tilde{n}$ での変分 注 39, ③ ρ_{ij} を含む n^1, $\tilde{n}^1$, $\hat{n}$ での変分 注 40

▶ $\tilde{E}$ 項の変分. (1.20) 式

① 項 $\Rightarrow -\frac{1}{2}\Delta\Psi_n(\vec{r})$

② 項 $\Rightarrow \int \frac{\delta(E_{xc}+E_H)}{\delta\tilde{n}} \times \frac{\partial\tilde{n}}{\partial\tilde{\rho}} d\vec{r} = (v_{xc}[\tilde{n}+\hat{n}+\tilde{n}_c] + v_H[\tilde{n}+\hat{n}+\tilde{n}_{zc}])\,\tilde{\Psi}_n(\vec{r})$

$$\tilde{v}_{\text{eff}}(\vec{r}) = v_{xc}[\tilde{n}+\hat{n}+\tilde{n}_c] + v_H[\tilde{n}+\hat{n}+\tilde{n}_{zc}] \tag{1.34}$$

③ 項 $\Rightarrow \frac{\delta(E_{xc}+E_H)}{\delta\hat{n}} \times \frac{\partial\hat{n}}{\partial\rho_{ij}}$

$$\frac{\partial\hat{n}}{\partial\rho_{ij}} = \sum_L \hat{Q}^L_{ij}(\vec{r}) \Rightarrow \int \tilde{v}_{\text{eff}}(\vec{r}) \times \sum_L \hat{Q}^L_{ij}(\vec{r})d\vec{r} \times |\tilde{p}_i\rangle\langle\tilde{p}_j| \tag{1.35}$$

▶ $\tilde{E}^1$ (1.21) 式の変分

③ 項のみ、まず、$\langle\tilde{\phi}_i| - \frac{1}{2}\Delta|\tilde{\phi}_j\rangle \times |\tilde{p}_i\rangle\langle\tilde{p}_j|$

$\hat{n}$ での変分 → 原子内積分項について.

$$\int (v_{xc}[\tilde{n}^1+\hat{n}+\tilde{n}_c] + v_H[\tilde{n}_{zc}+\tilde{n}^1+\hat{n}]) \times \sum_L \hat{Q}^L_{ij}(\vec{r})d\vec{r}^3 \times |\tilde{p}_i\rangle\langle\tilde{p}_j|$$

$\tilde{n}^1$ での変分

同様に（原子内）→ $\langle\tilde{\phi}_i|\tilde{v}_{\text{eff}}{}^1|\tilde{\phi}_j\rangle \times |\tilde{p}_i\rangle\langle\tilde{p}_j|$

以上まとめると

$$\langle\tilde{\phi}_i| - \frac{1}{2}\Delta + \tilde{v}_{\text{eff}}{}^1(\vec{r})|\tilde{\phi}_j\rangle \times |\tilde{p}_i\rangle\langle\tilde{p}_j| + \int \tilde{v}_{\text{eff}}{}^1(\vec{r}) \times \sum_L \hat{Q}^L_{ij}(\vec{r})d\vec{r}^3 \times |\tilde{p}_i\rangle\langle\tilde{p}_j| = \tilde{D}^1_{ij} \times |\tilde{p}_i\rangle\langle\tilde{p}_j| \tag{1.36}$$

$\tilde{v}_{\text{eff}}{}^1 = v_{xc}[\tilde{n}^1+\hat{n}+\tilde{n}_c] + v_H[\tilde{n}_{zc}+\tilde{n}^1+\hat{n}]$ ← 原子内のみ

► E^1 (1.22) 式の変分

③ 項のみ、まず、$\langle\phi_i| -\frac{1}{2}\Delta|\phi_j\rangle \times |\tilde{p}_i\rangle\langle\tilde{p}_j|$

n^1 での変分

$$\int \left(v_{xc}[n^1+n_c] + v_H[n_{zc}+n^1]\right) \langle\phi_i|\vec{r}\rangle\langle\vec{r}|\phi_j\rangle d\vec{r}^3 \times |\tilde{p}_i\rangle\langle\tilde{p}_j|$$

$$\downarrow$$

$$\left.\begin{aligned} &\langle\phi_i| -\frac{1}{2}\Delta + v_{\mathrm{eff}}{}^1(\vec{r})|\phi_j\rangle \times |\tilde{p}_i\rangle\langle\tilde{p}_j| \\ &v_{\mathrm{eff}}{}^1 = v_H[n_{zc}+n^1] + v_{xc}[n^1+n_c] \end{aligned}\right\} \tag{1.37}$$

以上まとめると.

(1.34), (1.35), (1.37), (1.36) 式

$\Downarrow$

$$\boldsymbol{H} = -\frac{1}{2}\Delta + \tilde{v}_{\mathrm{eff}}(\vec{r}) + \sum_{(i,j)} |\tilde{p}_i\rangle \left(\hat{D}_{ij} + D^1_{ij} - \tilde{D}^1_{ij}\right) \langle\tilde{p}_j| \tag{1.38}$$

$$\tilde{v}_{\mathrm{eff}}(\vec{r}) = v_H[\tilde{n}_{zc}+\tilde{n}+\hat{n}] + v_{xc}[\tilde{n}+\hat{n}+\tilde{n}_c] \quad \leftarrow (1.34)$$

$$\hat{D}_{ij} = \sum_L \int \tilde{v}_{\mathrm{eff}}(\vec{r})\hat{Q}^L_{ij}(\vec{r})d\vec{r}^3 \quad \leftarrow (1.35)$$

$$\left.\begin{aligned} &D^1_{ij} = \langle\phi_i| -\frac{1}{2}\Delta + v_{\mathrm{eff}}{}^1|\phi_j\rangle \\ &v_{\mathrm{eff}}{}^1 = v_H[n_{zc}+n^1] + v_{xc}[n^1+n_c] \end{aligned}\right\} \leftarrow (1.37)$$

$$\left.\begin{aligned} &\tilde{D}^1_{ij} = \langle\tilde{\phi}_i| -\frac{1}{2}\Delta + \tilde{v}_{\mathrm{eff}}{}^1|\tilde{\phi}_j\rangle + \sum_L \int_{\Omega_r} \tilde{v}_{\mathrm{eff}}{}^1(\vec{r})\hat{Q}^L_{ij}(\vec{r})d\vec{r}^3 \\ &\tilde{v}_{\mathrm{eff}}{}^1 = v_H[\tilde{n}_{zc}+\tilde{n}^1+\hat{n}] + v_{xc}[\tilde{n}^1+\hat{n}+\tilde{n}_c] \end{aligned}\right\} \leftarrow (1.36)$$

Atomic Forces: Hellmann-Feynman Theorem

$$\vec{F} = -\frac{dE_{tot}}{d\vec{t}_a} = -\frac{\partial}{\partial \vec{t}_a}\sum_n f_n \frac{\langle \tilde{\Psi}_n | H[\rho,\{\vec{t}_a\}] | \tilde{\Psi}_n \rangle}{\langle \tilde{\Psi}_n | S | \tilde{\Psi}_n \rangle} - \frac{\partial U(\vec{t}_a, Z_{ion})}{\partial \vec{t}_a}$$

$$= -\sum_n f_n \left\langle \tilde{\Psi}_n \left| \frac{\partial (H[\rho,\{\vec{t}_a\}] - \varepsilon_n S[\{\vec{t}_a\}])}{\partial \vec{t}_a} \right| \tilde{\Psi}_n \right\rangle - \frac{\partial U(\vec{t}_a, Z_{ion})}{\partial \vec{t}_a}$$

$$\vec{F}_1 = -\int (\tilde{n}(\vec{r}) + \hat{n}(\vec{r})) \times \frac{\partial v_H[\tilde{n}_{zc}]}{\partial \vec{t}_a} d\vec{r}^3 \quad \Leftarrow \quad v_H(\vec{r}) \; in \; \tilde{\upsilon}_{\mathrm{eff}}(\vec{r}) \; and \; \hat{D}_{ij}$$

$$\vec{F}_2 = -\sum_{(i,j),L} \rho_{ij} \int \tilde{\upsilon}_{\mathrm{eff}}(\vec{r}) \times \frac{\partial}{\partial \vec{t}_a} \hat{Q}_{ij}^L d\vec{r}^3 \quad \Leftarrow \quad \hat{Q}_{ij}^L(\vec{r}) \; in \; \hat{D}_{ij}$$

$$\vec{F}_3 = -\sum_{n,(i,j)} (\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1 - \varepsilon_n q_{ij}) \times f_n \left\langle \tilde{\Psi}_n \left| \frac{\partial |\tilde{p}_i\rangle\langle\tilde{p}_j|}{\partial \vec{t}_a} \right| \tilde{\Psi}_n \right\rangle$$

$$\vec{F}_{\mathrm{nlcc}} = -\frac{\delta E_{xc}}{\delta \tilde{n}_c} \times \frac{\delta \tilde{n}_c}{\delta \vec{t}_a} = -\int \upsilon_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] \times \frac{\partial \tilde{n}_c(\vec{r})}{\partial \vec{t}_a} d\vec{r}^3$$

9.3 Atomic Force の導出：Hellmann-Feynman の定理の証明

- $E_{\mathrm{tot}}[\{\vec{R}_a\}, \{\tilde{\Psi}_n\}]$ と表わしたとき、Atomic Force $\frac{dE_{\mathrm{tot}}}{d\vec{R}_a}$ は、$\vec{R}_a$ の直接依存項と、$\{\tilde{\Psi}_n\}$ を通じて依存する項に分けて考える.

$$-\vec{F}_a = \frac{dE_{\mathrm{tot}}}{d\vec{R}_a} = \frac{\partial E_{\mathrm{tot}}}{\partial \vec{R}_a} + \sum_n \left\{ \frac{\delta E_{\mathrm{tot}}}{\delta \tilde{\Psi}_n} \times \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} + \frac{\delta E_{\mathrm{tot}}}{\delta \tilde{\Psi}_n^*} \times \frac{\partial \tilde{\Psi}_n^*}{\partial \vec{R}_a} \right\} \tag{9.17}$$

- 間接依存項（(9.12) 式，(9.15) 式を用いる）

$$\sum_n \left\{ \frac{\delta E_{\mathrm{tot}}}{\delta \tilde{\Psi}_n} \times \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} + \frac{\delta E_{\mathrm{tot}}}{\delta \tilde{\Psi}_n^*} \times \frac{\partial \tilde{\Psi}_n^*}{\partial \vec{R}_a} \right\} = \sum_n \left\{ \langle \tilde{\Psi}_n | \boldsymbol{H} | \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} \rangle + \langle \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} | \boldsymbol{H} | \tilde{\Psi}_n \rangle \right\} \times f_n$$

$$= \sum_n \varepsilon_n \left\{ \langle \tilde{\Psi}_n | \boldsymbol{S} | \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} \rangle + \langle \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} | \boldsymbol{S} | \tilde{\Psi}_n \rangle \right\} \times f_n$$

$$= -\sum_n f_n \varepsilon_n \langle \tilde{\Psi}_n | \frac{\partial \boldsymbol{S}}{\partial \vec{R}_a} | \tilde{\Psi}_n \rangle \tag{9.18}$$

$$\left(\begin{array}{lcl} \because \langle \tilde{\Psi}_n | \boldsymbol{S} | \tilde{\Psi}_n \rangle = 1 \text{ 定数} & & \\ \frac{\partial}{\partial \vec{R}_a} \langle \tilde{\Psi}_n | \boldsymbol{S} | \tilde{\Psi}_n \rangle & = & 0, \\ \frac{\partial}{\partial \vec{R}_a} \langle \tilde{\Psi}_n | \boldsymbol{S} | \tilde{\Psi}_n \rangle & = & \langle \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} | \boldsymbol{S} | \tilde{\Psi}_n \rangle + \langle \tilde{\Psi}_n | \frac{\partial \boldsymbol{S}}{\partial \vec{R}_a} | \tilde{\Psi}_n \rangle + \langle \tilde{\Psi}_n | \boldsymbol{S} | \frac{\partial \tilde{\Psi}_n}{\partial \vec{R}_a} \rangle = 0 \end{array} \right)$$

► 直接依存項

(9.1) 式の E_{tot} 内の、V_{local}, $\hat{n}=\sum_a\sum_{ij}\rho^a_{ij}\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r})$ 内の $\hat{Q}^{lm}_{ij,a}(\vec{r})$, ρ^a_{ij} 内の $|\tilde{p}^a_i\rangle\langle\tilde{p}^a_j|$ が、$\{\vec{R}_a\}$ に直接依存する.

従って、

$$
\begin{aligned}
\frac{\partial E_{\mathrm{tot}}}{\partial \vec{R}_a} &= \int \frac{\partial V_{\mathrm{local}}(\vec{r})}{\partial \vec{R}_a}(\tilde{n}+\hat{n})d\vec{r}^3 + \int \tilde{v}_{\mathrm{eff}}(\vec{r})\sum_{ij}\rho^a_{ij}\sum_{lm}\frac{\partial \hat{Q}^{lm}_{ij,a}(\vec{r})}{\partial \vec{R}_a}d\vec{r}^3 \\
&+ \int \tilde{v}_{\mathrm{eff}}(\vec{r})\sum_{ij}\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r})d\vec{r}^3 \times \sum_n f_n\langle\tilde{\Psi}_n|\frac{\partial|\tilde{p}^a_i\rangle\langle\tilde{p}^a_j|}{\partial \vec{R}_a}|\tilde{\Psi}_n\rangle \\
&+ \sum_{ij}(D^1_{ij,a}-\tilde{D}^1_{ij,a})\sum_n f_n\langle\tilde{\Psi}_n|\frac{\partial|\tilde{p}^a_i\rangle\langle\tilde{p}^a_j|}{\partial \vec{R}_a}|\tilde{\Psi}_n\rangle \qquad (9.19)
\end{aligned}
$$

導出は、ハミルトニアンの導出と同様に行える. [注8]

一方、(9.18) 式は、以下に変形される

$$
\text{与式} = -\sum_n f_n\varepsilon_n\langle\tilde{\Psi}_n|\frac{\partial \boldsymbol{S}}{\partial \vec{R}_a}|\tilde{\Psi}_n\rangle = -\sum_{ij}\sum_n f_n\varepsilon_n q_{ij,a}\langle\tilde{\Psi}_n|\frac{\partial|\tilde{p}^a_i\rangle\langle\tilde{p}^a_j|}{\partial \vec{R}_a}|\tilde{\Psi}_n\rangle \qquad (9.20)
$$

[注8] (9.19) 式の第 2, 3 項は、E_{tot} を $\hat{n}$ で微分して $\hat{n}$ を $\vec{R}_a$ で微分. 第 4 項は、$E^1-\tilde{E}^1$ を ρ^a_{ij} で微分して、ρ^a_{ij} を $\vec{R}_a$ で微分.

以上から、Atomic Force は

$$
\begin{aligned}
-\vec{F}_a &= \int \frac{\partial V_{\mathrm{local}}(\vec{r})}{\partial \vec{R}_a}(\tilde{n}+\hat{n})d\vec{r}^3 \\
&+ \int \tilde{v}_{\mathrm{eff}}(\vec{r})\sum_{ij}\rho^a_{ij}\sum_{lm}\frac{\partial \hat{Q}^{lm}_{ij,a}(\vec{r})}{\partial \vec{R}_a}d\vec{r}^3 \\
&+ \sum_{ij}\sum_n(\hat{D}_{ij,a}+D^1_{ij,a}-\tilde{D}^1_{ij,a}-\varepsilon_n q_{ij,a})f_n\langle\tilde{\Psi}_n|\frac{\partial|\tilde{p}^a_i\rangle\langle\tilde{p}^a_j|}{\partial \vec{R}_a}|\tilde{\Psi}_n\rangle \qquad (9.21)
\end{aligned}
$$

積分はバルク（周期セル）.

以上により、Hellmann-Feynman の定理（及び $\boldsymbol{S}$ の寄与）が証明できた. [注9]

これは、結果的に、Kresse らの論文と同じ.（第 1 章参照）

Practical Procedure to Prepare the Functional Forms: Examples (Other forms are possible)

$$\tilde{\phi}_{lk}(r)=\begin{cases}\sum_{i=1}^{2}\alpha_i j(q_i r) & r<r_c^l\\ \phi_{lk}(r) & r>r_c^l\end{cases}$$

Smooth PS Partial Waves Using Spherical Bessel Functions, Continuously Connected to AE Partial Waves at r_c

$$\mathrm{v}^a_{local}(r)=A\frac{\sin(q_{\mathrm{loc}}r)}{r} \qquad r<r_{\mathrm{loc}}$$
$$=\mathrm{v}^a_{AE}(r) \qquad r\geq r_{\mathrm{loc}}$$

Screened Atomic Local Pseudo-Potential, Continuously Connected to Screened AE Potential ⇒Unscreening

Projectors are constructed by PS Partial Waves and Screened Local PP

$$\tilde{n}_c(r)=\sum_{i=1,2}B_i\frac{\sin(q_i r)}{r}$$

Partial Core Charge inside Some Radius, Continuously Connected to True Core Charge outside the Radius

$$g_l(r)=\sum_{i=1}^{3}\alpha_i^l j_l(q_i^l r)$$

Compensation Function Using Spherical Bessel Functions

Conditions to Determine the Coefficients $g_l(r_{\mathrm{comp}})=0$, $g_l'(r_{\mathrm{comp}})=0,\ g_l''(r_{\mathrm{comp}})=0$, $\int_0^{r_{\mathrm{comp}}} g_l(r)r^{l+2}dr=1$

Practical Procedure to Compute the Atomic Terms: Radial Mesh Integration inside Atomic Sphere

$$\phi_i(\vec{r})=\frac{\phi_{n_il_i}(r)}{r}Y_{l_im_i}(\hat{r})$$

$$\frac{\phi_{n_il_i}(r)}{r}:\ Radial\ Part$$

$$\left\langle\phi_i\right|-\frac{1}{2}\Delta\left|\phi_j\right\rangle$$
$$=\left(-\frac{1}{2}\right)\delta_{l_il_j}\delta_{m_im_j}\int_0^{r_{\mathrm{rad}}}\phi_{n_il_j}(r)\left[\frac{d^2}{dr^2}-\frac{l_j(l_j+1)}{r^2}\right]\phi_{n_jl_j}(r)dr$$
$$=\delta_{l_il_j}\delta_{m_im_j}\int_0^{r_{\mathrm{rad}}}\phi_{n_il_j}(r)\left[\varepsilon_j-V_{AE}(r)\right]\phi_{n_jl_j}(r)dr$$

$$\left\langle\phi_i\right|\upsilon_H[n_{zc}]\left|\phi_j\right\rangle=\delta_{l_il_j}\delta_{m_im_j}\int_0^{r_{\mathrm{rad}}}\upsilon_{\mathrm{H}}[n_{zc}]\phi_{n_il_j}(r)\phi_{n_jl_j}(r)dr$$

$$\iint_{\Omega r}\frac{\phi_i^*(\vec{r})\phi_j(\vec{r})\phi_k^*(\vec{r}')\phi_l(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'^3d\vec{r}^3$$
$$=\sum_{LM}\frac{4\pi}{2L+1}G^{LM}_{l_im_il_jm_j}(-1)^M G^{L,-M}_{l_km_kl_lm_l}$$
$$\times\int_0^{r_{\mathrm{rad}}}dr\left[\int_0^r dr'\left(\frac{r'^L}{r^{L+1}}\right)\phi_{n_il_i}(r)\phi_{n_jl_j}(r)\phi_{n_kl_k}(r')\phi_{n_ll_l}(r')\right.$$
$$\left.+\int_r^{r_{\mathrm{rad}}}dr'\left(\frac{r^L}{r'^{L+1}}\right)\phi_{n_il_i}(r)\phi_{n_jl_j}(r)\phi_{n_kl_k}(r')\phi_{n_ll_l}(r')\right]$$

$$\overline{E_H[n^1]}=\frac{1}{2}\iint\frac{n^1(\vec{r})n^1(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'d\vec{r}$$

This term contains the final equation.

Practical Procedure to Compute the Atomic Terms:
Radial Mesh Integration inside Atomic Sphere

$$\tilde{\phi}_i(\vec{r}) = \frac{\tilde{\phi}_{n_i l_i}(r)}{r} Y_{l_i m_i}(\hat{r})$$

$$\frac{\tilde{\phi}_{n_i l_i}(r)}{r} : \textit{Radial Part}$$

$$\left\langle \tilde{\phi}_i \left| -\frac{1}{2}\Delta \right| \tilde{\phi}_j \right\rangle = \left(-\frac{1}{2}\right) \delta_{l_i l_j} \delta_{m_i m_j} \int_0^{r_{\mathrm{rad}}} \tilde{\phi}_{n_i l_i}(r) \left[\frac{d^2}{dr^2} - \frac{l_j(l_j+1)}{r^2} \right] \tilde{\phi}_{n_j l_j}(r) dr$$

$$= \delta_{l_i l_j} \delta_{m_i m_j} \int_0^{r_{\mathrm{rad}}} \tilde{\phi}_{n_i l_i}(r) \left[\varepsilon_j - V_j(r) \right] \tilde{\phi}_{n_j l_j}(r) dr$$

$$\left\langle \tilde{\phi}_i \left| \upsilon_H[\tilde{n}_{zc}] \right| \tilde{\phi}_j \right\rangle = \delta_{l_i l_j} \delta_{m_i m_j} \int_0^{r_{\mathrm{rad}}} \upsilon_H[\tilde{n}_{zc}](r) \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r) dr$$

$$\overline{E_H[\tilde{n}^1 + \hat{n}]} = \frac{1}{2} \iint \frac{(\tilde{n}^1 + \hat{n})(\tilde{n}^1 + \hat{n})}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}$$

This term contains the following three-types of integrations.

$$\iint_{\Omega r} \frac{\tilde{\phi}_i^*(\vec{r}) \tilde{\phi}_j(\vec{r}) \sum_L \hat{Q}_{kl}^L(\vec{r}')}{|\vec{r} - \vec{r}'|} dr^3 d\vec{r}'^3$$

$$= \sum_{LM} \frac{4\pi}{2L+1} G^{LM}_{l_i m_i l_j m_j} (-1)^M q_{kl}^{L,-M}$$

$$\times \int_0^{r_{\mathrm{rad}}} dr \left[\int_0^r dr' \left(\frac{r'^{L+2}}{r^{L+1}} \right) g_L(r') \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r) + \int_r^{r_{\mathrm{rad}}} dr' \left(\frac{r^L}{r'^{L-1}} \right) g_L(r') \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r) \right]$$

$$\iint_{\Omega r} \frac{\tilde{\phi}_i^*(\vec{r}) \tilde{\phi}_j(\vec{r}) \tilde{\phi}_k^*(\vec{r}') \tilde{\phi}_l(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'^3 d\vec{r}^3$$

$$= \sum_{LM} \frac{4\pi}{2L+1} G^{LM}_{l_i m_i l_j m_j} (-1)^M G^{L,-M}_{l_k m_k l_l m_l}$$

$$\times \int_0^{r_{\mathrm{rad}}} dr \left[\int_0^r dr' \left(\frac{r'^L}{r^{L+1}} \right) \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r) \tilde{\phi}_{n_k l_k}(r') \tilde{\phi}_{n_l l_l}(r') + \int_r^{r_{\mathrm{rad}}} dr' \left(\frac{r^L}{r'^{L+1}} \right) \tilde{\phi}_{n_i l_i}(r) \tilde{\phi}_{n_j l_j}(r) \tilde{\phi}_{n_k l_k}(r') \tilde{\phi}_{n_l l_l}(r') \right]$$

$$\iint \frac{\sum_L \hat{Q}_{ij}^L(\vec{r}) \sum_{L'} \hat{Q}_{kl}^{L'}(\vec{r}')}{|\vec{r} - \vec{r}'|} dr^3 d\vec{r}'^3$$

$$= \sum_{LM} \frac{4\pi}{2L+1} (-1)^M q_{ij}^{LM} q_{kl}^{L,-M}$$

$$\times \int_0^{r_{\mathrm{rad}}} dr \left[\int_0^r dr' \left(\frac{r'^{L+2}}{r^{L-1}} \right) g_L(r) g_L(r') + \int_r^{r_{\mathrm{rad}}} dr' \left(\frac{r^{L+2}}{r'^{L-1}} \right) g_L(r) g_L(r') \right]$$

AIST

Outline of Lecture

1. **Pseudo-Potentials and Projectors 1) & 2)**
2. **Transformation Theory: Wave Functions, Expectation Values and Charge Density Distribution 3) & 4)**
3. **Formulation of Total Energy: Kinetic Energy, Exchange-Correlation Energy, Hartree Energy and Compensation Charge 3) & 4)**
4. **Hamiltonian, Kohn-Sham Equation, and Atomic Forces 4)**
5. **Representation by Plane-Wave Basis Set**
6. **Stress Tensor by Nielsen-Matrin Scheme 5)**
7. **Efficient Scheme to Obtain Ground-State Electronic Structure**

1) P.E. Blöchl, PRB 41 (1990) 5414,
2) D. Vanderbilt, PRB 41 (1990) 7892,
3) P.E. Blöchl, PRB 50 (1994) 17953,
4) G. Kresse and D. Joubert, PRB59 (1999) 1758,
5) O.H. Nielsen and R.M. Martin, PRB 32 (1985) 3780

Detailed Formulation ⇒ See *PAW Note* by QMAS Group

AIST

Representation by Plane-Wave Basis Set: Usage of the Symmetry

$\vec{k}\ in\ B.Z. \Rightarrow \vec{k}\ in\ I.P. \&\ Rotation\ \mathbf{R}$

Projector Function

$$\rho_{ij} = \sum_{n}^{occ} \sum_{\vec{k}\in B.Z.} f_{\vec{k}n} \langle \tilde{\Psi}_{\vec{k}n} | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\Psi}_{\vec{k}n} \rangle$$

k-Space Integration throughout Brillouin Zone (B.Z.)

$$\rho_{ij} = \sum_{n}^{occ} \sum_{\vec{k}\in I.P.} f_{\vec{k}n} \langle \tilde{\Psi}_{\vec{k}n} | \sum_{\mathbf{R}} \{\mathbf{R}|\vec{t}_s\}^{-1} \left(|\tilde{p}_i\rangle\langle\tilde{p}_j| \right) | \tilde{\Psi}_{\vec{k}n} \rangle$$

k-Space Integration in Irreducible Part (I.P.) in B.Z. by Using Symmetry. R: Rotation Matrix of Symmetric Element

Rotation of Spherical Harmonics

$$Y_{lm}(\mathbf{R}r) = \sum_{m'} Y_{lm'}(\hat{r}) \times D^l_{m'm}(\mathbf{R})$$

$$D^l_{m'm}(\alpha\beta\gamma) = e^{-i\alpha m'} d^l_{m'm}(\beta) e^{-i\gamma m}$$

Necessity to Rotate the Projector (Spherical Harmonics Y_{lm}) by R

$$|\tilde{p}_i\rangle = \frac{\tilde{P}_{n_i l_i}(r)}{r} Y_{l_i m_i}(\hat{r})$$

$$d^l_{m'm}(\beta) = \left[\frac{(l-m)!(l+m')!}{(l+m)!(l-m')!}\right]^{\frac{1}{2}} \frac{1}{(m'-m)!} \left(\cos\frac{\beta}{2}\right)^{2l-(m'-m)} \times \left(-\sin\frac{\beta}{2}\right)^{m'-m}$$
$$\times {}_2F_1\left(m'-l; -m-l; m'-m+1; -\tan^2\frac{\beta}{2}\right) \quad for \quad m' \geq m$$

$$d^l_{m'm}(\beta) = [(l+m)!(l-m)!(l+m')!(l-m')!]^{\frac{1}{2}}$$
$$\times \sum_k \frac{(-1)^k}{(l-m'-k)!(l+m-k)!(m'-m+k)!k!} \left(\cos\frac{\beta}{2}\right)^{2l-(m'-m)-2k}$$
$$\times \left(-\sin\frac{\beta}{2}\right)^{m'-m+2k}$$

α, β,γ: Euler Angles of R

See M.E. Rose, *Elementary Theory of Angular Momentum*

Representation by Plane-Wave Basis Set: Wave Functions and Projectors

$\{\vec{R}\}: Lattice\ Vector \quad \{\vec{G}\}: Reciprocal\ Lattice\ Vector$

$\{\vec{t}_a\}: Atomic\ Position\ Vector\ in\ the\ Cell \quad \Omega_c: Cell\ Volume$

$$|\vec{k}+\vec{G}\rangle = \Omega^{-\frac{1}{2}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$ **Plane Wave Basis**

$$\tilde{\Psi}_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C^n_{\vec{k}+\vec{G}} |\vec{k}+\vec{G}\rangle$$ **Pseudo Wave Function**

$$|\Psi_{\vec{k}n}(\vec{r})\rangle = \sum_{\vec{G}} C^n_{\vec{k}+\vec{G}} |\vec{k}+\vec{G}\rangle + \sum_i \{\Phi^{\vec{k}}_i(\vec{r}) - \tilde{\Phi}^{\vec{k}}_i(\vec{r})\} \sum_{\vec{G}} \langle \tilde{p}_i | \vec{k}+\vec{G}\rangle C^n_{\vec{k}+\vec{G}}$$ **True Wave Function**

$$\Phi^{\vec{k}}_i(\vec{r}) = \sum_R N^{-\frac{1}{2}} e^{i\vec{k}\cdot(\vec{t}_a+\vec{R})} |\phi_i(\vec{r}-\vec{t}_a-\vec{R})\rangle$$ **Bloch Sum of AE (PS) Partial Waves**

$$|\tilde{p}_i\rangle = P_i(r) Y_{l_i m_i}(\hat{r}) \qquad P_i(r) = \frac{\tilde{P}_{n_i l_i}(r)}{r}$$ **Projector at Each Atomic Site**

$$|\tilde{p}_i\rangle = \sum_{\vec{R}} |\tilde{p}_i(\vec{r}-\vec{t}_a-\vec{R})\rangle = \sum_{\vec{R}} P_i(|\vec{r}-\vec{t}_a-\vec{R}|) Y_{l_i m_i}(r-t_a-R)$$ **Projector in Supercell (Crystal) System**

$$\langle \vec{k}+\vec{G} | \tilde{p}_i \rangle = 4\pi\Omega_c^{-\frac{1}{2}} (-i)^{l_i} e^{-i\vec{G}\cdot\vec{t}_a} Y_{l_i m_i}(k+G) \int_0^\infty r^2 P_i(r) j_{l_i}(|\vec{k}+\vec{G}|r) dr$$

$$\langle \tilde{p}_i | \vec{k}+\vec{G} \rangle = 4\pi\Omega_c^{-\frac{1}{2}} (i)^{l_i} e^{i\vec{G}\cdot\vec{t}_a} Y_{l_i m_i}{}^*(k+G) \int_0^\infty r^2 P_i(r) j_{l_i}(|\vec{k}+\vec{G}|r) dr$$

Plane-Wave Expression of the Projector

Representation by Plane-Wave Basis Set: Projector Function and Charge Density Distribution

Projector Function at Atom a

$$\rho_{ij}^{a}=\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in\mathrm{I.P.}}f_{\vec{k}n}\sum_{\mathbf{R}}\Bigg[\sum_{m_i'}\sum_{m_j'}D_{m_i'm_i}^{l_i}(\mathbf{R})D_{m'_jm_j}^{l_j}{}^{*}(\mathbf{R})$$

$$\times\Bigg\{\left[\sum_{\vec{G}}\left\langle\tilde{p}_i(\vec{t}_b;m_i')\middle|\vec{k}+\vec{G}\right\rangle C_{\vec{k}+\vec{G}}^{n}\right]^{*}\left[\sum_{\vec{G}}\left\langle\tilde{p}_j(\vec{t}_b;m_j')\middle|\vec{k}+\vec{G}\right\rangle C_{\vec{k}+\vec{G}}^{n}\right]$$

$$+(-1)^{m_i'+m_j'}\left[\sum_{\vec{G}}\left\langle\tilde{p}_i(\vec{t}_b;-m_i')\middle|\vec{k}+\vec{G}\right\rangle C_{\vec{k}+\vec{G}}^{n}\right]\left[\sum_{\vec{G}}\left\langle\tilde{p}_j(\vec{t}_b;-m_j')\middle|\vec{k}+\vec{G}\right\rangle C_{\vec{k}+\vec{G}}^{n}\right]^{*}\Bigg\}\Bigg]$$

$\tilde{p}_i(\vec{t}_b;m_j)$: *Projector of the Same Atom at* $\vec{t}_b$ *Translated by* $\{\mathbf{R}\,|\,\vec{t}_{\mathbf{R}}\}^{-1}$ *from Atom a at* $\vec{t}_a$ *and with* $m=m_j$

R: Rotation Matrix of the Symmetric Element

Valence Charge Density

$$\tilde{n}(\vec{r})=\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in\mathrm{B.Z.}}f_{\vec{k}n}\left|\tilde{\Psi}_{\vec{k}n}(\vec{r})\right|^2=\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in\mathrm{I.P.}}f_{\vec{k}n}\sum_{\mathbf{R}}\left\{\left|\tilde{\Psi}_{\mathbf{R}\vec{k}n}(\vec{r})\right|^2+\left|\tilde{\Psi}_{-\mathbf{R}\vec{k}n}(\vec{r})\right|^2\right\}=\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in\mathrm{I.P.}}2f_{\vec{k}n}\sum_{\mathbf{R}}\sum_{\vec{G}}\left|C_{\mathbf{R}\vec{k}+\vec{G}}{}^{n}\right|^2$$

$$n^1(\vec{r})=\sum_{\vec{R}}\sum_{\vec{t}_a}\sum_{i,j}\rho_{ij}^{a}\,\phi_i^{*}(\vec{r}-\vec{t}_a-\vec{R})\phi_j(\vec{r}-\vec{t}_a-\vec{R})\qquad \tilde{n}^1(\vec{r})=\sum_{\vec{R}}\sum_{\vec{t}_a}\sum_{i,j}\rho_{ij}^{a}\,\tilde{\phi}_i^{*}(\vec{r}-\vec{t}_a-\vec{R})\tilde{\phi}_j(\vec{r}-\vec{t}_a-\vec{R})$$

Compensation Charge Density

$$\hat{n}(\vec{r})=\sum_{\vec{R}}\sum_{\vec{t}_a}\sum_{i,j}\rho_{ij}^{a}\sum_{lm}\hat{Q}_{ij}^{lm}(\vec{r}-\vec{t}_a-\vec{R})\qquad \hat{Q}_{ij}^{lm}(\vec{r}-\vec{t}_a-\vec{R})=q_{ij,a}^{lm}\times g_l\left(\left|\vec{r}-\vec{t}_a-\vec{R}\right|\right)\times Y_{lm}(r-t_a-R)$$

$$\hat{n}(\vec{r})=\sum_{\vec{G}}\hat{n}(\vec{G})\,e^{i\vec{G}\cdot\vec{r}}$$ **Fourier Components**

Representation by Plane-Wave Basis Set: Total Energy

$$E_{tot}=E_{kin}+E_{xc}+E_{H}+E_{local}+E^{1}-\tilde{E}^{1}+E_{i-i}$$

$$E_{kin}=\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in\mathrm{I.P.}}f_{\vec{k}n}\sum_{\mathbf{R}}\left\{\left\langle\tilde{\Psi}_{\mathbf{R}\vec{k}n}\middle|-\frac{1}{2}\Delta\middle|\tilde{\Psi}_{\mathbf{R}\vec{k}n}\right\rangle+\left\langle\tilde{\Psi}_{-\mathbf{R}\vec{k}n}\middle|-\frac{1}{2}\Delta\middle|\tilde{\Psi}_{-\mathbf{R}\vec{k}n}\right\rangle\right\}$$

$E_{i\text{-}i}$: Ion-Ion Electrostatic Energy

$$\left\langle\tilde{\Psi}_{\mathbf{R}\vec{k}n}\middle|-\frac{1}{2}\Delta\middle|\tilde{\Psi}_{\mathbf{R}\vec{k}n}\right\rangle=\frac{1}{2}\sum_{\vec{G}}\left|\vec{k}+\mathbf{R}^{-1}\vec{G}\right|^2\left|C_{\vec{k}+\mathbf{R}^{-1}\vec{G}}^{n}\right|^2=\frac{1}{2}\sum_{\vec{G}}\left|\vec{k}+\vec{G}\right|^2\left|C_{\vec{k}+\vec{G}}^{n}\right|^2\qquad\left\langle\tilde{\Psi}_{-\mathbf{R}\vec{k}n}\middle|-\frac{1}{2}\Delta\middle|\tilde{\Psi}_{-\mathbf{R}\vec{k}n}\right\rangle=\frac{1}{2}\sum_{\vec{G}}\left|\vec{k}+\vec{G}\right|^2\left|C_{\vec{k}+\vec{G}}^{n}\right|^2$$

$$E_{xc}=\int\varepsilon_{xc}\left(\tilde{n}(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_c(\vec{r})\right)\left(\tilde{n}(\vec{r})+\hat{n}(\vec{r})+\tilde{n}_c(\vec{r})\right)d\vec{r}$$

$n(G)$, $V_H(G)$, $V_{loc}(G)$: Fourier Components

$$E_H=\frac{1}{2}\int V_H(\vec{r})n(\vec{r})d\vec{r}^{\,3}=\frac{1}{2}\Omega_c\sum_{\vec{G}\neq0}V_H(\vec{G})n(-\vec{G})$$

$$V_{loc}(\vec{r})=\sum_{\vec{R}}\sum_{\vec{t}_a}\mathrm{v}_{loc}^{a}(\vec{r}-\vec{t}_a-\vec{R})=\sum_{\vec{G}}V_{loc}(\vec{G})\,e^{i\vec{G}\cdot\vec{r}}$$

$$E_{local}=\int V_{loc}(\vec{r})n(\vec{r})d\vec{r}=\Omega_c\sum_{\vec{G}\neq0}V_{loc}(\vec{G})n(-\vec{G})$$

V^{a}_{loc}: Unscreened Atomic Local PP

$$n(\vec{r})=\tilde{n}(\vec{r})+\hat{n}(\vec{r})=\sum_{\vec{G}}n(\vec{G})e^{i\vec{G}\cdot\vec{r}}\qquad V_H(\vec{G}):\ \textit{From Poisson Equation of}\ n(\vec{G})$$

$$E^1=\sum_{\vec{t}_a}\sum_{i,j}\rho_{ij}^{a}\left\langle\phi_i^{a}\middle|-\frac{1}{2}\Delta\middle|\phi_j^{a}\right\rangle+\sum_{\vec{t}_a}\overline{E_{xc}\left[n^1+n_c\right]}+\sum_{\vec{t}_a}\overline{E_H\left[n^1(\vec{r}-\vec{t}_a)\right]}+\sum_{\vec{t}_a}\int_{\Omega_r}\upsilon_H[n_{zc}]n^1(\vec{r}-\vec{t}_a)d\vec{r}^{\,3}$$

$$\tilde{E}^1=\sum_{\vec{t}_a}\sum_{i,j}\rho_{ij}^{a}\left\langle\phi_i^{a}\middle|-\tfrac{1}{2}\Delta\middle|\tilde{\phi}_j^{a}\right\rangle+\sum_{\vec{t}_a}\overline{E_{xc}\left[\tilde{n}^1+\hat{n}+\tilde{n}_c\right]}+\sum_{\vec{t}_a}\overline{E_H\left[\tilde{n}^1+\hat{n}\right]}+\sum_{\vec{t}_a}\int_{\Omega_r}\upsilon_H[\tilde{n}_{zc}](\tilde{n}^1+\hat{n})d\vec{r}^{\,3}$$

Representation by Plane-Wave Basis Set: Atomic Terms inside Atomic Sphere

$$E^1=\sum_{\vec{t}_a}\sum_{i,j}\rho^a_{ij}\left\langle\phi^a_i\left|-\tfrac{1}{2}\Delta\right|\phi^a_j\right\rangle+\sum_{\vec{t}_a}\overline{E_{xc}\left[n^1+n_c\right]}+\sum_{\vec{t}_a}\overline{E_H\left[n^1\left(\vec{r}-\vec{t}_a\right)\right]}+\sum_{\vec{t}_a}\int_{\Omega_r}\upsilon_H\left[n_{zc}\right]n^1\left(\vec{r}-\vec{t}_a\right)d\vec{r}^3$$

The 3rd term contains this type of integration

$$\frac{e^2}{2}\sum_{i,j}\sum_{k,l}\rho^a_{ij}\rho^a_{kl}\iint_{\Omega_r}\frac{\phi^{a^*}_i(\vec{r})\phi^a_j(\vec{r})\phi^{a^*}_k(\vec{r}')\phi^a_l(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}^3d\vec{r}'^3$$

$$=\frac{e^2}{2}\sum_{i,j}\sum_{k,l}\rho^a_{ij}\rho^a_{kl}\times V^a_{ij;kl}$$

The 4th term contains this type of integration

$$\int_{\Omega_r}\upsilon_H\left[n_{zc}\right](r)\sum_{ij}\rho^a_{ij}\,\phi^{a^*}_i(\vec{r})\phi^a_j(\vec{r})d\vec{r}^3$$

$$=\sum_{i,j}\rho^a_{ij}\left\langle\phi^a_i\left|\upsilon_H\left[n_{zc}\right]\right|\phi^a_j\right\rangle$$

$$=\sum_{i,j}\rho^a_{ij}\times\delta_{l_il_j}\delta_{m_im_j}\times\int_0^{r_{\mathrm{rad}}}\upsilon_H\left[n_{zc}\right](r)\times\phi^a_{n_il_i}(r)\phi^a_{n_jl_j}(r)dr$$

$$\tilde{E}^1=\sum_{\vec{t}_a}\sum_{i,j}\rho^a_{ij}\left\langle\phi^a_i\left|-\tfrac{1}{2}\Delta\right|\tilde{\phi}^a_j\right\rangle+\sum_{\vec{t}_a}\overline{E_{xc}\left[\tilde{n}^1+\hat{n}+\tilde{n}_c\right]}+\sum_{\vec{t}_a}\overline{E_H\left[\tilde{n}^1+\hat{n}\right]}+\sum_{\vec{t}_a}\int_{\Omega_r}\upsilon_H\left[\tilde{n}_{zc}\right]\left(\tilde{n}^1+\hat{n}\right)d\vec{r}^3$$

The 3rd term contains this type of integration

$$\frac{e^2}{2}\sum_{i,j}\sum_{k,l}\rho^a_{ij}\rho^a_{kl}\times\left[\iint_{\Omega_r}\frac{\tilde{\phi}^*_i\tilde{\phi}_j\tilde{\phi}^*_k\tilde{\phi}_l}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}^3d\vec{r}'^3+\iint_{\Omega_r}\frac{\tilde{\phi}^*_i\tilde{\phi}_j\sum_{lm}\hat{Q}^{lm}_{kl,a}(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}^3d\vec{r}'^3\right.$$

$$\left.+\iint\frac{\tilde{\phi}^*_k\tilde{\phi}_l\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}^3d\vec{r}'^3+\iint_{\Omega_r}\frac{\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r}')\sum_{lm}\hat{Q}^{lm}_{kl,a}(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}^3d\vec{r}'^3\right]$$

Representation by Plane-Wave Basis Set: Hamiltonian and Kohn-Sham Equation

$$H=-\tfrac{1}{2}\Delta+\tilde{\upsilon}_{\mathrm{eff}}(\vec{r})+\sum_{\vec{R}}\sum_{\vec{t}_a}\sum_{i,j}\left|\tilde{p}_i\left(\vec{r}-\vec{t}_a-\vec{R}\right)\right\rangle\left(\hat{D}^a_{ij}+D^a_{ij}-\tilde{D}^a_{ij}\right)\left\langle\tilde{p}_j\left(\vec{r}-\vec{t}_a-\vec{R}\right)\right|$$

$$\hat{D}^a_{ij}=\int\tilde{\upsilon}_{\mathrm{eff}}(\vec{r})\sum_{lm}\hat{Q}^{lm}_{ij,a}\left(\vec{r}-\vec{t}_a\right)d\vec{r}^3$$

$$=\Omega_c\sum_{\vec{G}}\tilde{\upsilon}_{\mathrm{eff}}\left(\vec{G}\right)\times Q_{ij,a}\left(-\vec{G}\right)$$

Integration in the Crystal (Supercell)

$$D^a_{ij}=\left\langle\phi^a_i\left|-\tfrac{1}{2}\Delta\right|\phi^a_j\right\rangle+\left\langle\phi^a_i\left|\upsilon_H\left[n_{nz}\right]\right|\phi^a_j\right\rangle$$

$$+\left\langle\phi^a_i\left|\upsilon_H\left[n^1\right]\right|\phi^a_j\right\rangle+\left\langle\phi^a_i\left|\upsilon_{xc}\left[n^1+n_c\right]\right|\phi^a_j\right\rangle$$

Integration inside Each Atomic Sphere

$$\tilde{D}^a_{ij}=\left\langle\tilde{\phi}^a_i\left|-\tfrac{1}{2}\Delta\right|\tilde{\phi}^a_j\right\rangle+\left\langle\tilde{\phi}^a_i\left|\upsilon_H\left[\tilde{n}_{zc}\right]\right|\tilde{\phi}^a_j\right\rangle$$

$$+\left\langle\tilde{\phi}^a_i\left|\upsilon_H\left[\tilde{n}^1+\hat{n}\right]\right|\tilde{\phi}^a_j\right\rangle+\left\langle\tilde{\phi}^a_i\left|\upsilon_{xc}\left[\tilde{n}^1+\hat{n}+\tilde{n}_c\right]\right|\tilde{\phi}^a_j\right\rangle$$

$$+\int_{\Omega_r}d\vec{r}^3\left\{\upsilon_H\left[\tilde{n}_{zc}\right]+\upsilon_H\left[\tilde{n}^1+\hat{n}\right]+\upsilon_{xc}\left[\tilde{n}^1+\hat{n}+\tilde{n}_c\right]\right\}\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r})$$

$$S=1+\sum_{\vec{R}}\sum_{\vec{t}_a}\sum_{i,j}\left|\tilde{p}_i\left(\vec{r}-\vec{t}_a-\vec{R}\right)\right\rangle q_{ij,a}\left\langle\tilde{p}_j\left(\vec{r}-\vec{t}_a-\vec{R}\right)\right|$$

$$q_{ij,a}=\left\langle\phi^a_i\middle|\phi^a_j\right\rangle-\left\langle\tilde{\phi}^a_i\middle|\tilde{\phi}^a_j\right\rangle$$

Integration within r_c

Outline of Lecture

1. **Pseudo-Potentials and Projectors** 1) & 2)
2. **Transformation Theory: Wave Functions, Expectation Values and Charge Density Distribution** 3) & 4)
3. **Formulation of Total Energy: Kinetic Energy, Exchange-Correlation Energy, Hartree Energy and Compensation Charge** 3) & 4)
4. **Hamiltonian, Kohn-Sham Equation, and Atomic Forces** 4)
5. **Representation by Plane-Wave Basis Set**
6. **Stress Tensor by Nielsen-Matrin Scheme** 5)
7. **Efficient Scheme to Obtain Ground-State Electronic Structure**

1) P.E. Blöchl, PRB 41 (1990) 5414,
2) D. Vanderbilt, PRB 41 (1990) 7892,
3) P.E. Blöchl, PRB 50 (1994) 17953,
4) G. Kresse and D. Joubert, PRB59 (1999) 1758,
5) O.H. Nielsen and R.M. Martin, PRB 32 (1985) 3780

Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Stress Tensor in Plane-Wave Basis Expression: General Rules to Derive the Expression

$$\sigma_{\alpha\beta} = \frac{1}{\Omega_c}\frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\alpha\beta}}$$

Definition of Stress Tensor

Ω_c : *Cell Volume* $\quad \varepsilon_{\alpha\beta}$: *Strain Tensor*

Uniform Deformation of the Crystal by Strain Tensor

$$\vec{R} \Rightarrow (\mathbf{I}+\boldsymbol{\varepsilon})\vec{R} \qquad \frac{\partial |\vec{R}|^2}{\partial \varepsilon_{\alpha\beta}} = 2R_\alpha R_\beta \qquad \frac{\partial R_\gamma}{\partial \varepsilon_{\alpha\beta}} = \delta_{\alpha\gamma} R_\beta$$

$$\vec{G} \Rightarrow (\mathbf{I}-\boldsymbol{\varepsilon})\vec{G} \qquad \frac{\partial |\vec{G}|^2}{\partial \varepsilon_{\alpha\beta}} = -2G_\alpha G_\beta \qquad \frac{\partial G_\gamma}{\partial \varepsilon_{\alpha\beta}} = -\delta_{\alpha\gamma} G_\beta$$

$$\frac{\partial \Omega_c}{\partial \varepsilon_{\alpha\beta}} = \delta_{\alpha\beta}\Omega_c \qquad \frac{\partial \Omega_c^{\ -1}}{\partial \varepsilon_{\alpha\beta}} = -\delta_{\alpha\beta}\Omega_c^{\ -1}$$

Nielsen & Martin,
PRB 32 (1985) 3780

Stress Tensor in Plane-Wave Basis (Reciprocal-Space) Expression

$$E_{tot}=E_{kin}+E_{xc}+E_{H}+E_{local}+E^1-\tilde{E}^1+E_{i-i} \qquad E_{non-local}=E^1-\tilde{E}^1$$

$$\frac{\partial E_{kin}}{\partial \varepsilon_{\alpha\beta}}=(-2)\sum_{n}^{\mathrm{occ}}\sum_{\vec{k}\in \mathrm{I.P.}} f_{\vec{k}n}\sum_{\mathbf{R}}\sum_{\vec{G}}\left|C^{n}_{\vec{k}+\mathbf{R}^{-1}\vec{G}}\right|^2\left[\mathbf{R}\left(\vec{k}+\mathbf{R}^{-1}\vec{G}\right)\right]_{\alpha}\left[\mathbf{R}\left(\vec{k}+\mathbf{R}^{-1}\vec{G}\right)\right]_{\beta}$$

$$=(-2)\sum_{\mathbf{R}}\sum_{\gamma,\delta}R_{\alpha\gamma}R_{\beta\delta}\sum_{n}^{occ}\sum_{\vec{k}\in \mathrm{I.P.}} f_{\vec{k}n}\sum_{\vec{G}}\left|C^{n}_{\vec{k}+\vec{G}}\right|^2(\vec{k}+\vec{G})_{\gamma}(\vec{k}+\vec{G})_{\delta}$$

R: Rotation Matrix of the Symmetric Element

$$\frac{\partial E_{xc}}{\partial \varepsilon_{\alpha\beta}}=\delta_{\alpha\beta}\Omega_c\sum_{\vec{G}}\varepsilon_{xc}(\vec{G})n(\vec{G})^{*}-\delta_{\alpha\beta}\Omega_c\sum_{\vec{G}}\mu_{xc}(\vec{G})\tilde{n}(\vec{G})^{*}$$

$$+\Omega_c\sum_{\vec{G}}\mu_{xc}(\vec{G})\left(\frac{\partial \hat{n}(\vec{G})^{*}}{\partial \varepsilon_{\alpha\beta}}+\frac{\partial \tilde{n}_c(\vec{G})^{*}}{\partial \varepsilon_{\alpha\beta}}\right)$$

LDA Form

$$n(\vec{r})=\tilde{n}(\vec{r})+\hat{n}(\vec{r})=\sum_{\vec{G}}n(\vec{G})\,e^{i\vec{G}\cdot\vec{r}}$$

$$n(\vec{G})=\tilde{n}(\vec{G})+\hat{n}(\vec{G})$$

$$\frac{\partial E_{H}}{\partial \varepsilon_{\alpha\beta}}=-\delta_{\alpha\beta}E_H+\Omega_c\sum_{\vec{G}\neq 0}\frac{4\pi e^2\left|n(\vec{G})\right|^2}{\left|\vec{G}\right|^2}\times\frac{G_{\alpha}G_{\beta}}{\left|\vec{G}\right|^2}$$

$$+\frac{1}{2}\Omega_c\sum_{\vec{G}\neq 0}\frac{4\pi e^2}{\left|\vec{G}\right|^2}\left\{\left(\delta_{\alpha\beta}\hat{n}(\vec{G})+\frac{\partial \hat{n}(\vec{G})}{\partial \varepsilon_{\alpha\beta}}\right)n^{*}(\vec{G})+\mathrm{c.c.}\right\}$$

Stress Tensor in Plane-Wave Basis (Reciprocal-Space) Expression

$$E_{tot}=E_{kin}+E_{xc}+E_{H}+E_{local}+E^1-\tilde{E}^1+E_{i-i} \qquad E_{non-local}=E^1-\tilde{E}^1$$

$$\frac{\partial E_{local}}{\partial \varepsilon_{\alpha\beta}}=\Omega_c\sum_{\vec{G}\neq 0}V_{\mathrm{loc}}(\vec{G})\left(-\delta_{\alpha\beta}\tilde{n}^{*}(\vec{G})+\frac{\partial \hat{n}^{*}(\vec{G})}{\partial \varepsilon_{\alpha\beta}}\right)$$

$$+\sum_{\vec{G}\neq 0}n^{*}(\vec{G})\frac{G_{\alpha}G_{\beta}}{\left|\vec{G}\right|}\times 4\pi\sum_{\vec{\tau}_a}e^{-i\vec{G}\cdot\vec{\tau}_a}\int_0^{\infty}V^{a}_{loc}(r)\times r^3\times j_1\left(\left|\vec{G}\right|r\right)dr$$

V^a_{loc}: Unscreened Atomic Local PP

$$\frac{\partial E_{non\text{-}local}}{\partial \varepsilon_{\alpha\beta}}=\sum_{\vec{\tau}_a}\sum_{ij}\left(\frac{\partial \rho^a_{ij}}{\partial \varepsilon_{\alpha\beta}}\right)\left(K^a_{ij}+V^a_{ij}+\sum_{kl}e^2\rho^a_{kl}W^a_{ij:kl}\right)$$

$$+\sum_{\vec{\tau}_a}\sum_{ij}\left(\frac{\partial \rho^a_{ij}}{\partial \varepsilon_{\alpha\beta}}\right)\int_{\Omega_a}\left\{\mu_{xc}\left(n^1_a+n^a_c\right)\phi_i^{a*}(\vec{r})\phi_j^a(\vec{r})\right.$$

$$\left.-\mu_{xc}\left(\tilde{n}^1_a+\hat{n}^a+\tilde{n}^a_c\right)\times\left(\tilde{\phi}_i^{a*}(\vec{r})\tilde{\phi}_j^a(\vec{r})+\sum_{lm}\hat{Q}^{lm}_{ij,a}(\vec{r})\right)\right\}d\vec{r}^{\,3}$$

$$K^a_{ij},\ V^a_{ij}\ \ and\ \ W^a_{ij:lk}$$

Atomic Terms of Atom a

$$\frac{\partial \hat{n}(\vec{G})}{\partial \varepsilon_{\alpha\beta}},\ \frac{\partial \tilde{n}_c(\vec{G})}{\partial \varepsilon_{\alpha\beta}}\ \ and\ \ \frac{\partial \rho_{ij}}{\partial \varepsilon_{\alpha\beta}}$$

Details are given in *PAW Note.*

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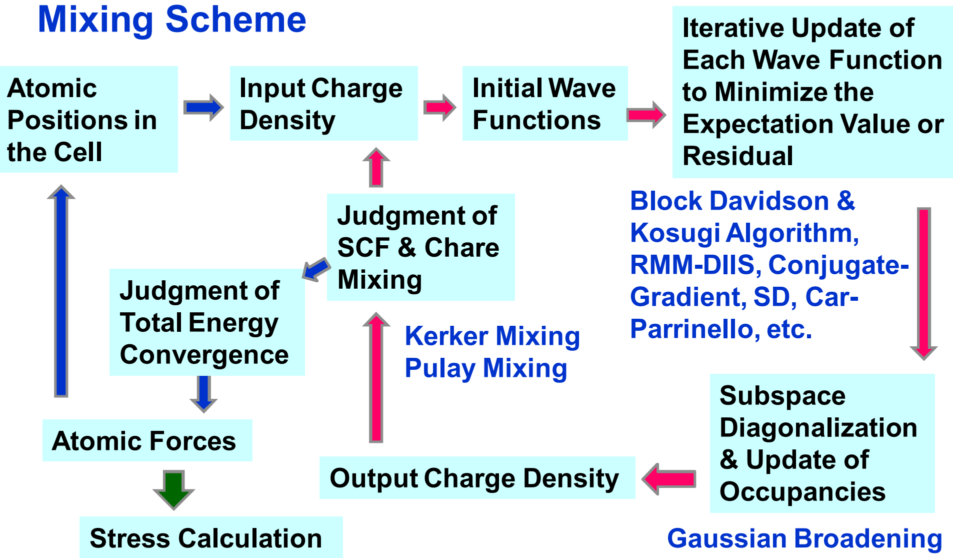
Detailed Formulation ⇒ See *PAW Note* by QMAS Group

Procedure to Obtain the Electronic Ground State by Iterative Schemes coupled with a Charge Mixing Scheme



How to Obtain the Electronic Ground State Efficiently by Iterative Schemes

Total-Energy Minimization in DFT

$$F = E_{tot}[\{\varphi_i\}] - \sum_{ij} \lambda_{ij}(\langle \varphi_i | \varphi_j \rangle - \delta_{ij})$$

Gradient or Residual

$$\frac{\delta F}{\delta \varphi_i^*} = \frac{\delta E_{tot}}{\delta \varphi_i^*} - \sum_j \lambda_{ij}\varphi_j = H\varphi_i - \lambda_i \varphi_i = (H - \lambda_i)\varphi_i = -g_i$$

$$\varphi_i = \varphi_i^0 + \delta\varphi_i \qquad \frac{\delta F}{\delta \varphi_i^*} = (H-\lambda_i)\varphi_i = (H-\lambda_i)(\varphi_i^0 + \delta\varphi_i) = (H-\lambda_i)\delta\varphi_i$$

$$\delta\varphi_i = H_s^{-1}(H-\lambda_i)\varphi_i = -H_s^{-1} g_i \qquad M \times N_{pw}^2 \Rightarrow M^2 \times N_{pw}$$

$$\varphi_i^0 = \varphi_i - \delta\varphi_i = \varphi_i - K(H-\lambda_i)\varphi_i = \varphi_i + Kg_i$$

***K*: Preconditioning**

$$\varphi_i'' = \varphi_i - \sum_{j<i} \langle \varphi_j' | \varphi_i \rangle \varphi_j' \qquad \varphi_i' = \varphi_i'' / |\varphi_i''|$$

Gram-Schmidt Orthogonalization

①Steepest Descent Method, Conjugate-Gradient Method, ②RMM-DIIS Method, ③Block Davidson Method, Kosugi Method, etc.

Comparison between Steepest Descent and Conjugate-Gradient Schemes

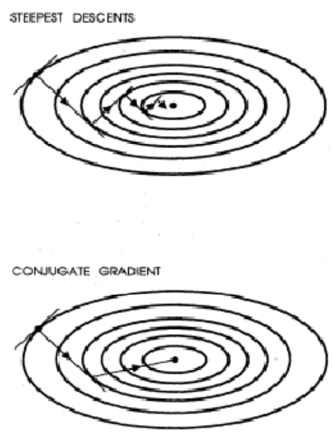


FIG. 14. Schematic illustration of two methods of convergence to the center of an anisotropic harmonic potential. Top: steepest-descents method requires many steps to converge. Bottom: Conjugate-gradients method allows convergence in two steps.

Gradient

$$g_i^m = -(H - \lambda_i^m)\varphi_i^m$$

$$\varphi_i^{m+1} = \varphi_i^m + \gamma K g_i^m \qquad \textbf{SG}$$

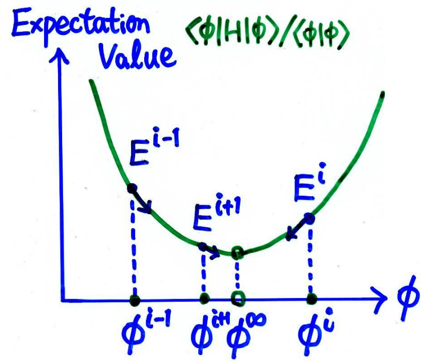
$$\varphi_i^{m+1} = \varphi_i^m + \alpha\phi_i^m \qquad \textbf{CG}$$

$$\phi_i^m = K g_i^m + \gamma_m \phi_i^{m-1}$$

$$\gamma_m = \frac{\langle g_i^m | g_i^m \rangle}{\langle g_i^{m-1} | g_i^{m-1} \rangle}$$

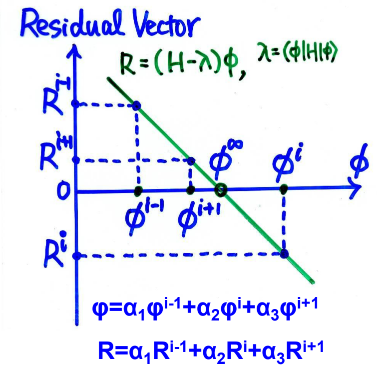
Comparison between Conjugate-Gradient and RMM-DIIS Schemes

Conjugate-Gradient or Steepest Descent Scheme



Minimization of Expectation Value.
Update by Gradient - $(H-\lambda)\varphi$

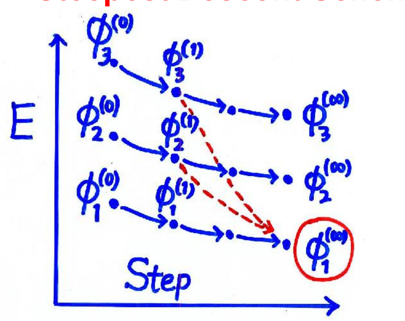
RMM-DIIS Scheme (Pulay)



Minimization of Residual:
$R=(H-\lambda)\varphi$. φ is Updated So As to Minimize $\langle R|R\rangle$.

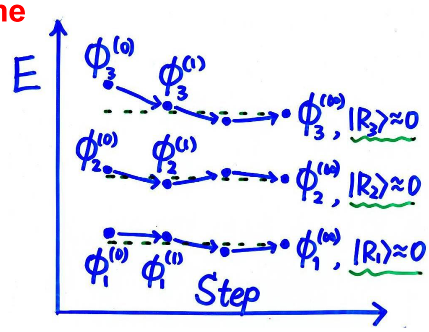
Comparison between Conjugate-Gradient and RMM-DIIS Schemes

Conjugate-Gradient or Steepest Descent Scheme



All the States Converge to the Same Bottom State if No Explicit Orthogonalization.
Explicit Orthogonalization is Essential.

RMM-DIIS Scheme



Each State Can Converge to a Near Eigen State with R=0. No Need of Frequent Orthogonalization. Each State can be Updated Independently in Each CPU.

Block Davidson Scheme & Kosugi Algorithm

$$\delta\varphi_i^m = -H_s^{-1}(H-\lambda_i^m)\varphi_i^m = H_s^{-1} g_i^m \qquad N_{pw} \times N_{pw}$$

$$\varphi_i^{m+1} = \varphi_i^m + \delta\varphi_i^m$$

$$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle \quad H\phi_i = \varepsilon_i \phi_i \quad \phi_i = \sum_j C_{ij}\varphi_j \qquad M \times M$$

Subspace Diagonalization $\{\varphi_i\} \Rightarrow \{\phi_i\}$

Block Davidson Scheme

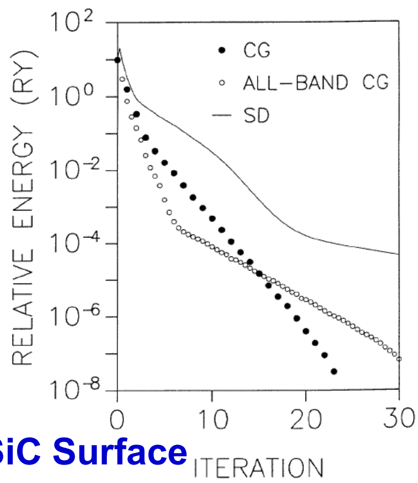
$$\{\varphi_i, \delta\varphi_i\} \quad H_{ij} = \langle \varphi_i | H | \varphi_j \rangle \quad H_{i,j+M} = \langle \varphi_i | H | \delta\varphi_j \rangle$$

$$2M \times 2M$$

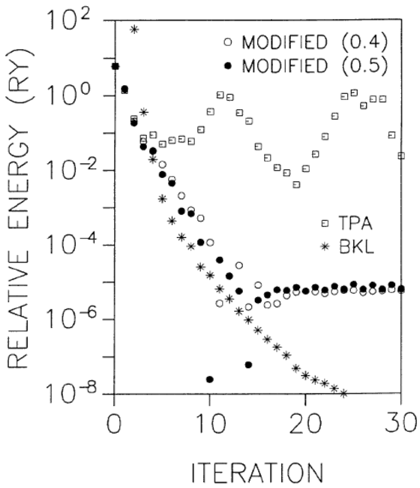
Kosugi Algorithm

$$\{\varphi_i, \delta\varphi_i\}_{i=1,m_1} \quad \{\varphi_i, \delta\varphi_i\}_{i=m_1+1,m_2} \qquad 2m_1 \times 2m_1$$

Comparison between Conjugate-Gradient and Steepest Descent Schemes



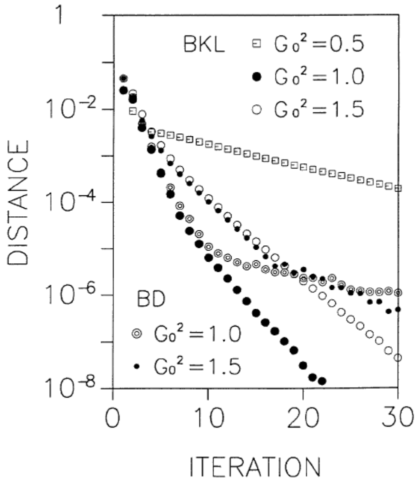
SiC Surface

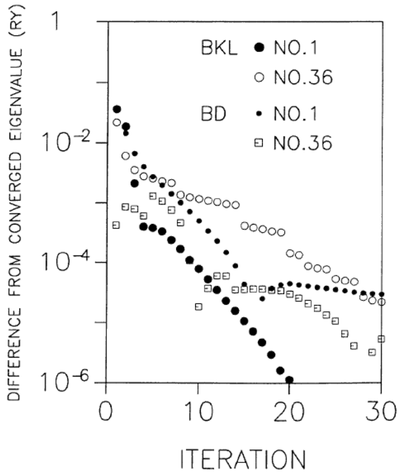


M. Kohyama, *MSMSE* 4 (1996) 397

SiC/Al Interface

Comparison between Conjugate-Gradient and Block Davidson Schemes





Dependence on the Parameters of Kerker Scheme

M. Kohyama, *MSMSE* 4 (1996) 397 **SiC/Al Interfaces**

Efficient Charge Mixing Scheme in Self-Consistent Iterations

$$F = E_{tot}[\{\varphi_i\}] - \sum_{ij} \lambda_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij})$$

$$\frac{\delta F}{\delta \varphi_i^*} = \frac{\delta E_{tot}}{\delta \varphi_i^*} - \sum_j \lambda_{ij} \varphi_j = H\varphi_i - \lambda_i \varphi_i = (H - \lambda_i)\varphi_i$$

$$H[\rho_{in}]\varphi_i = \lambda_i \varphi_i \Longleftrightarrow \rho_{out} = \sum_i f_i |\varphi_i|^2$$

$$\rho_{in}^{new} = \Xi(\rho_{in}^{old}, \rho_{out}^{old})$$

$$\rho_{in}^{new}(\vec{G}) = \rho_{in}^{old}(\vec{G}) + A\frac{|\vec{G}|^2}{|\vec{G}|^2 + G_0^2}(\rho_{out}^{old}(\vec{G}) - \rho_{in}^{old}(\vec{G}))$$ **Kerker Mixing**

$$\rho_{in}^{m} = \Xi(\rho_{in}^{m-n} \sim \rho_{in}^{m-1}, \rho_{out}^{m-n} \sim \rho_{out}^{m-1})$$ **Pulay Mixing**

Parallelization by MPI

$$H\varphi_i = \lambda_i \varphi_i \quad \{\varphi_i\} \quad \varphi_i \Rightarrow$$ **Each Node**

$$H\varphi_i \quad N_{pw} \times N_{pw} \Rightarrow N_{pw} log N_{pw}$$ **FFT in Each Node**

$$\delta\varphi_i^m = -H_s^{-1}(H-\lambda_i^m)\varphi_i^m = H_s^{-1} g_i^m \qquad \varphi_i^{m+1} = \varphi_i^m + \delta\varphi_i^m$$

Independent Update of Each Wave Function in Each Node, But Necessity of Mutual Orthogonalization

$$\varphi_i'' = \varphi_i - \sum_{j<i} \langle \varphi_j' | \varphi_i \rangle \varphi_j' \qquad \varphi_i' = \varphi_i'' / |\varphi_i''|$$ **Gram-Schmidt Orhogonalization**

$$M^2 N_{pw}$$

Necessity of Large Data Communication among Nodes

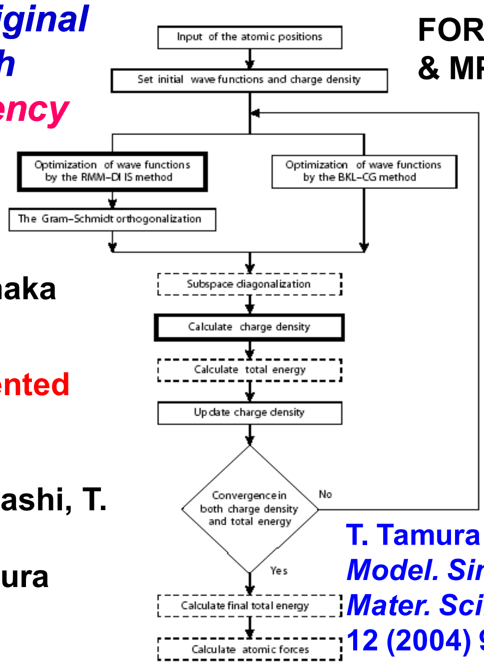
Development of Original Ab Initio Codes with High Parallel Efficiency

FORTRAN & MPI

Norm-Conserving PP Version "KAMIKAZE"

by M. Kohyama, S. Tanaka and T. Tamura (2001-)

PAW (Projector Augmented Wave) Version "QMAS (Qauntum MAterials Simulator)" by S. Ishibashi, T. Tamura, S. Tanaka, M. Kohyama and K. Terakura (2004-)



T. Tamura *et al.*, *Model. Simul. Mater. Sci. Eng.* 12 (2004) 945

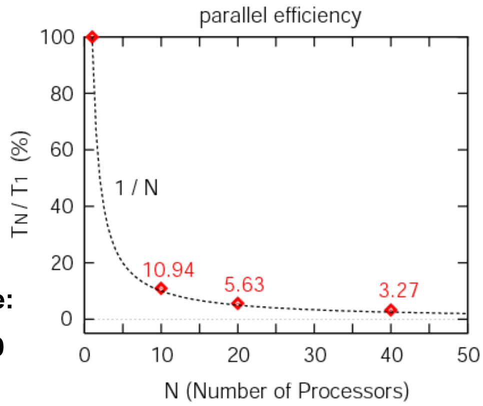
Efficiency of Parallel Computation RMM-DIIS: QMAS(PAW) Version

SiO_2 72-Atom Cell

N_{pw}=12915
384 Electrons

Cluster Machine:

Intel Xeon × 449 Node



Ratio T_N/T_1: 10.94% (10 Nodes: Ideal 10%), 5.63% (20 Nodes: Ideal 5%), 3.27% (40 Nodes: Ideal 2.5%)
Efficiency δ: 99%, α: 76%

Even for Large Numbers of Nodes, Parallel Efficiency is Very Good. For N=40, δ=99% and α=76%