The 32th CMD workshop
”Practice of ESopt”

Basic theory

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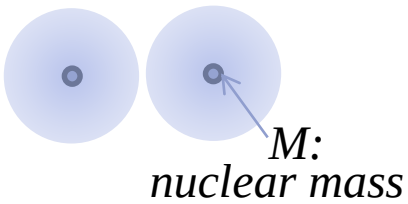
Born-Oppenheimer approximation

- Based on difference in the mass, separation of the quantum mechanical motion is done. (the error scales as $(m/M)^{6/4}$.)

Cf. S. Takahashi, K. Takatsuka, J. Chem. Phys. ***124****, 144101 (2006).*

$$\left\{\hat{H}_{el}+\hat{H}_{el-ion}+\hat{H}_{ion-ion}\right\}\left|\Psi\right\rangle\otimes\left|\Phi_{ion}\left(\left\{\mathbf{R}_I\right\}\right)\right\rangle$$
$$=\left\{E+E_{ion-ion}\right\}\left|\Psi\right\rangle\otimes\left|\Phi_{ion}\left(\left\{\mathbf{R}_I\right\}\right)\right\rangle.$$



- Existence of stable materials allows us to fix positions for the mass centers of nuclei. Then,

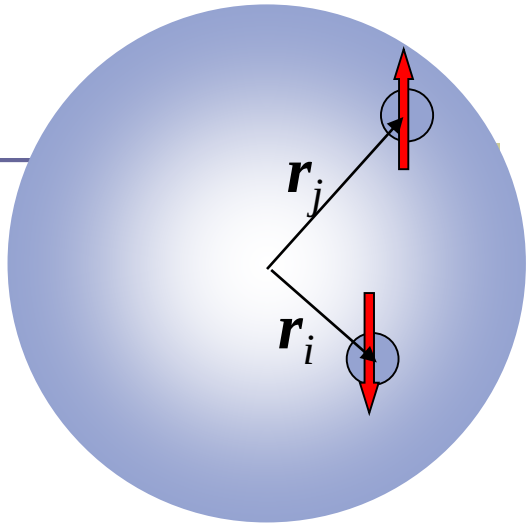
Multiply $\left\langle\left\{\mathbf{R}_I\right\}\right|$ to the Schrödinger equation from the left,

and define the external potential $v_{ext}(\mathbf{r})=\sum_{I=1}^{N_{ion}}\frac{Z_I e^2}{\left|\mathbf{r}-\mathbf{R}_I\right|}$ for the electrons, we have,

$$\left[-\sum_{\sigma}\int d^3r\left(\frac{\hbar^2}{2m}\right)\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})\nabla^2\hat{\psi}_{\sigma}(\mathbf{r})+\iint d^3r d^3r'\frac{e^2:\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}'):}{\left|\mathbf{r}-\mathbf{r}'\right|}+\int d^3r v_{ext}(\mathbf{r})\hat{n}(\mathbf{r})\right]\left|\Psi\right\rangle$$
$$=E\left|\Psi\right\rangle.$$

The Coulomb gauge is fixed as the photon propagator in a steady state.

Hamiltonian



- Static state of electron system:
  - Represented by potential:

$$v_{ext}(\mathbf{r}_i) \qquad V(\boldsymbol{r}_i, \boldsymbol{r}_j) = \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}.$$

  - Cf: Ehrenfest's theorem $\frac{d}{dt}\langle\Psi|\mathbf{p}|\Psi\rangle = \langle\Psi|-\nabla v_{ext}(\mathbf{r})|\Psi\rangle$

- The Hamiltonian
  - Velocities of electrons < the velocity of light,
  - In a steady material, internal gauge field behaves as the Coulomb potential.

$$H = -\sum_{i=1}^{N}\left(\frac{\hbar^2}{2m}\right)\nabla_{\mathbf{r}_i}^2 + \sum_{\langle i,j\rangle}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i).$$

A practice

- Let's have an expression of the energy by v_{ext}.

$$E_{ext} = \int \prod_l d^3 r_l \sum_{\sigma_l = \pm 1} \Psi^*(\{\mathbf{r}_l, \sigma_l\}) \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) \Psi(\{\mathbf{r}_l, \sigma_l\})$$

$$= N \int \prod_l d^3 r_l \sum_{\sigma_l = \pm 1} v_{ext}(\mathbf{r}_1) \left|\Psi(\{\mathbf{r}_l, \sigma_l\})\right|^2$$

$$= \int d^3 r v_{ext}(\mathbf{r}) N \int \prod_l d^3 r_l \sum_{\sigma_l = \pm 1} \delta(\mathbf{r} - \mathbf{r}_1) \left|\Psi(\{\mathbf{r}_l, \sigma_l\})\right|^2$$

$$= \int d^3 r v_{ext}(\mathbf{r}) \int \prod_l d^3 r_l \sum_{\sigma_l = \pm 1} \Psi^*(\{\mathbf{r}_l, \sigma_l\}) \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \Psi(\{\mathbf{r}_l, \sigma_l\})$$

$$= \int d^3 r v_{ext}(\mathbf{r}) \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r}).$$

- Variation of the energy w.r.t. v_{ext}, we have the expression in the next page.
- [Problem] Derive the above expression in a different smart manner.

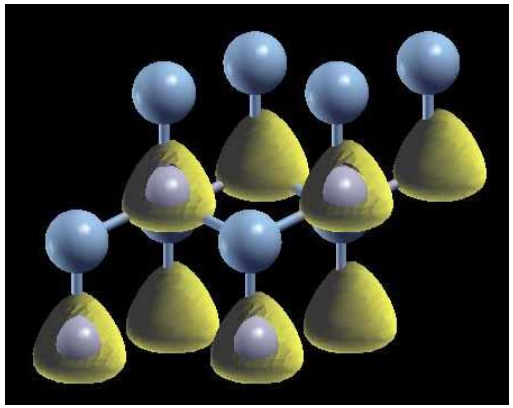
The density determining "order"

- Energy as a functional of v_{ext}: $E[v_{\text{ext}}]$.
- A functional derivative:

$$E[v_{ext}+\delta v_{ext}]-E[v_{ext}]=\int d^3r\,\frac{\delta E[v_{ext}]}{\delta v_{ext}(\mathbf{r})}\delta v_{ext}(\mathbf{r})+O(\delta^2)$$

$$=\int d^3r\,\delta v_{ext}(\mathbf{r})n(\mathbf{r})+O(\delta^2). \qquad (1)$$

- The order parameter : $n(\mathbf{r})$.



K.Kusakabe and I. Maruyama, J. Phys. A: Math. Theor. 44 (2011) 135305.

A theorem in quantum mechnics

- Consider two potentials, $v_1(\boldsymbol{r})$ and $v_2(\boldsymbol{r})$, which are different more than a constant from each other.
- Let $|\Psi_1>$ and $|\Psi_2>$ be an eigen state of a system by $v_1(\boldsymbol{r})$ and that by $v_2(\boldsymbol{r})$, respectively.
- Then, $|\Psi_1>$ cannot be an eigen state of $v_2(\boldsymbol{r})$ and vice versa.

Proof: The unique continuation theorem for the Poisson equation tells us that the statement above is correct. See the next page.

A proof

- When our system is treated by the Born-Oppenheimer approximation, nuclei are treated as fixed point charges.
- v_1 (and v_2 also) follows the Poisson equation.
- Suppose that ψ is a solution of both of two Schrödinger equations given by v_1 and v_2, where v_1 and v_2 are different from each other more than a constant.
- We have $v_1 \psi = (v_2 + \text{const.}) \psi$.
- Let N be the number of electrons.
- We may find an open set S in $\mathbb{R}^3$, where

$$\psi(\boldsymbol{r}_1 + \boldsymbol{r}, \sigma_1, \boldsymbol{r}_2, \sigma_2, \cdots, \boldsymbol{r}_N, \sigma_N) \neq 0$$

  for $\boldsymbol{r} \in S$.
- In S, we have $v_1(\boldsymbol{r}) = v_2(\boldsymbol{r}) + \text{const.}$
- By the unique continuation theorem, we conclude that $v_1(\boldsymbol{r}) = v_2(\boldsymbol{r}) + \text{const}$ in $\mathbb{R}^3$.
- This conclusion contradicts to the assumption.

Hohenberg-Kohn's theorem

- By the last theorem, we have a next inequality which is a contradiction.

$$
\begin{aligned}
E_1 &= \langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle + \int d^3 r n v_1 \\
&= \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle \\
&= \langle \Psi_2 | T + V_{ee} | \Psi_2 \rangle + \int d^3 r n v_1 \\
&= \langle \Psi_2 | T + V_{ee} | \Psi_2 \rangle + \int d^3 r n v_2 + \int d^3 r n (v_1 - v_2) \\
&= \langle \Psi_2 | H_2 | \Psi_2 \rangle + \int d^3 r n (v_1 - v_2) \\
&< \langle \Psi_1 | H_2 | \Psi_1 \rangle + \int d^3 r n (v_1 - v_2) \\
&= \langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle + \int d^3 r n v_2 + \int d^3 r n (v_1 - v_2) \\
&= \langle \Psi_1 | H_1 | \Psi_1 \rangle = E_1 .
\end{aligned}
$$

- This implies existence of "one-to-one correspondence between the potential and the electron density". (by Hohenberg and Kohn (1964))

A logic tells physics

- Fixed positions of nuclei give a scalar potential v_i.
- When $v_2 \neq v_1$ + const., $\Psi_1 \neq \Psi_2$, where Ψ_i is a ground state for a problem by v_i. (by the unique continuation theorem.)
- In this case, $n_1 \neq n_2$. (Proof by Hohenberg & Kohn.) Namely,
  - If "$n_1=n_2=n$" and "$\Psi_1 \neq \Psi_2$", then

$$E_1 = \langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle + \int d^3 r n v_1 = \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle = \langle \Psi_2 | T + V_{ee} | \Psi_2 \rangle + \int d^3 r n v_1$$

$$= \langle \Psi_2 | T + V_{ee} | \Psi_2 \rangle + \int d^3 r n v_2 + \int d^3 r n (v_1 - v_2) = \langle \Psi_2 | H_2 | \Psi_2 \rangle + \int d^3 r n (v_1 - v_2)$$

$$< \langle \Psi_1 | H_2 | \Psi_1 \rangle + \int d^3 r n (v_1 - v_2) = \langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle + \int d^3 r n v_2 + \int d^3 r n (v_1 - v_2) = \langle \Psi_1 | H_1 | \Psi_1 \rangle = E_1.$$

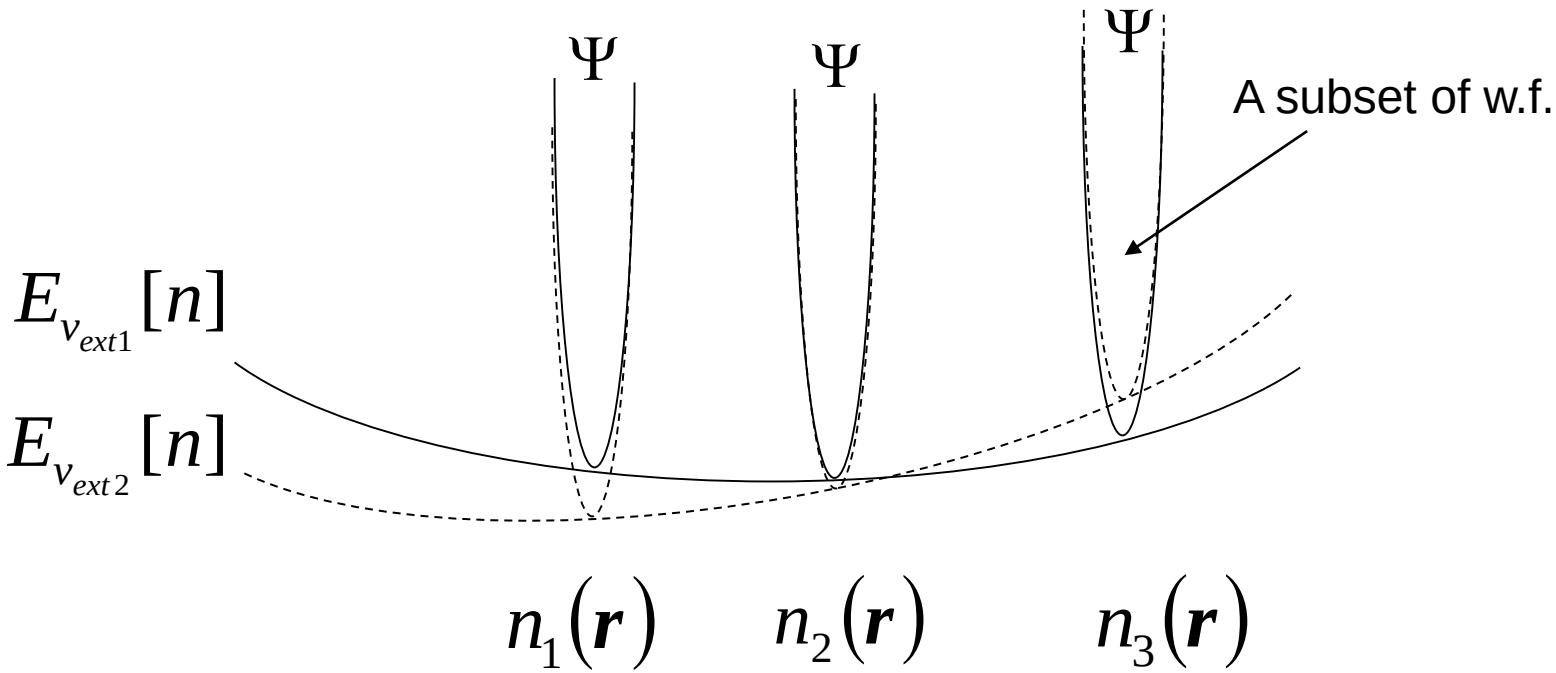
$$\textit{Thus,} \quad E_1 < E_1, \quad \textit{which} \quad \textit{is} \quad \textit{a} \quad \textit{contradiction.}$$

- Thus, we have a one to one correspondence between v and n.
- Namely, n gives v, the Hamiltonian, and the wave function of the ground state Ψ with energy $E[n]$.

Variational energy

$$E_0 = \min_n \left\{ F[n] + \int n(\mathbf{r}) \cdot v_{ext}(\mathbf{r}) d\mathbf{r} \right\}$$

$$= \min_n \left\{ \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int n(\mathbf{r}) \cdot v_{ext}(\mathbf{r}) d\mathbf{r} \right\} = \min_n E_{v_{ext}}[n]. \qquad (2)$$



This definition of the density functional theory does not rely on HK.

$$
\begin{aligned}
E_0 &= \langle \Psi_{GS} | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi_{GS} \rangle + \int n_{GS}(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \\
&= \min_n \left\{ \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \right\} \\
&= \min_n \left\{ \min_{\Psi' \to n(\mathbf{r})} \langle \Psi' | \hat{T} | \Psi' \rangle + F[n] - F_T[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \right\} \\
&= \min_n \left\{ \min_{\Psi' \to n(\mathbf{r})} \left\{ \langle \Psi' | \hat{T} | \Psi' \rangle + F[n_{\Psi'}] - F_T[n_{\Psi'}] \right. \right. \\
&\qquad \left. \left. + \int n_{\Psi'}(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \right\} \right\} \\
&= \min_{\Psi'} \left\{ \langle \Psi' | \hat{T} | \Psi' \rangle + \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + F[n_{\Psi'}] \right. \\
&\qquad \left. - \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' - F_T[n_{\Psi'}] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \right\} \\
&= \boxed{\begin{aligned} &\min_{\Psi'} \left\{ \langle \Psi' | \hat{T} | \Psi' \rangle + \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{xc}[n_{\Psi'}] \right. \\ &\left. + \int n_{\Psi'}(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r \right\} \end{aligned}} \\
&= \min_{\Psi'} G_T[\Psi']. \qquad (3)
\end{aligned}
$$

Definition of E_{xc}[n].

Derive differential equations

- First, set up a differentiable energy functional.

$$E_{xc}[n] \Rightarrow \overline{E}_{xc}[n] \qquad G_T[\Psi] \Rightarrow \overline{G}_T[\Psi]$$

- Derive a determining equations, which are to be self-consistent equations.

$$\frac{\delta}{\delta\langle\Psi|}\left\{\overline{G}_T[\Psi] - E\left(\langle\Psi|\Psi\rangle - 1\right)\right\} = 0, \qquad \left\{\hat{T} + \int d^3r v_{eff}(\mathbf{r})\hat{n}(\mathbf{r})\right\}|\Psi\rangle = E|\Psi\rangle,$$

$$\Rightarrow v_{eff}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta\overline{E}_{xc}[n]}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}),$$

$$n(\mathbf{r}) = \sum_{\sigma}\langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle.$$

The local density approximation I.

Let's start from the Kohn-Sham equation.

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + \quad v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right\}\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \ .$$

Here, v_{ext} is the static electron-ion potential, v_H is the Hartree potential given by

$$v_H(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\frac{e^2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ ,$$

and v_{xc} is given by the functional derivative

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \ .$$

The electron charge density $\rho(\mathbf{r})$ is given as

$$\rho(\mathbf{r}) = 2\sum_i |\phi_i(\mathbf{r})|^2 \ ,$$

for a non-magnetic system. (In case of magnetic materials, we might utilize a local-spin-density approximation which provides us an effective model with a spin-dependent orbital $\phi_{i,\sigma}$.)

The local density approximation II.

We need to evaluate E_{xc} and v_{xc} by approximate methods. The simplest method is to use the local-density approximation (LDA).

In LDA, E_{xc} is constructed from the exchange-correlation energy per electron at a point $\mathbf{r}$ in an inhomogeneous electron gas, $\varepsilon_{xc}(\rho(\mathbf{r}))$, which is given by that of the homogeneous electron gas with the density ρ.

$$E_{xc}[\rho(\mathbf{r})] = \int \mathrm{d}\mathbf{r}\, \varepsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}) \ .$$

The functional derivative of E_{xc} in LDA is obtained via the next calculation.

$$\begin{aligned} \delta E_{xc}[\rho(\mathbf{r})] &= \int \mathrm{d}\mathbf{r}\, \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r}) \\ &= \int \mathrm{d}\mathbf{r}\, \left.\frac{d\varepsilon_{xc}(\rho)\rho}{d\rho}\right|_{\rho=\rho(\mathbf{r})} \delta\rho(\mathbf{r}) \end{aligned}$$

Thus v_{xc} is given by,

$$v_{xc}(\mathbf{r}) = \left.\frac{d\varepsilon_{xc}(\rho)\rho}{d\rho}\right|_{\rho=\rho(\mathbf{r})}$$

The local density approximation III.

The LDA energy functional is given by several authors. For example,

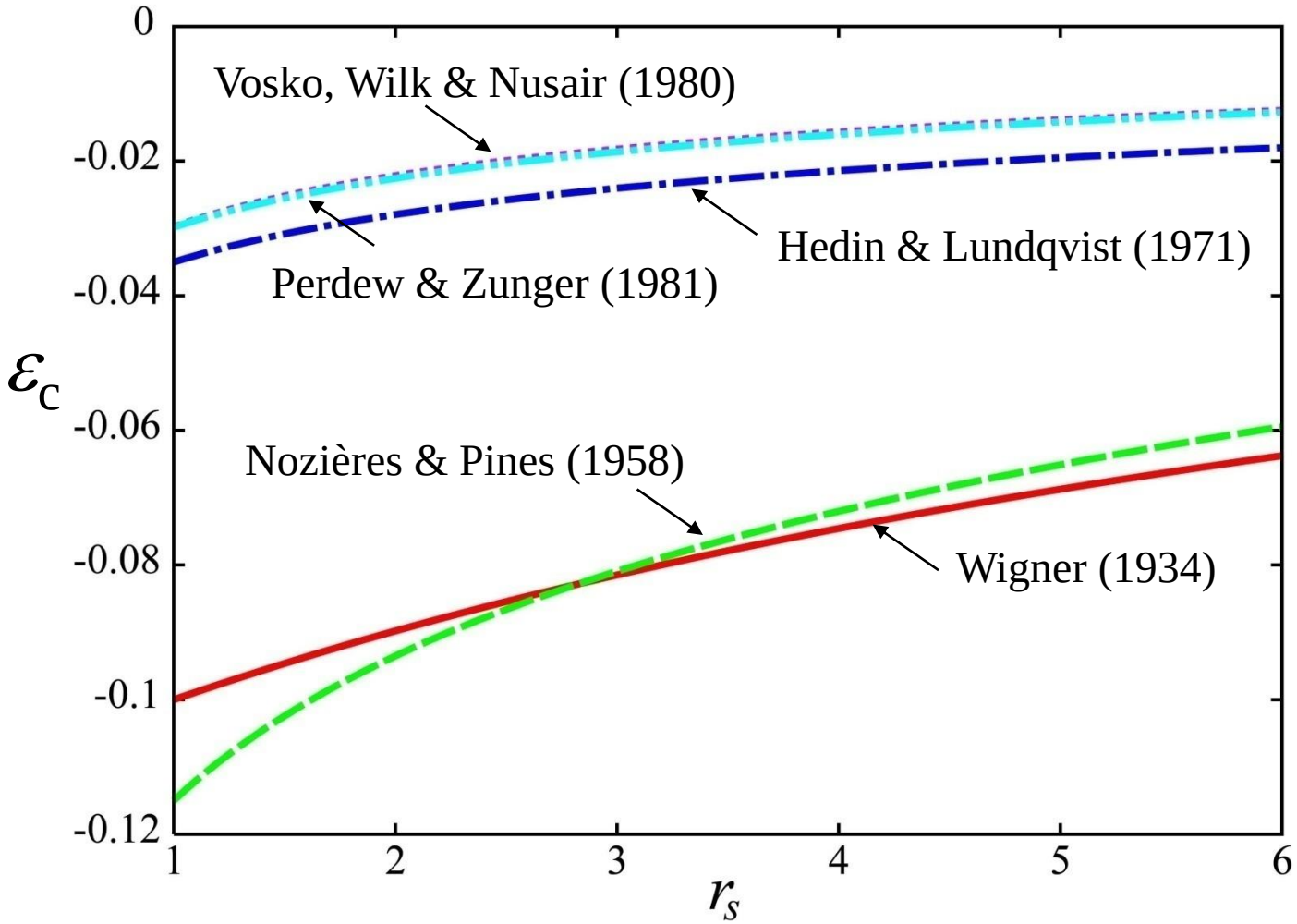
1. Wigner (1938)
2. Kohn and Sham (1965)
3. Hedin and Lundqvist (1971),
4. Vosko, Wilk and Nusair (1980),
5. Perdew and Zunger (1981)

These parametrizations use interpolation formulas to link exact results for the exchange-correlation energy of the high-density limit of the electron gas (given by RPA) and the exchange-correlation energy of intermediate and low-density electron gases obtained by some approximation methods or the Quantum Monte-Carlo calculation.

Note: there are many attempts to overcome LDA, which include the Generalized Gradient Approximation (GGA), meta GGA.

Correlation energy density for LDA

Let's introduce r_s by $\frac{N_e}{V} = 1/\left(\frac{4\pi}{3} r_s^3\right)$ We may divide ε_{xc} as, $\varepsilon_{xc}(r_s) = \varepsilon_x(r_s) + \varepsilon_c(r_s)$.



The plane-wave expansion I.

The Bloch theorem tells us that each wavefunction is given by,

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{n,\mathbf{k}}(\mathbf{r}) \ .$$

Here, $\mathbf{k}$ is a wave vector in the first Brillouin zone and $u_{n,\mathbf{k}}(\mathbf{r})$ is a periodic function satisfying $u_{n,\mathbf{k}}(\mathbf{r}+\mathbf{l}) = u_{n,\mathbf{k}}(\mathbf{r})$. $\mathbf{l}$ is a lattice vector. A band index is represented by n.

Since $u_{n,\mathbf{k}}$ can be expanded as

$$u_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \phi_{n,\mathbf{k}}(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{r}) \ ,$$

with the reciprocal lattice vectors $\mathbf{G}$, we have a plane-wave expansion of $\phi_{n,\mathbf{k}}$

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \phi_{n,\mathbf{k}}(\mathbf{G}) \exp(i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}) \ .$$

The plane-wave expansion II.

Using the momentum-space representation, the Kohn-Sham equation reads,

$$\sum_{\mathbf{G}'}\left[\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G},\mathbf{G}'}+v_{ext}(\mathbf{G}-\mathbf{G}')+v_H(\mathbf{G}-\mathbf{G}')+v_{xc}(\mathbf{G}-\mathbf{G}')\right]\phi_{n,\mathbf{k}}(\mathbf{G}')$$
$$=\sum_{\mathbf{G}'}H_{\mathbf{k}}(\mathbf{G},\mathbf{G}')\phi_{n,\mathbf{k}}(\mathbf{G}')=\varepsilon_{n,\mathbf{k}}\phi_{n,\mathbf{k}}(\mathbf{G})$$

We can obtain eigenvalues $\varepsilon_{n,\mathbf{k}}$ and eigenvectors $\phi_{n,\mathbf{k}}$ by diagonalizing a Hamiltonian matrix $H_{\mathbf{k}}(\mathbf{G},\mathbf{G}')$.

- Dimension of the matrix can be O(10^3) or O(10^4).
- The diagonalization is often performed using the Housholder method or the conjugate gradient method (CG).

However,

- the process to find the ground state is regarded as an optimization process for the energy functional in the function space.

  The Car-Parrinello method (Conceptually different idea)

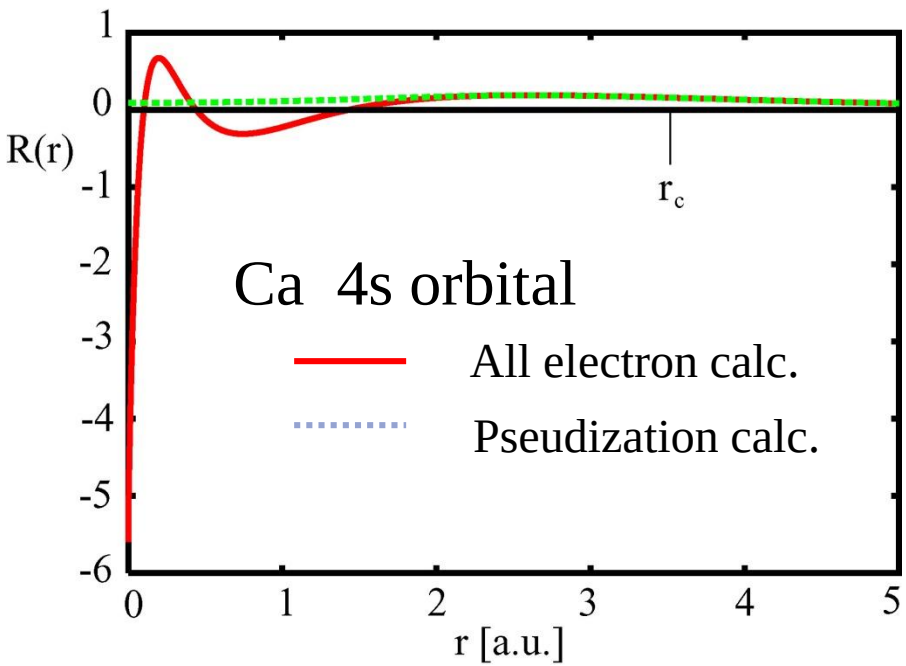
The pseudopotential I.

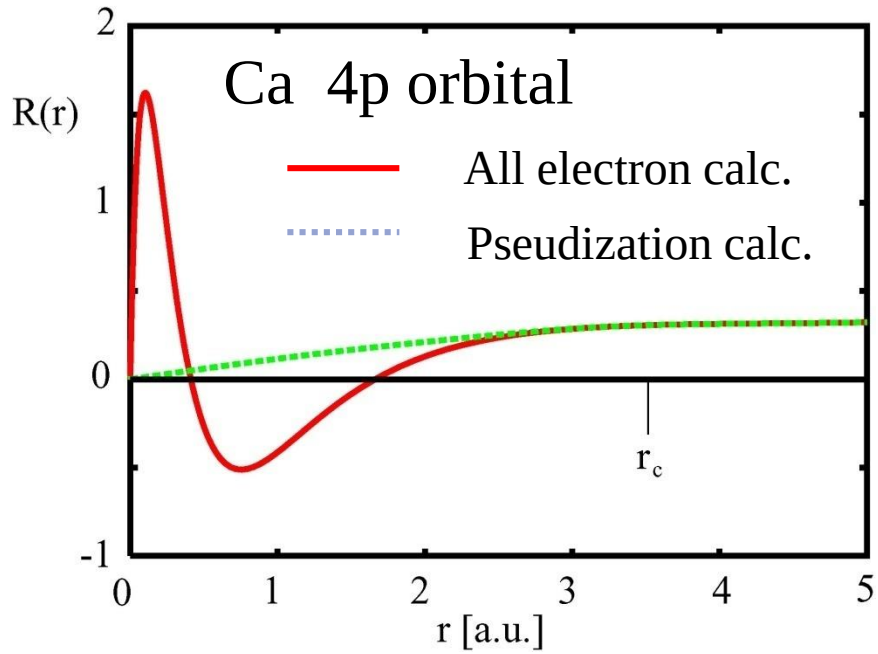
To construct a pseudopotential, we need a pseudo-wavefunction whose radial wave function R_l^{PP} satisfies $\varepsilon_l^{PP} = \varepsilon_l^{AE}$ and,

$$R_l^{PP}(r) = R_l^{AE}(r) \qquad \text{for } r > r_{cl}$$

and

$$\int_0^{r_{cl}} |R_l^{PP}(r)|^2 r^2 dr = \int_0^{r_{cl}} |R_l^{AE}(r)|^2 r^2 dr$$





The pseudopotential II.

The norm-conserving property of the pseudo-potential ensures that the logarithmic derivative D_l of the wavefunction is maintaind up to its first order derivative against the energy, when we construct the pseudo potential.

D_l is defined as,

$$D_l(\varepsilon) = \frac{1}{R_l(r;\varepsilon)} \frac{\partial R_l(r;\varepsilon)}{\partial r}\bigg|_{r=r_{cl}} .$$

The Kohn-Sham equation in a polar coordinate is,

$$\left\{ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{l(l+1)\hbar^2}{2mr^2} + v_{\text{eff}}(r) \right\} rR_l(r;\varepsilon) = \varepsilon r R_l(r;\varepsilon) .$$

We are searching for v_{eff}^{PP} which satisfies that artificial $\frac{\partial D_l^{PP}}{\partial \varepsilon}$ of the pseudo wavefunctions is the same as the $\frac{\partial D_l^{AE}}{\partial \varepsilon}$. The condition is identical to the norm conserving condition as follows.

The pseudopotential III.

Making a derivative of the Kohn-Sham equation with respect to ε. Multiply $rR_l(r;\varepsilon)$ to the result and subtract $r\frac{\partial R_l(r;\varepsilon)}{\partial \varepsilon}$ times the Kohn-Sham equation, we have,

$$\{rR_l(r;\varepsilon)\}^2 = -\frac{\hbar^2}{2m}\left[rR_l(r;\varepsilon)\frac{\partial^2}{\partial r^2}r\frac{\partial R_l(r;\varepsilon)}{\partial \varepsilon} - r\frac{\partial R_l(r;\varepsilon)}{\partial \varepsilon}\frac{\partial^2}{\partial r^2}rR_l(r;\varepsilon)\right] .$$

Integrate this expression with respect to r from 0 to r_{cl}, we have

$$\int_0^{r_{cl}} |R_l(r;\varepsilon)|^2 r^2 dr = -\frac{\hbar^2}{2m}\{rR_l(r;\varepsilon)\}^2 \left.\frac{\partial D_l}{\partial \varepsilon}\right|_{r=r_{cl}} .$$

Thus, if we keep continuity of the pseudo potential and the norm conserving condition, the resulting pseudo potential reproduces the all electron results up to the first order derivative around the reference energy where the pseudo wavefunction is given.

The pseudopotential IV.

Once the pseudo-wavefunction is obtained, the screened pseudopotential is recovered by inversion of the radial equation,

$$V_{scr,l}^{PP}(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_l^{PP}(r)}\frac{d^2}{dr^2}[rR_l^{PP}(r)] \ .$$

To make a pseudopotential which is tranferable for a variety of environment, we make an ionic pseudopotential by unscreening.

$$V_{ion,l}^{PP}(r) = V_{scr,l}^{PP}(r) - V_H^{PP}(r) - V_{xc}^{PP}(r) \ .$$

Here V_H^{PP} and V_{xc}^{PP} are the Hartree and the exchange-correlation potentials calculated from the valence pseudo-wavefunctions. This is the unscreening process.

The pseudopotential V.

The ionic pseudopotential operator is given as,

$$\hat{V}_{ion}^{PP}(r) = V_{ion,local}^{PP}(r) + \sum_l V_{nonlocal,l}\hat{P}_l \ ,$$

where $V_{ion,local}^{PP}(r)$ is the local potential and

$$V_{nonlocal,l}(r) = V_{ion,l}^{PP}(r) - V_{ion,local}^{PP}(r)$$

is the semilocal potential for the angular-momentum component l and $\hat{P}_l$ projects out the lth angular-momentum component.

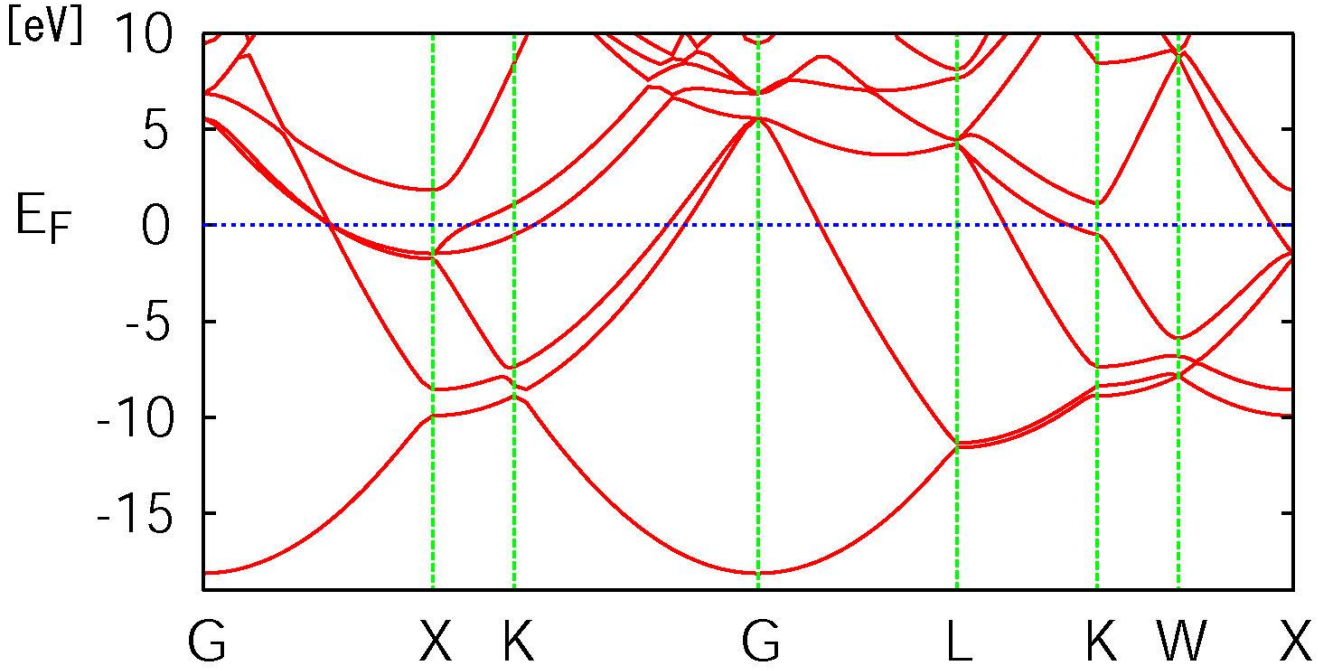
The semilocal potential can be transformed into a nonlocal form by the Kleinman-Bylander construction,

$$V_{nonlocal,l}^{KB}(r) = \frac{|V_{nonlocal,l}(r)\Phi_l^{PP,0}(r)\rangle\langle\Phi_l^{PP,0}(r)V_{nonlocal,l}(r)|}{\langle\Phi_l^{PP,0}(r)|V_{nonloal,l}(r)|\Phi_l^{PP,0}(r)\rangle} \ ,$$

where $\Phi_l^{PP,0}(r)$ is the atomic pseudo-wavefunction.

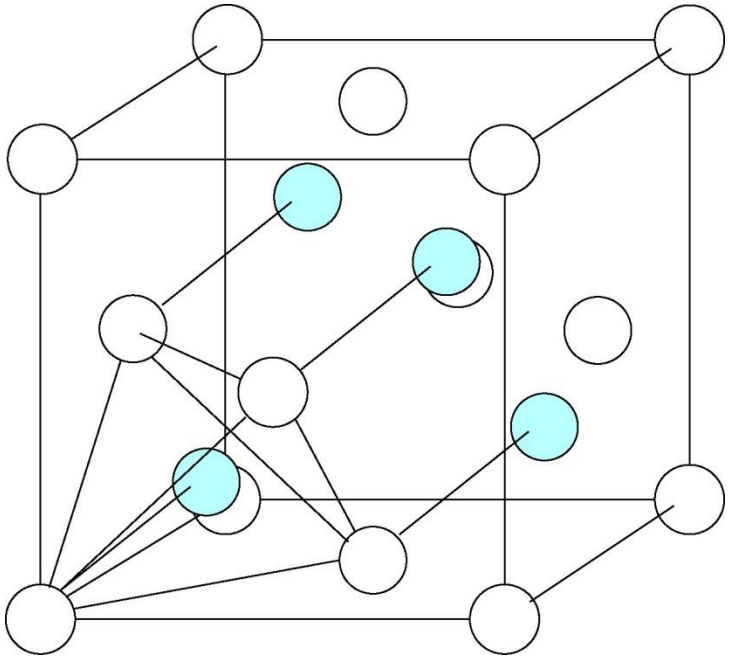
Application for a metal

- The band structure of Al (FCC)
  - The plane-wave expansion with a pseudo-potential
  - GGAPBE96

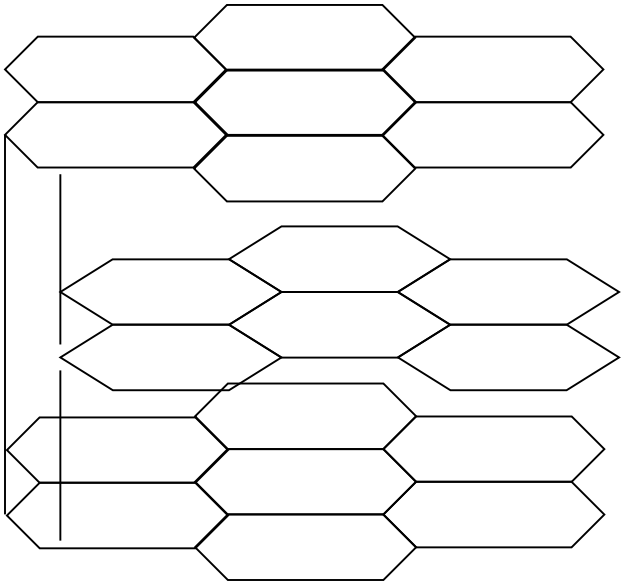


Covalent crystals I.

- Diamond and Graphite as covalent crystals.

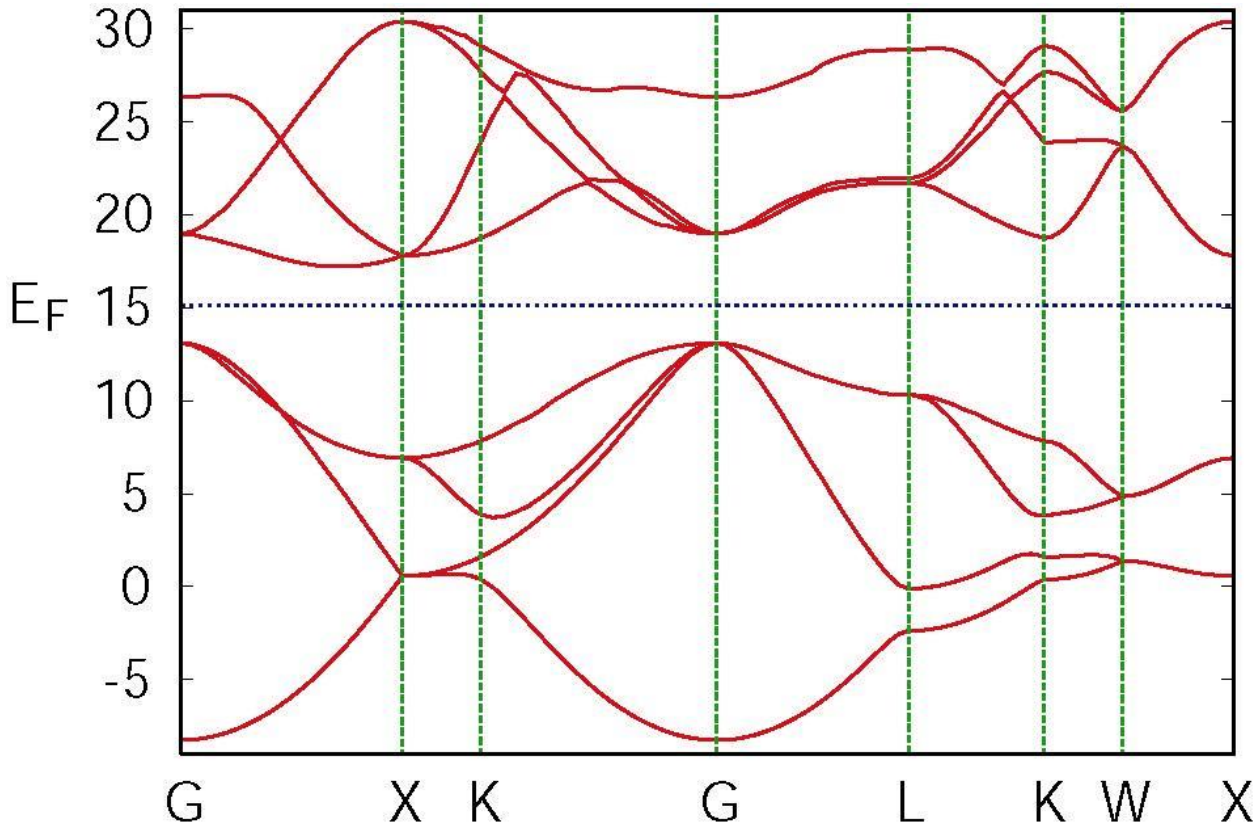


Diamond structure



Graphite structure

Band structure of cubic diamond



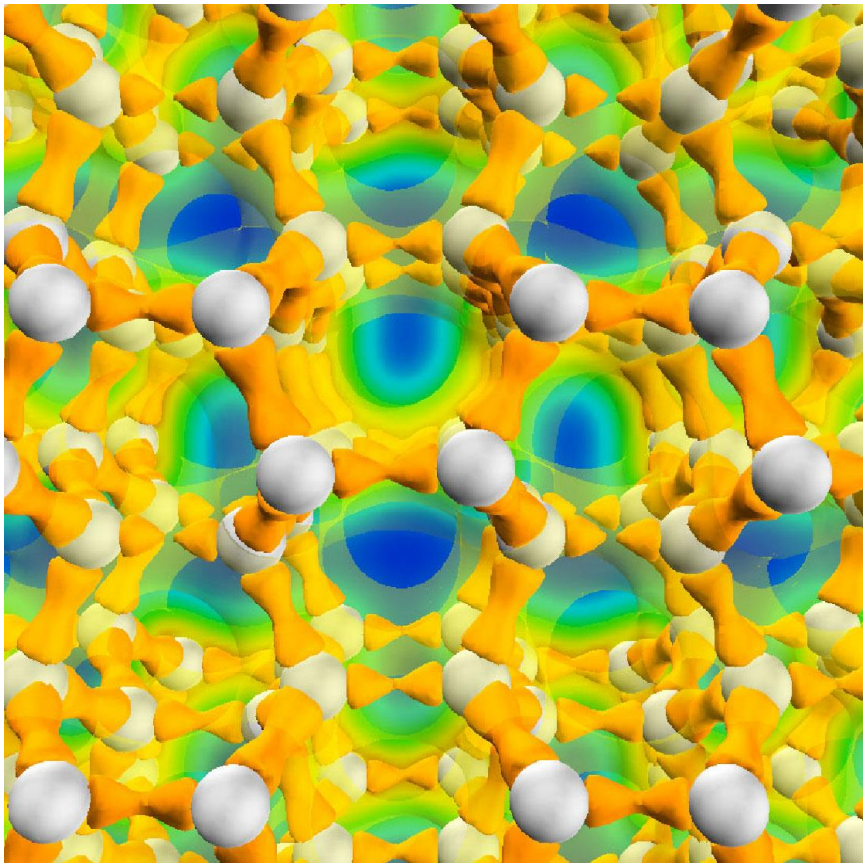
σ^* bands (anti-bonding bands)

σ bands (bonding bands)

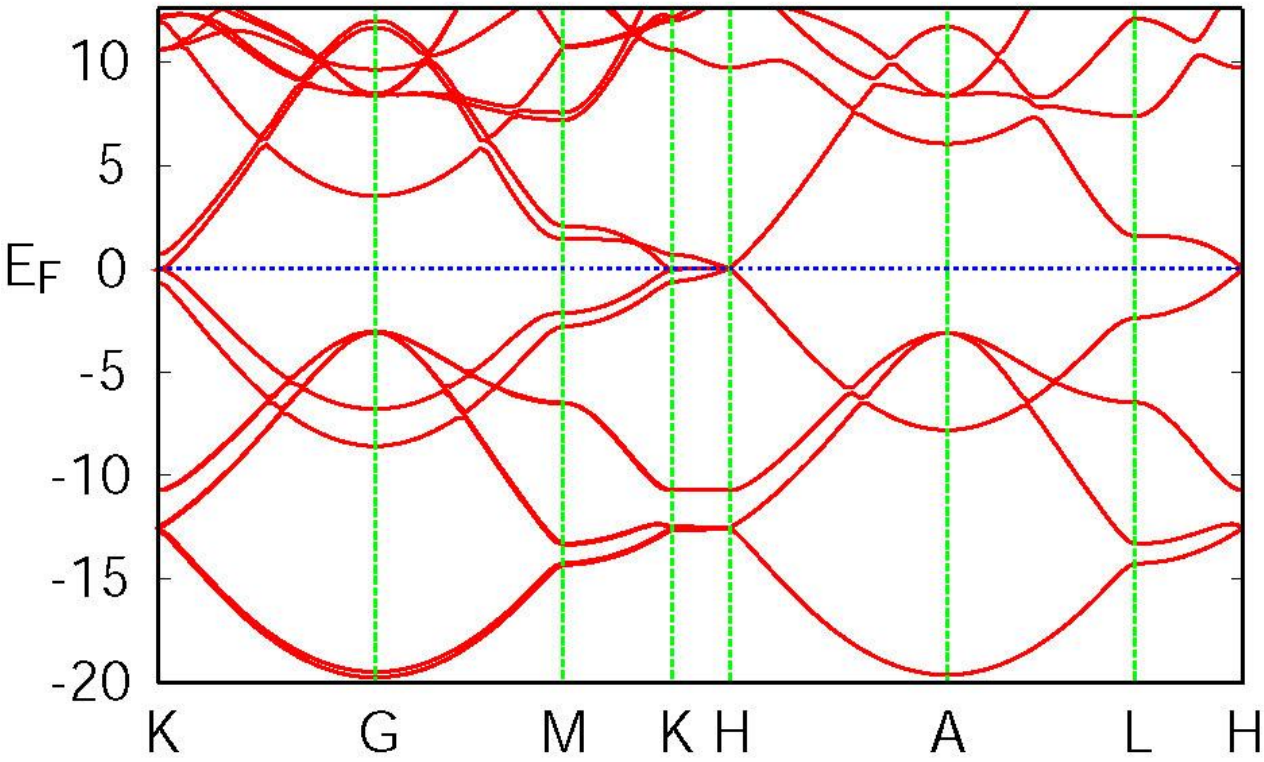
An energy gap appears and the system is a wide-gap semiconductor.

Bonding charge in hex-diamond

- In a covalent crystal, we can see charge density of electrons at each bond connection.
- Yellow object represents charge density and white spheres are carbons.



Band structure of graphite



σ^* bands (anti-bonding bands)

π^* bands (anti-bonding)

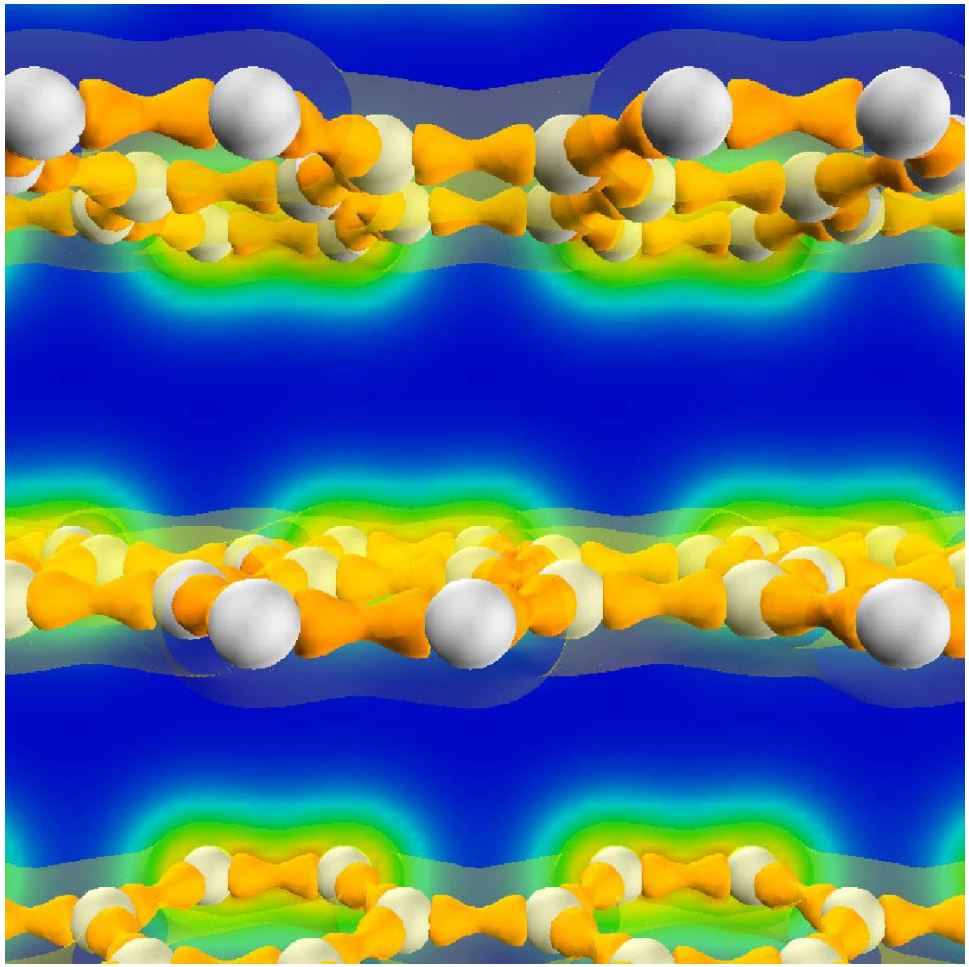
π bands (bonding bands)

σ bands (bonding bands)

The π-band is half-filled and there are small Fermi pockets both for electrons and holes. (Semimetal)

Bonding charge in graphite

- Bonding charge comes from σ-electrons.
- This system is a semimetal where the Fermi surface is made of π-bands.



Techniques in the molecular dynamics

- Constant-Temperature Scheme (Nosè & Hoover)
  - Average of the kinetic energy is made constant by introduction of interaction between the system and an imaginative heat bath.
  - An equation of motion with dissipative term written by an artificial variable is solved.
- Constant-Pressure Scheme (Parrinello & Rahman)
  - The volume (cell parameters) of the system is made a variable.
  - MD and structural optimization is performed using the enthalpy, H=E+PV.

Realization of realistic situation

The Hellmann-Feynman force

The force acting on the I-th atom $\mathbf{F}_I$ is given by,

$$\begin{aligned}\mathbf{F}_I &= -\frac{dE}{d\mathbf{R}_I} \\ &= -\sum_i \left[\langle \phi_i | (\frac{d}{d\mathbf{R}_I} H) | \phi_i \rangle + (\frac{d}{d\mathbf{R}_I} \langle \phi_i |) H | \phi_i \rangle + \langle \phi_i | H (\frac{d}{d\mathbf{R}_I} | \phi_i \rangle \right] .\end{aligned}$$

Here $E = \Sigma_i \langle \phi_i | H | \phi_i \rangle$ is the Kohn-Sham energy.

When each electronic wave function ϕ_i is an eigenstate of the Hamiltonian, $H|\phi_i\rangle = \varepsilon_i |\phi_i\rangle$, the last two terms (called the Pulay force) in the above expression cancel with each other. This is because,

$$\sum_i \left[(\frac{d}{d\mathbf{R}_I} \langle \phi_i |) H | \phi_i \rangle + \langle \phi_i | H (\frac{d}{d\mathbf{R}_I} | \phi_i \rangle \right] = \sum_i \varepsilon_i \frac{d\langle \phi_i | \phi_i \rangle}{d\mathbf{R}_I} = 0$$

Thus the expression of the force becomes,

$$\mathbf{F}_I = -\sum_i \langle \phi_i | \frac{dH}{d\mathbf{R}_I} | \phi_i \rangle = -\frac{\partial E}{\partial \mathbf{R}_I}$$

The internal stress I

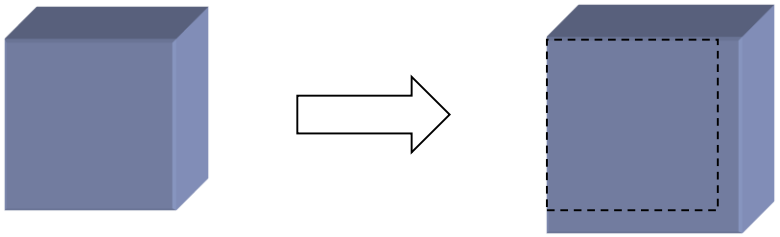
The expression of internal quantum stress is given by the same variational method as force. We consider a many-electron system in a certain unit cell with volume Ω_{cell}. The total energy is $E(\{\psi_{\mathbf{k},i}(\mathbf{r})\}, \{\mathbf{R}_I\})$. The variational principle tells us that the ground state energy E_{tot} is the minimum of $E(\{\psi_{\mathbf{k},i}(\mathbf{r})\}, \{\mathbf{R}_I\})$ with respect to $\{\psi_{\mathbf{k},i}(\mathbf{r})\}, \{\mathbf{R}_I\}$.

To derive the stress, we introduce a symmetric (rotation-free) two-rank strain tensor, ε. The infinitesimal homogeneous scaling given by ε is applied as,

$$\begin{aligned} \mathbf{R}_I &\rightarrow \mathbf{R}'_I = (1+\varepsilon)\mathbf{R}_I, \\ \psi_{\mathbf{k},i}(\mathbf{r}) &\rightarrow \psi_{\mathbf{k},i}(\mathbf{r}') = \det(1+\varepsilon)^{\frac{1}{2}}\psi_{\mathbf{k},i}(\mathbf{r}). \end{aligned}$$

The ground state energy changes as,

$$E_{tot} \rightarrow E(\varepsilon) = E_{tot} + \Delta E(\varepsilon).$$



The internal stress II

The shift in energy $\Delta E(\varepsilon)$ is expanded in a series of the power of ε. The stress in the stress tensor σ is defined as the coefficient of the first order in the series and thus we have,

$$\begin{aligned} \Delta E(\varepsilon) &= -\mathrm{Tr}(\sigma\varepsilon)\Omega_{cell} + O(\varepsilon^2), \\ \sigma_{\alpha\beta} &= -\frac{1}{\Omega_{cell}} \frac{\partial E(\varepsilon)}{\partial \varepsilon_{\alpha\beta}}\bigg|_{\varepsilon\to 0}. \end{aligned} \tag{1}$$

If the strain and the stress are isotropic, the above expression reduces to the well-known theromdynamic formula, $P = -\dfrac{dE}{d\Omega_{cell}}$.

Due to introduction of the strain tensor $\varepsilon_{\alpha\beta}$, which is a symmetric tensor, we have a modified $\mathbf{G}$ to be $(1-\varepsilon)\mathbf{G}$ in the first order and Ω_{cell} becomes $\det(1+\varepsilon)\Omega_{cell}$. Since $\Omega_{cell}n(\mathbf{G})$ and $S_I(\mathbf{G})$ are invariant, we have the next expressions.

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{kin} + \sigma_{\alpha\beta}^{el-el} + \sigma_{\alpha\beta}^{xc} + \sigma_{\alpha\beta}^{local} + \sigma_{\alpha\beta}^{non-local} + \sigma_{\alpha\beta}^{\alpha} + \sigma_{\alpha\beta}^{ewald}.$$

$$\sigma_{\alpha\beta}^{kin} = 2\sum_{\mathbf{k},\mathbf{G},i} |\psi_i(\mathbf{k}+\mathbf{G})|^2 (\mathbf{k}+\mathbf{G})_\alpha (\mathbf{k}+\mathbf{G})_\beta,$$

$$\sigma_{\alpha\beta}^{el-el} = -\frac{1}{2}\sum_{\mathbf{G}}{}' \frac{4\pi|n(\mathbf{G})|^2}{|\mathbf{G}|^2}\left(\frac{2\mathbf{G}_\alpha\mathbf{G}_\beta}{|\mathbf{G}|^2} - \delta_{\alpha\beta}\right),$$

$$\sigma_{\alpha\beta}^{xc} = \delta_{\alpha\beta}\frac{1}{\Omega_{cell}}\int_{\Omega_{cell}} d\mathbf{r} n(\mathbf{r})(\mu_{xc}(n) - \varepsilon_{xc}(n)),$$

$$\sigma_{\alpha\beta}^{local} = -\sum_{\mathbf{G},I}{}' n^*(\mathbf{G}) S_I(\mathbf{G}) \frac{\partial V_I^{local}(\mathbf{G})}{\partial \varepsilon_{\alpha\beta}},$$

$$\sigma_{\alpha\beta}^{non-local} = -2\sum_{\mathbf{k},i}\sum_{\mathbf{G},\mathbf{G}'}\sum_{I,l} S_I(\mathbf{G}-\mathbf{G}')\psi_{\mathbf{k},i}^*(\mathbf{G})\psi_{\mathbf{k},i}(\mathbf{G}')\frac{\partial \delta\hat{V}_I^l(\mathbf{k}+\mathbf{G},\mathbf{k}'+\mathbf{G}')}{\partial\varepsilon_{\alpha\beta}}$$

$$\sigma_{\alpha\beta}^{\alpha} = \delta_{\alpha\beta} n^*(\mathbf{0})\sum_I \alpha_I, \qquad \sigma_{\alpha\beta}^{ewald} - \frac{1}{\Omega_{cell}}\frac{\partial\gamma_{ewald}}{\partial\varepsilon_{\alpha\beta}}.$$

We have introduced a reference coordinate of atomic positions, $\mathbf{q}_I$, which satisfies $\mathbf{R}_I(t) = (1+\varepsilon)\mathbf{q}_I(t)$.

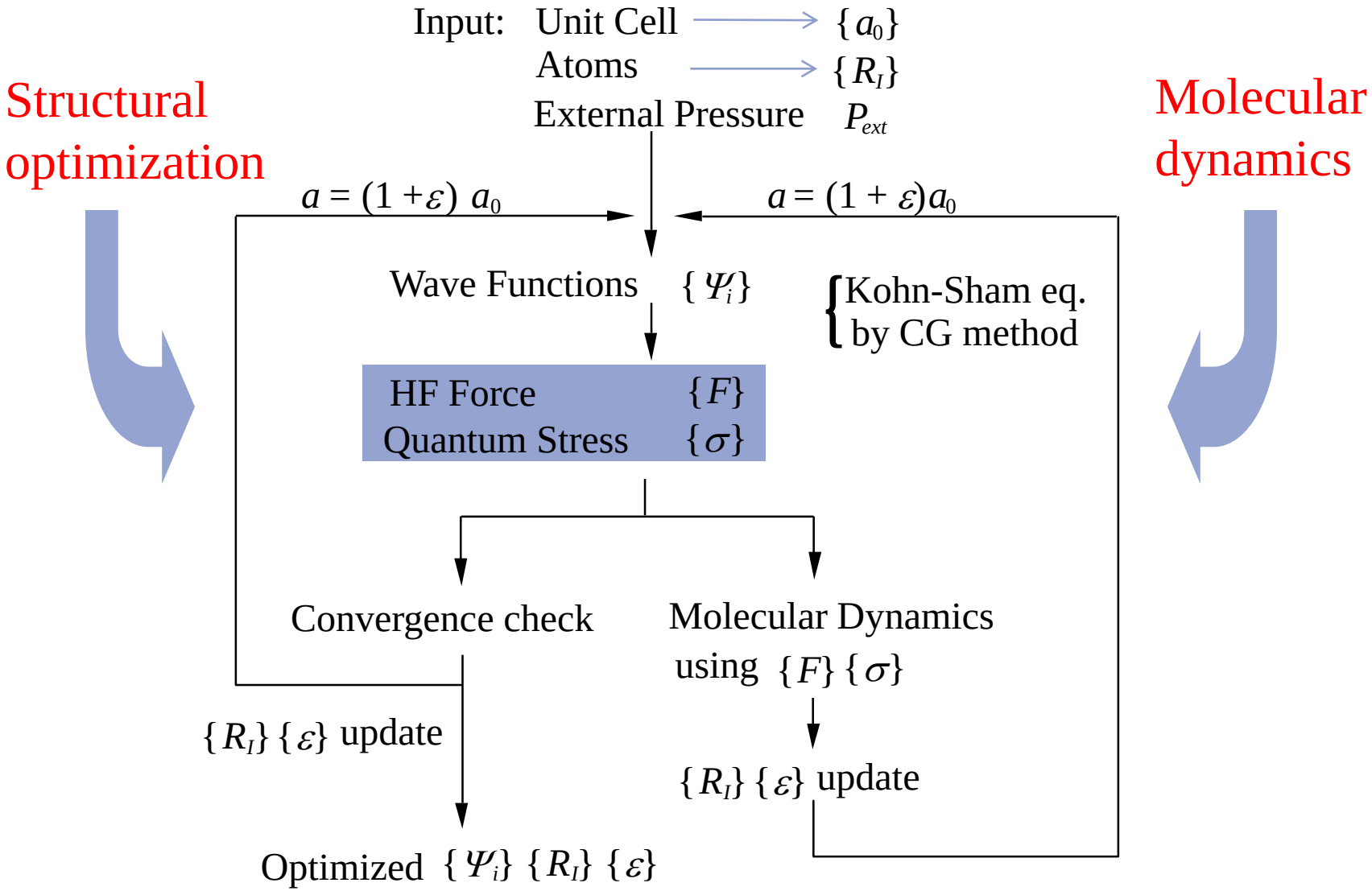
The equations of motion for CP-FPMD

Here, we introduce the reference coordinates $\mathbf{q}_I$ for the position of atoms and let $\mathbf{R}_I(t) = (1+\varepsilon)\mathbf{q}_I(t)$.

The Lagrangian proposed by Wentzcovitch is utilized. The equations of motion are given by the followings.

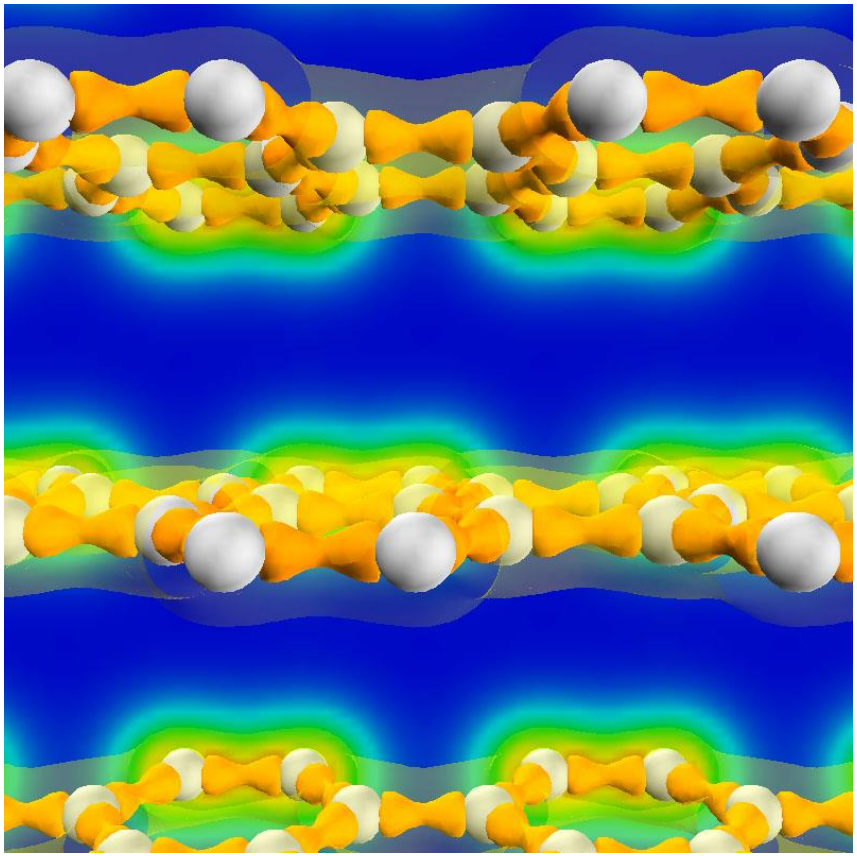
$$
\begin{aligned}
L &= \sum_I \frac{1}{2} m_I^t \dot{\mathbf{q}}_I d \dot{\mathbf{q}}_I - E_{tot}(\{\mathbf{q}_I\}(t), \varepsilon) + \frac{1}{2} W \mathrm{Tr}({}^t\dot{\varepsilon}\dot{\varepsilon}) - P_{ext}\Omega_{cell}, \\
\ddot{\mathbf{q}} &= -\frac{1}{m_I}(1+\varepsilon)^{-1}\mathbf{F}_I - d^{-1}\dot{d}\dot{\mathbf{q}}_I, \\
\ddot{\varepsilon} &= \frac{\Omega_{cell}}{W}(\Pi - P_{ext})^t(1+\varepsilon)^{-1}, \\
\Pi &= \frac{1}{\Omega_{cell}} \sum_I m_I \mathbf{v}_I^t \mathbf{v}_I - \frac{1}{\Omega_{cell}} \frac{\partial E_{tot}}{\partial \varepsilon}.
\end{aligned}
$$

The calculation scheme of FPMD at a constant pressure

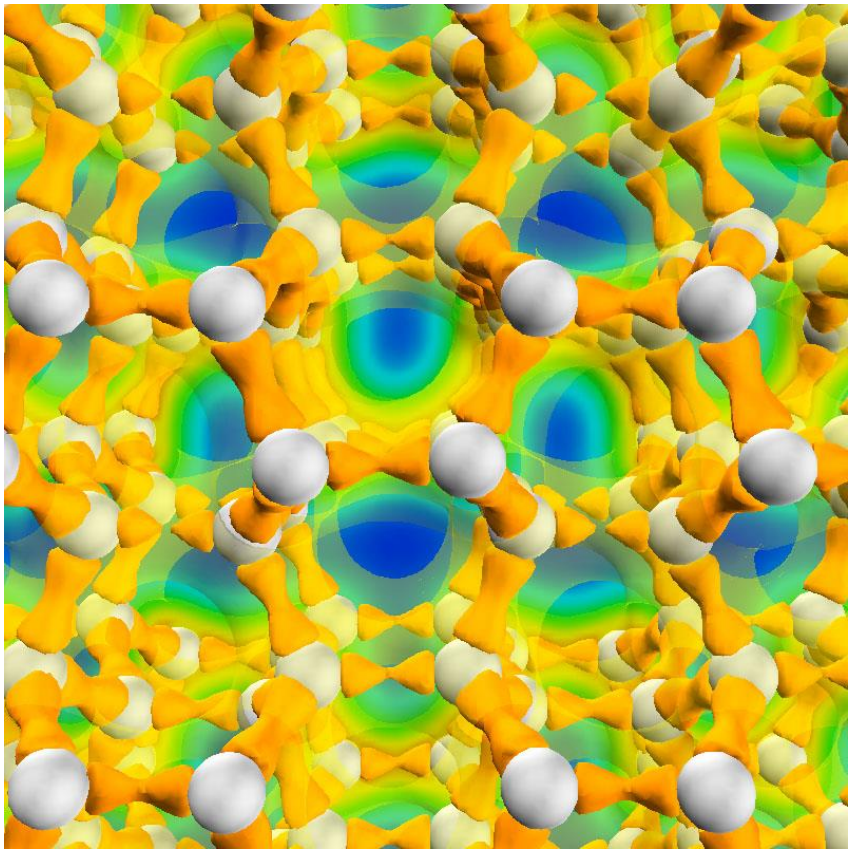


Graphite-diamond transformation in a FPMD simulation

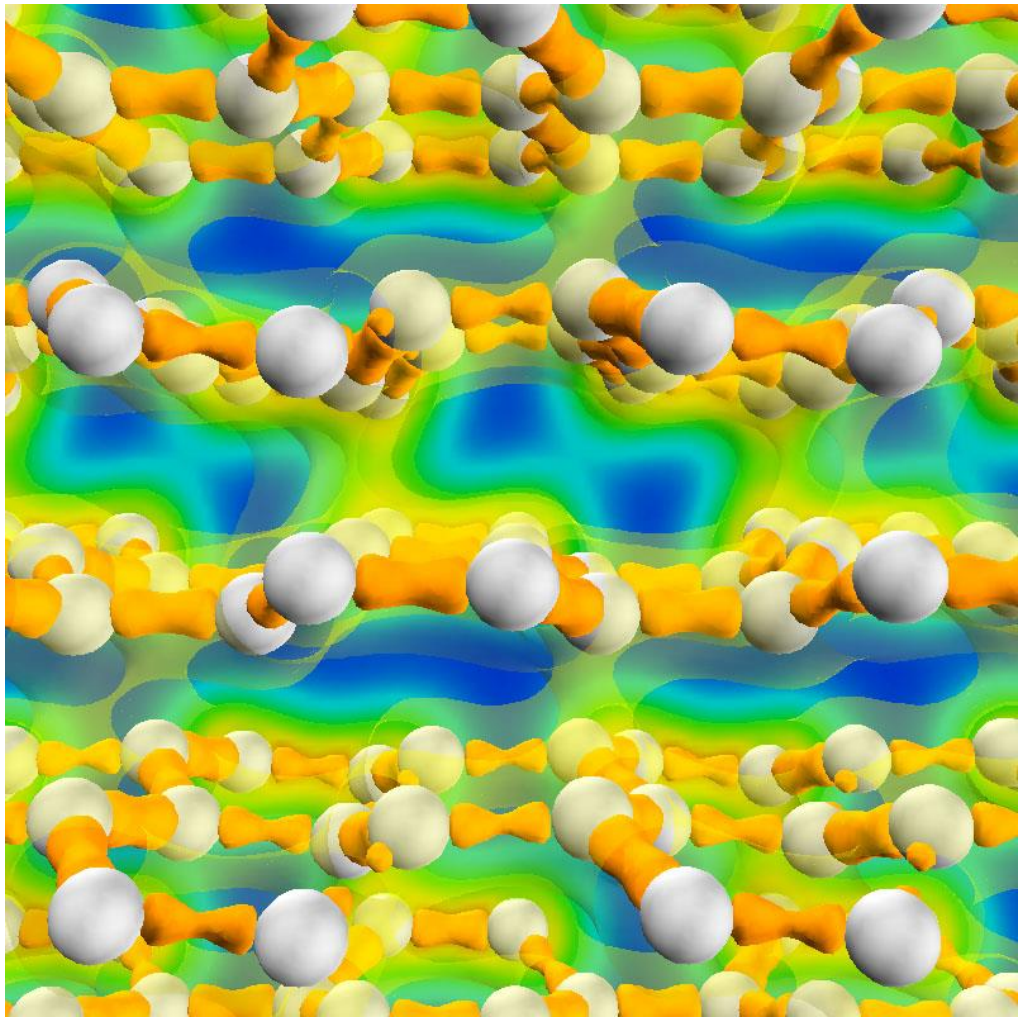
At ambient pressure



At high pressure



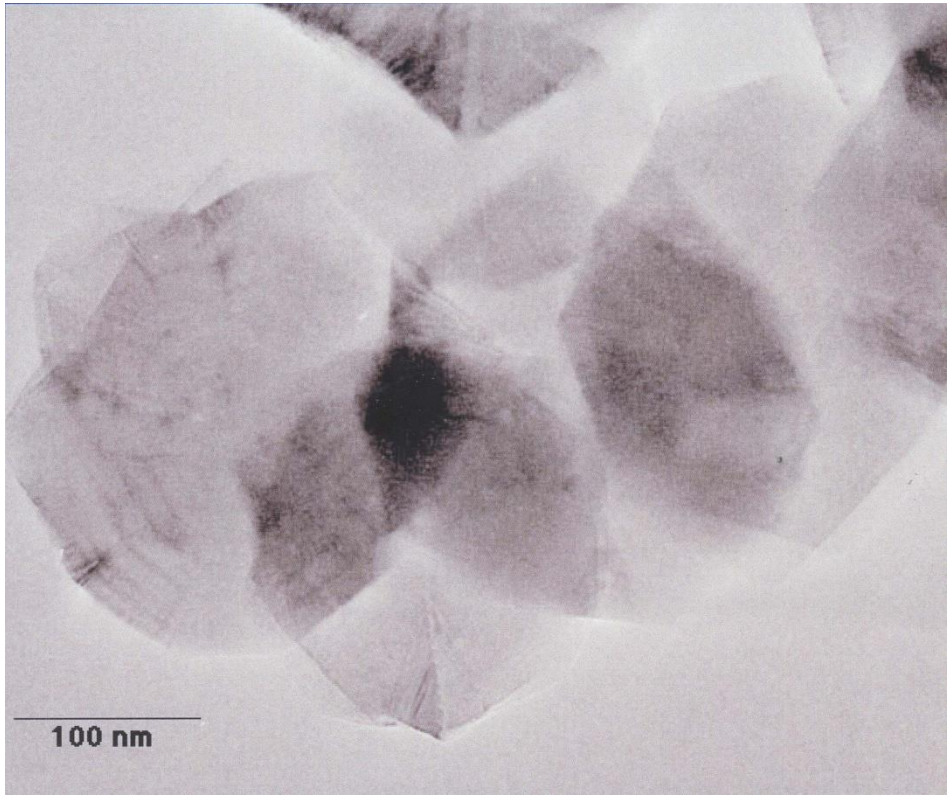
Formation of new bondings at the transformation



- White objects are carbon atoms and yellow iso-surfaces represent charge density of electrons.
- We see new bonding represented by bonding charge between graphite layers.
- Sliding of layers occurs due to formation of sp3 bond connections.

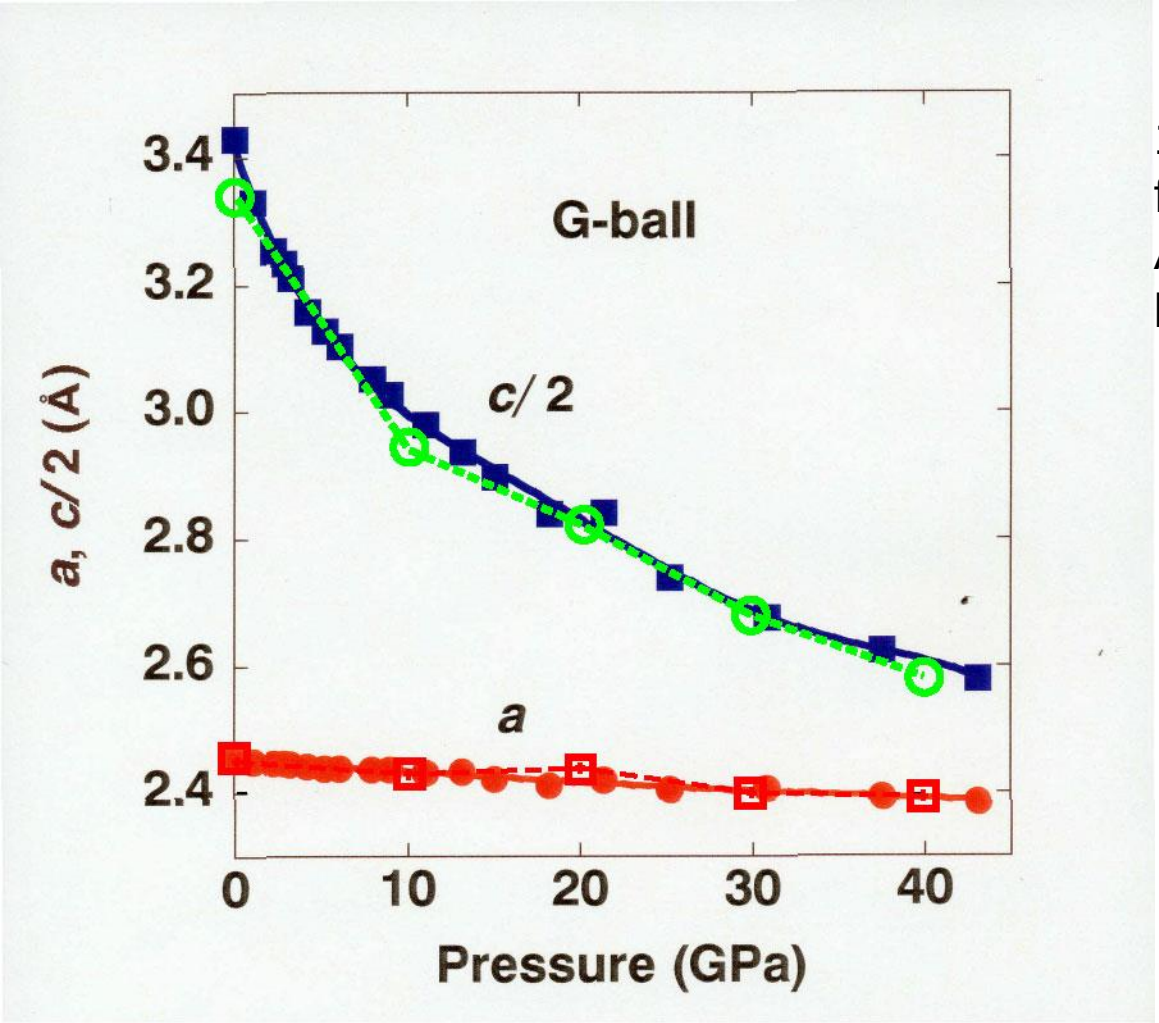
Graphitic structure stable in 40GPa range

- G-ball has a concentric structure made of graphitic sheets.
- The ball does not show any structural transformation up to ~ 40GPa.
- The conductance of the ball becomes high at high pressure.



TEM image of the graphite ball by F. Kokai et al. (2001).

Lattice constants of graphitic system in high pressure



Exp: by Nakayama et al.

1. Calculation has been done for hexagonal graphite with AB stacking of graphene layers.

2. Since we assume the graphite structure in calc., no phase transformation is seen and the structure is meta-stable up to 60GPa.

What is ESopt?

- Based on “opt” by ISSP, Univ. of Tokyo, we revised the program to have Esopt.
  - Plane wave expansion method.
  - Pseudo potential (Norm-conserving P.P.)
  - Exchange correlation: PW91
- Some merits of “opt” succeed to ESopt.
  - Readability of the source code
  - Optimization of the wavefunction by the original CG method

Characteristics of basis sets for DFT calculation

- Plane-wave expansion method with pseudo-potentials
  - Since plane waves are independent of position of atoms, the result is accurate with respect to the valence electrons.
  - Accuracy of the calculation is determined by the maximum energy of plane waves.
  - The kinetic energy is diagonal in the Fourier space, while the potential energy is diagonal in the real space. FFT is used to connect two spaces.
  - The Hellmann-Feynman force and the quantum stress are easily obtained.
- FLAPW (Full-potential linearlized augmented plane wave)
  - The wave functions in an atomic sphere are expanded in spherical waves. Otherwise, they are written in the plane waves.
  - Accuracy is determined by number of spherical waves and the maximum energy of plane waves.
  - Less ambiguity compared to the pseudo-potential method.
  - Pulay force has to be evaluated.