第34回CMDワークショップ

第一原理計算の基礎

大阪大学 大学院基礎工学研究科
物質創成専攻 未来物質領域
草部 浩一

Concept: Motion of electrons

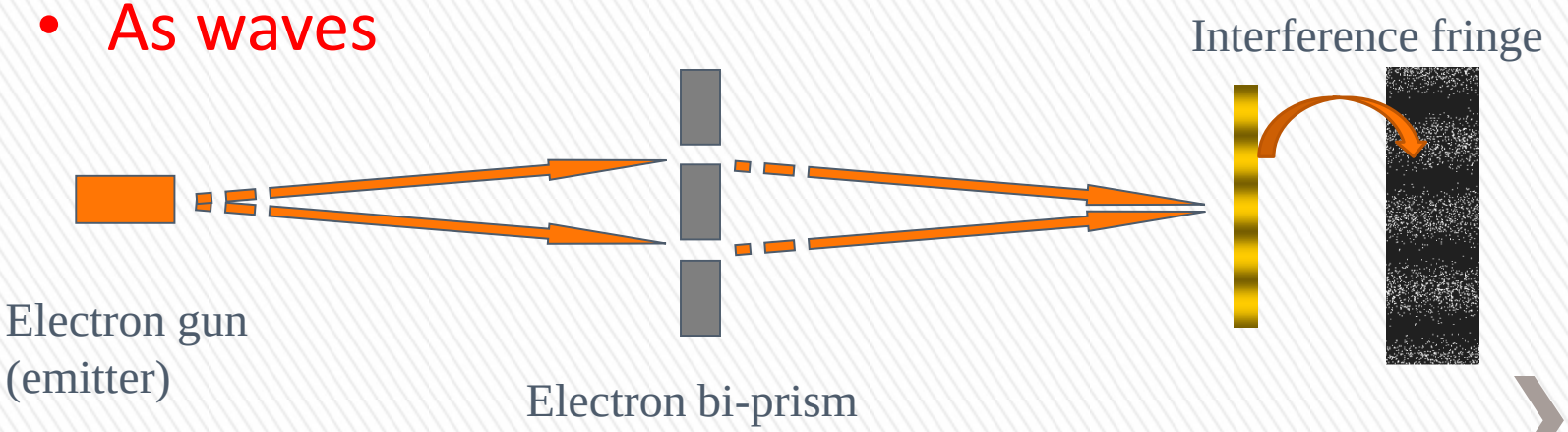
- As particles

$$p = \frac{h}{\lambda} = \hbar k, \quad k = 2\pi / \lambda.$$

p : momentum,
l : wave length,
k : wave number,
h : the Planck constant.

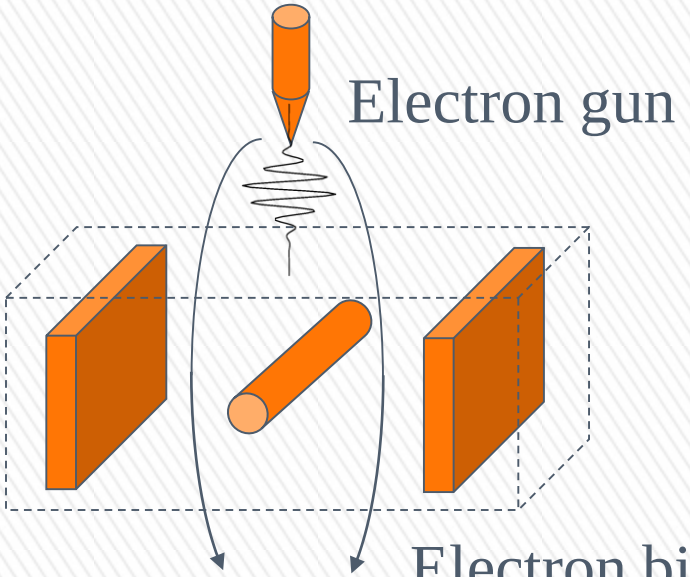
Schematic picture of an electron

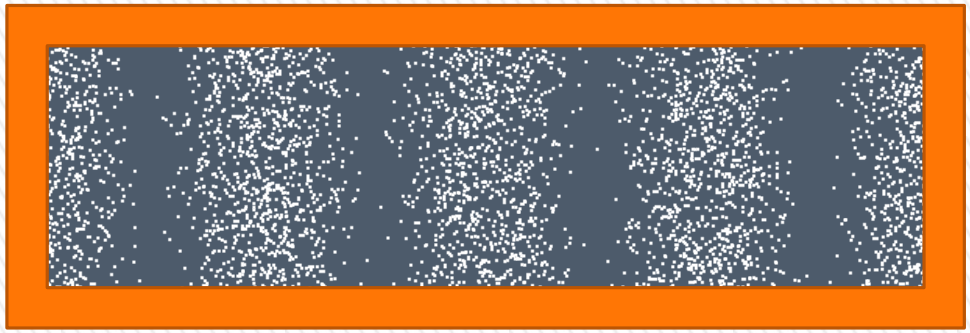
- As waves



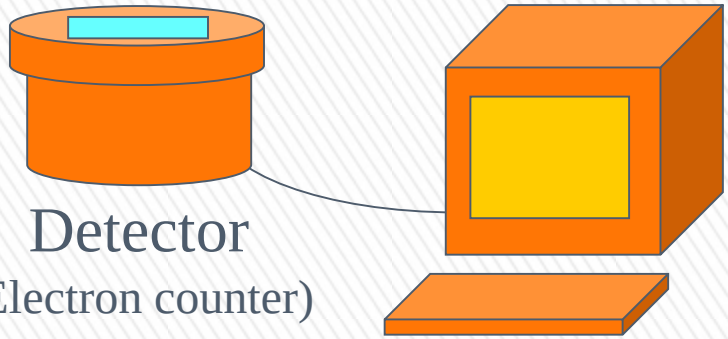
An electron moves as a wave, found to be a particle.

Interference of electron wave





Cf. 外村彰著「量子力学への招待」
"Introduction to quantum mechanics",
A. Tonomura (Iwanami shoten, in Japanese)

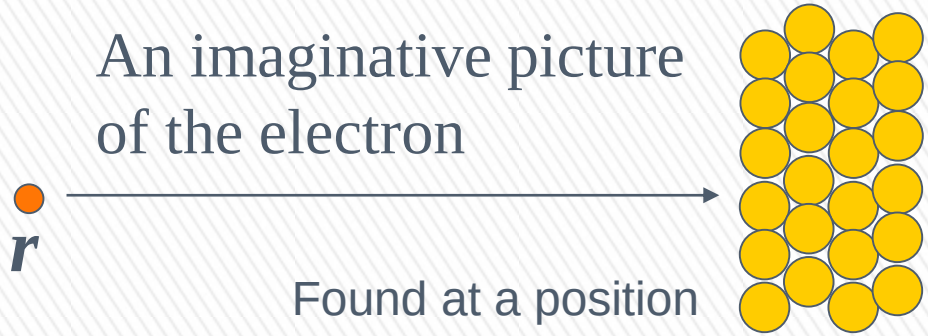


Interference fringe

Electron is a wave!
It's a quantum particle.

Why are these pictures different?

An imaginative picture of the electron

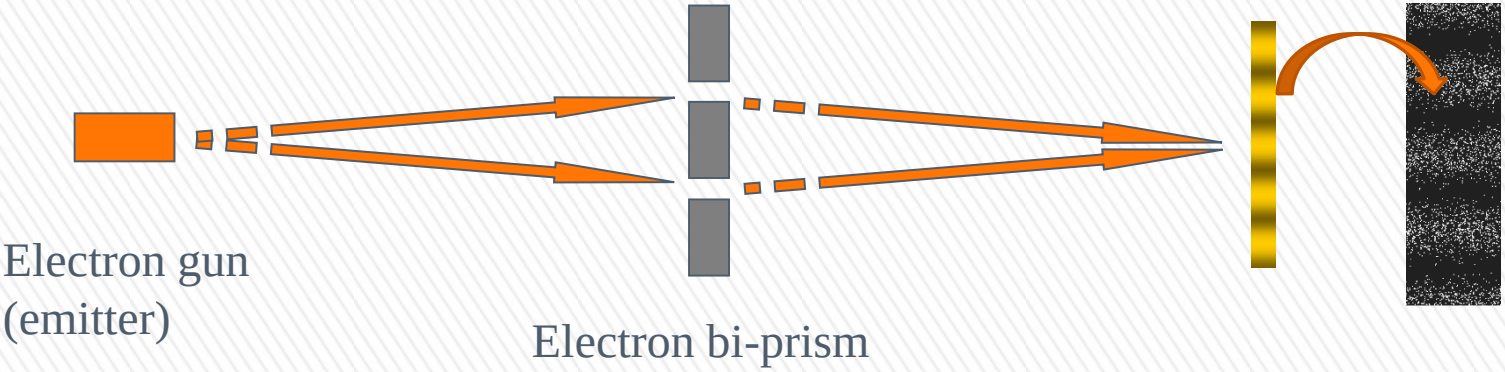


Position : $\boldsymbol{r}$

Momentum : $\boldsymbol{p}=m\dfrac{d\boldsymbol{r}}{dt}$

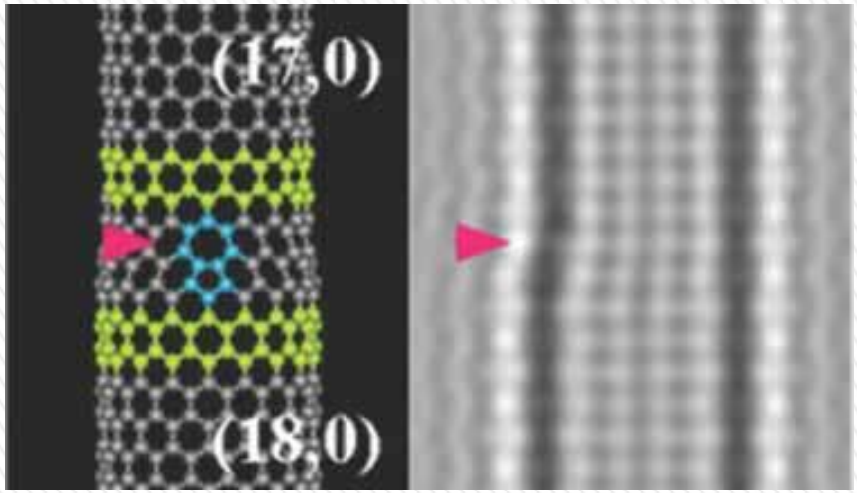
Both determined at a time t

An electron as a wave, which is in ‘a scattering state’.

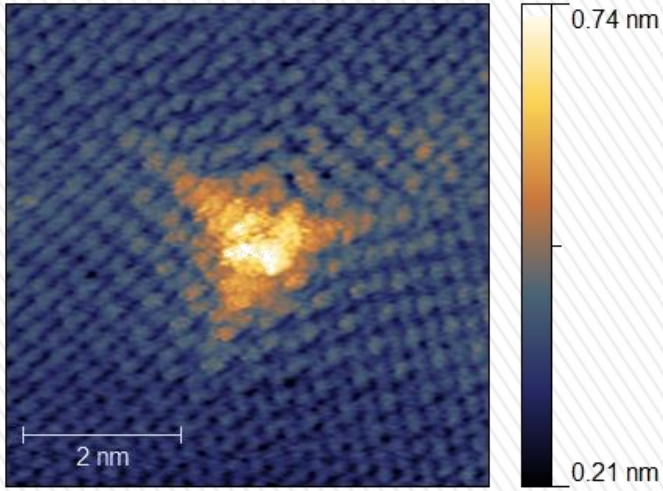


Particle position at the time t is not determined to be any specific state at $\boldsymbol{r}$.
The state with ‘a group velocity’ is composed of a superposition of ’$\boldsymbol{p}$ states’.

Direct imaging of “electron wave”



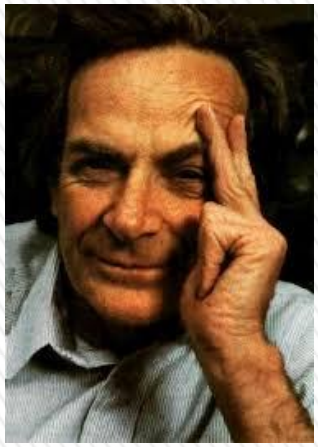
A. Hashimoto, K. Suenaga, A. Gloter, K. Urita & S. Iijima, *Nature* **430**, 870 - 873 (2004).



Cf. M. Ziatdinov, et al., *Phys. Rev. B* **89**, 155405-1-15 (2014).

Therefore, we recognize “existence of the electron wave”.

Concepts in QED

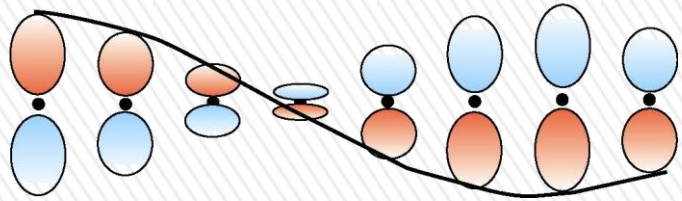


- I am rather delighted that we must resort to such peculiar rules and strange reasoning in order to understand Nature, and I enjoy telling people about it.
- There is no “wheels and gears” beneath this analysis of Nature; if you want to understand *Her*, this is what you have to take.

“QED THE STRANGE THEORY OF LIGHT AND MATTER”
Richard P. Feynman (Princeton Univ. Press, 1985.)

Wavefunction: a representation

A Bloch wave



State

- The coordinates

$$\mathbf{r} = (x, y, z), \qquad \sigma = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

$$(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \ldots, \mathbf{r}_N, \sigma_N) = (x_1, \ldots, x_N).$$

- Wavefunction : an amplitude by projection

$$\Psi(\mathbf{r}) = \langle \mathbf{r} | \cdot | \Psi \rangle = \langle \mathbf{r} | \Psi \rangle,$$

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \ldots, \mathbf{r}_N, \sigma_N)$$

$$= \langle \mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \ldots, \mathbf{r}_N, \sigma_N | \Psi \rangle.$$

State vector

$|\Psi\rangle$

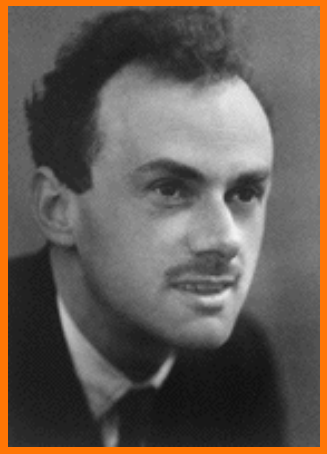
$|\mathbf{r}\rangle$

The state may be measured by the coordinates.

What is $|\Psi\rangle$?

$$|\Psi_{S=0}\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right] = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

$|\Psi_{S=0}\rangle$ by



Prof. P.A.M. Dirac

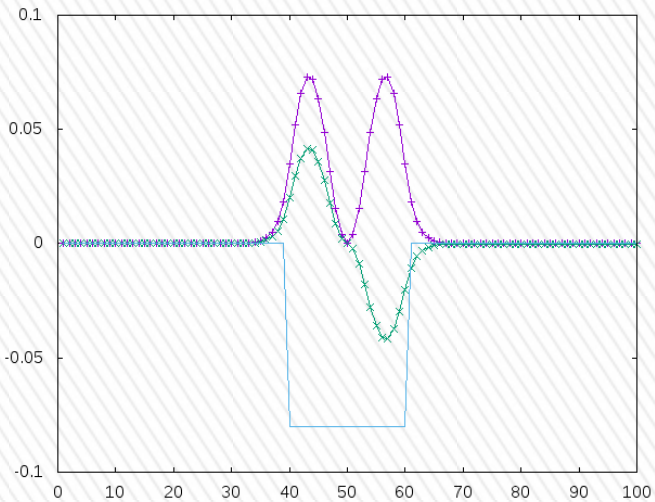
is

"A vector" !

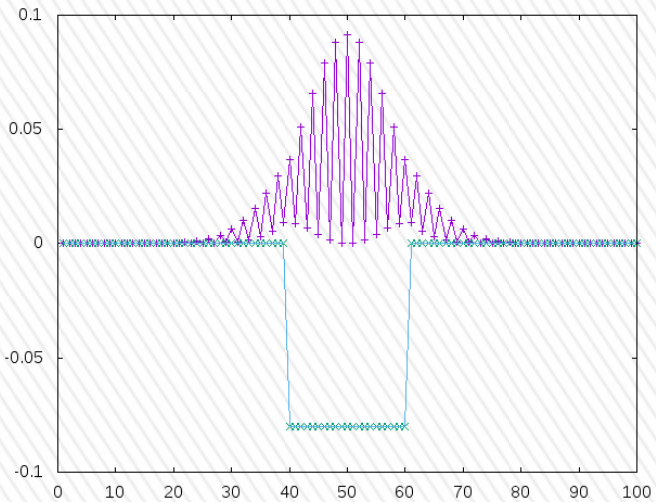
with a name "Ψ" added to the symbol.

Action of state vectors

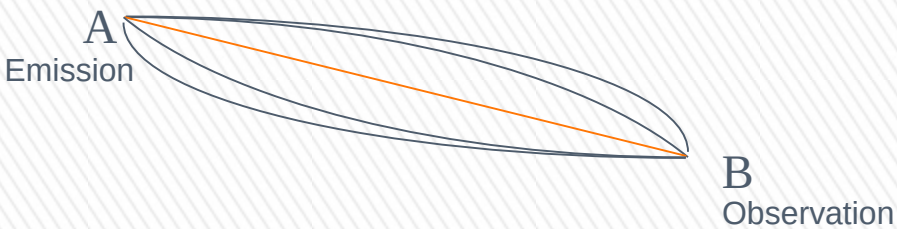
An eigen state



A transient state



A state vector shows ‘transition to the other state’.



Experimentally, we only see ‘the action’ as amplitudes.

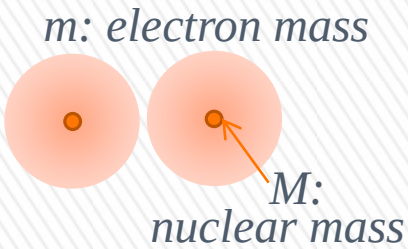
When a time coordinate is fixed for a system, a Hamiltonian operator is determined by ‘the gauge fixing’.

Separation of degrees of freedom

- 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 (or "distribution") of the mass center. Then, we may also make use of "existence of the order" in the material *a priori*.

The order is given by "the charge distribution of each species".
In relativistic form, it is by "distribution of the 4-current".

Born–Oppenheimer approximation

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

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

$$\hat{H}|\Psi\rangle$$

Here, this operator is a two-component Fermion field operator.

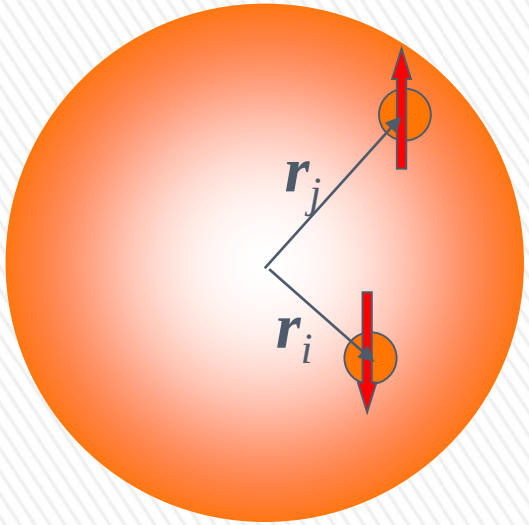
$$= \left[-\sum_\sigma \int d^3r \left(\frac{\hbar^2}{2m}\right) \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla^2 \hat{\psi}_\sigma(\mathbf{r}) + \iint d^3r d^3r' \frac{e^2 : \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}'):}{|\mathbf{r}-\mathbf{r}'|} + \int d^3r v_{ext}(\mathbf{r})\hat{n}(\mathbf{r}) \right] |\Psi\rangle$$

$$= E|\Psi\rangle.$$

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

Therefore, in a “well-defined” precise description of the quantum mechanical motion of electron, we may start from the electron Hamiltonian in the equation above.

Hamiltonian



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

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

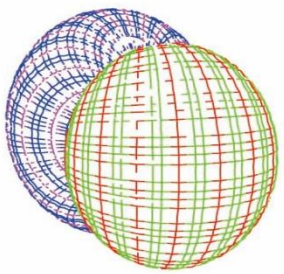
  - Cf: Ehrenfest's theorem $\frac{d}{dt}\langle \Psi | \mathbf{p} | \Psi \rangle = \langle \Psi | -\nabla v_{ext}(\mathbf{r}) | \Psi \rangle$

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

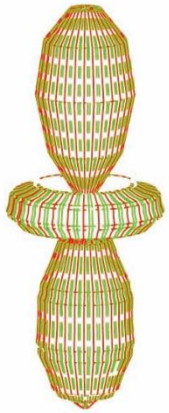
$$H = -\sum_{i=1}^{N} \left(\frac{\hbar^2}{2m} \right) \nabla_{\mathbf{r}_i}^2 + \sum_{\langle i,j \rangle} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i).$$

Electrons in a potential

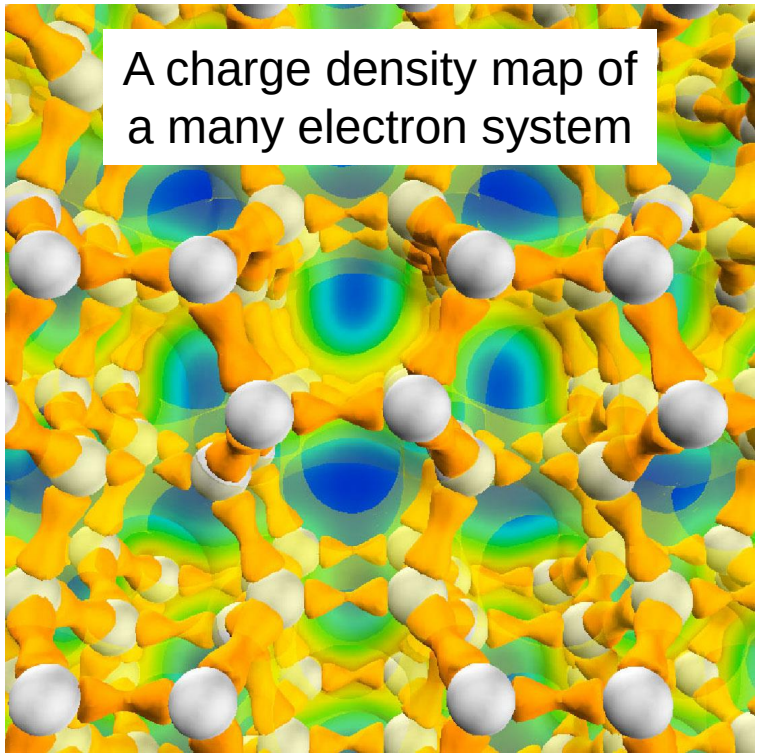
$2p$



$3d$



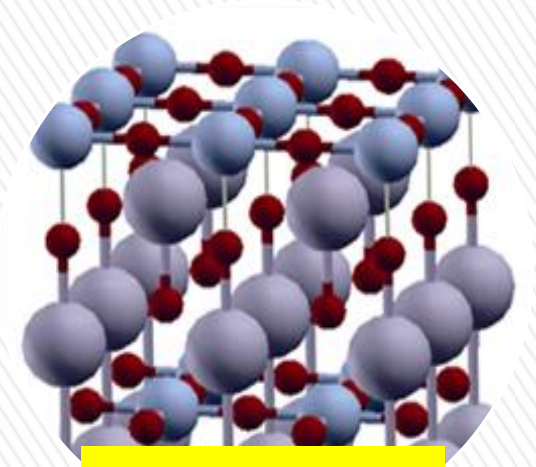
Single electron wavefunctions in steady states.



- Therefore, charge density should be determined.

Quantum mechanical calculations

Many-body theory need “a basis functions to make an expansion”.



DFT calc.

Utilization of the DFT single-particle orbitals has no more difficulty in our theory of “multi-referenced DFT”.

Model calc.

- Models of strongly correlated electron systems
  - Hubbard, Anderson
- Effective-mass theory

Perturbation Green-function

- GW+vertex correction
- Spectral DFT
  - Dynamical Mean field theory (DMFT)
  - Dynamical cluster approximation (DCA, CDMFT)

Monte-Carlo method

- Diffusion Monte Carlo
- Path integral QMC
- Projector QMC
- Continuous time loop algorithm

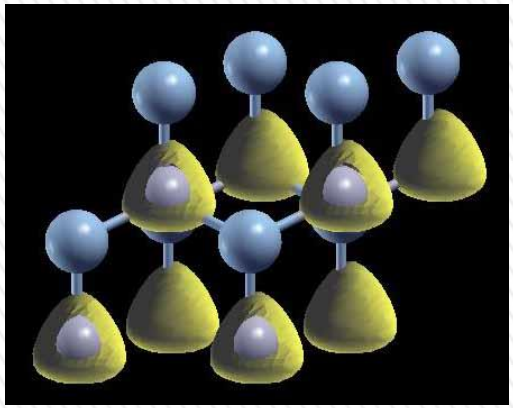
The density determining "order"

- 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 mechanics

- 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

Note: you can find that the next proof is easily extended for a wider class of Hamiltonians appearing in a model space.

- When our system is treated by the Born-Oppenheimer approximation, nuclei is treated as fixed point charges.
- v_1 and v_2 follows the Poisson equation.
- Suppose that ψ is a solution of two Schrödinger equation 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

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

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

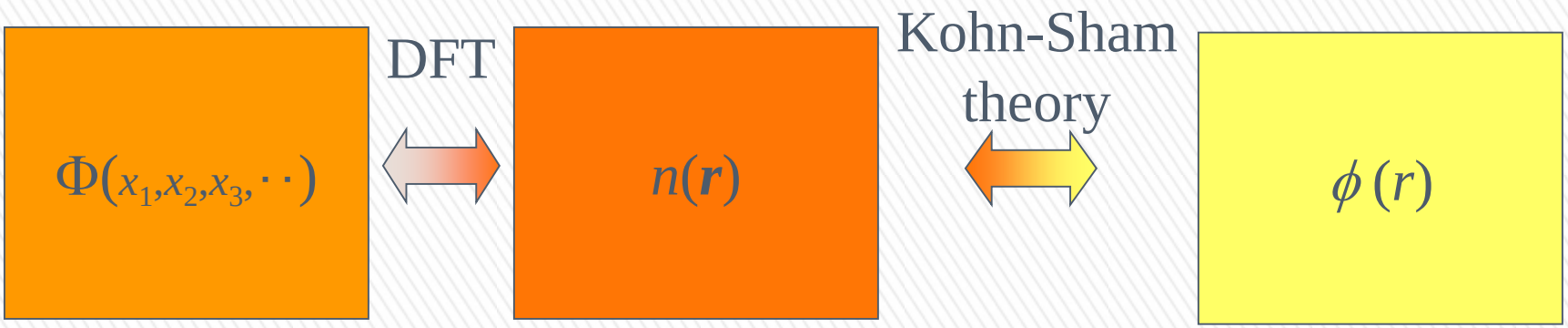
$$< \langle \Psi_1 | H_2 | \Psi_1 \rangle + \int d^3 r n (v_1 - v_2) = \langle \Psi_1 | T + V_{ee} | \Psi_1 \rangle + \int d^3 r n v_2 + \int d^3 r n (v_1 - v_2) = \langle \Psi_1 | H_1 | \Psi_1 \rangle = E_1.$$

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

- 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 $E[n]$.

Idea by Kohn and Sham

- Density as a variable



- Search optimum $n(\boldsymbol{r})$ by referencing "another wave function $\phi(\boldsymbol{r})$". (by Kohn & Sham (1965))

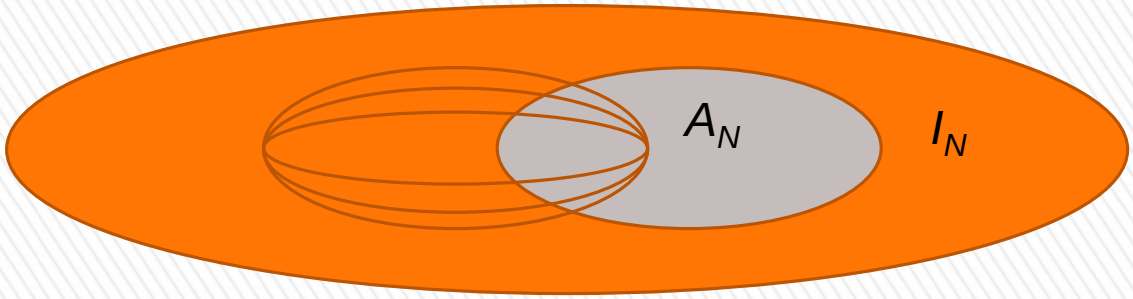
- Caution 1 by Harriman : $\forall n(r) \in I_N, \exists \phi_i(r) \text{s.t.} \{\phi_i(r)\} \to n(r).$
- Caution 2 by Lieb : $A_N \subset I_N, \quad A_N \neq A_N'.$

We need other energy functionals than the Hohenberg-Kohn functional.

A set of density

- V−representable density : A_N
  - Density of a ground state, which is an eigenstate of an interacting Hamiltonian operator for an external potential $v_{\mathrm{ext}}(\boldsymbol{r})$.

When N>1



- N−representable density : I_N
  - Density satisfying next three conditions.

$$n(\mathbf{r}) \geq 0, \quad \int n(\mathbf{r}) d\mathbf{r} = N, \quad \int \left| \nabla n(\mathbf{r})^{1/2} \right|^2 d\mathbf{r} < \infty.$$

Energy as a functional of density

- The Levy-Lieb universal energy density functional

  $\hat{T}$: kinetic energy operator, $\hat{V}_{ee}$: electron-electron interaction.

  Since $\hat{T}+\hat{V}_{ee}$ is a positive quadratic form,

$$F[n]=\min_{\Psi\to n}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle.$$

- The Lieb energy functional

  For a density, $n(\mathbf{r})\geq 0,$ which is ensemble-V (EV) representable,

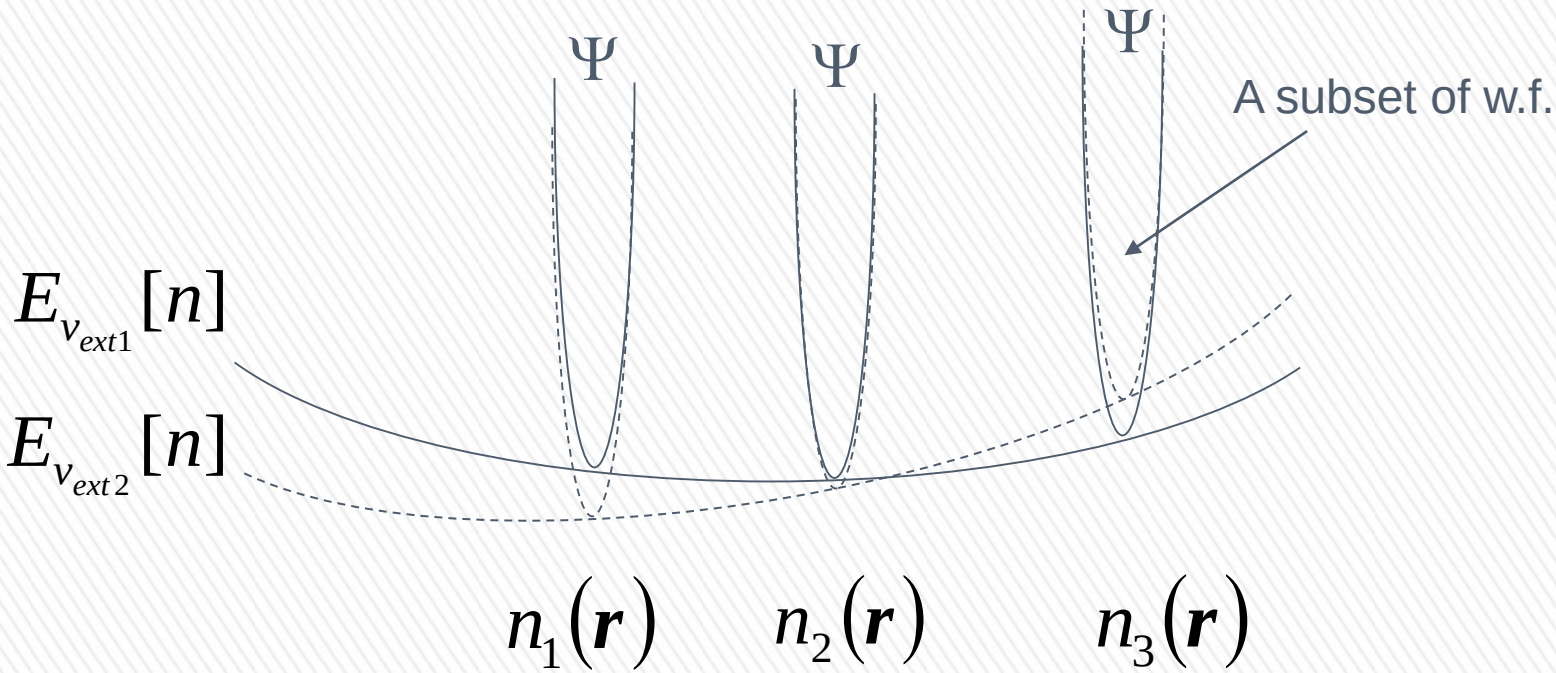
$$F_L[n]=\inf_{\hat{\Gamma}\to n}\operatorname{tr}\hat{\Gamma}\left(\hat{T}+\hat{V}_{ee}\right),$$

  $\hat{\Gamma}$: density matrix.

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.

The Kohn–Sham scheme

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

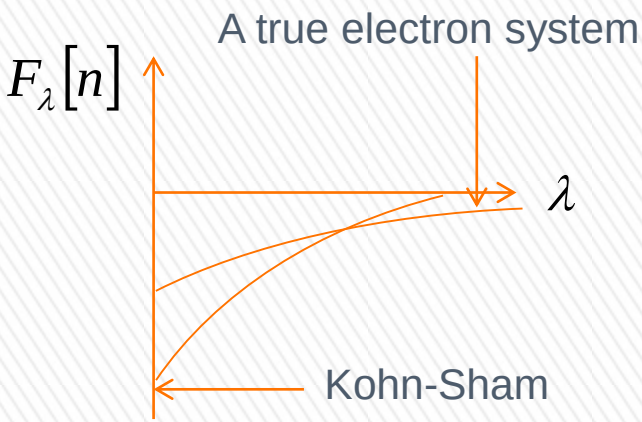
Definition of E_{xc}[n].

Two cautions on Kohn–Sham scheme

Modified energy functional and phase transition points.

$$F_\lambda[n] = \min_{\Psi' \to n} \langle \Psi' | \hat{T} + \lambda \hat{V}_{ee} | \Psi' \rangle.$$

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



Ex. Metal ↔ Mott insulator,
Kramers doublet ↔ local Kondo singlet

See also contents of 13th lecture.

of "Theory in Materials Science @ ES-OU".

Differentiability of the Lieb functional is shown in the following conditions, only.

- $n(\mathbf{r})$ is an EV-representable,
- Direction $n_1(\mathbf{r})$ is an EV-rep.,
- $n(\mathbf{r}) > 0$, and $n_1(\mathbf{r}) > 0$,
- Second order derivatives of $n_1(\mathbf{r})$, $n(\mathbf{r})$, and G.S. w.f., are square integrable.

⇒ Special directional derivative of $F_L[n]$ is given.

P.E. Lammert, Int. J. Quant. Chem. **107**, 1943 (2007).

Note that functional derivative is considered with variation out of H^1 in general sense, if one do not make a caution on the domain.

DFT & LDA/GGA

Definition of energy functional

Hohenberg-Kohn theorem

Harriman-Lieb construction
Levy-Lieb constrained min.

Lieb functional with definition of the domain

Model functional introduced, then, we have the steps !

Kohn-Sham variational method

Many-body perturbation theory using K-S orbitals

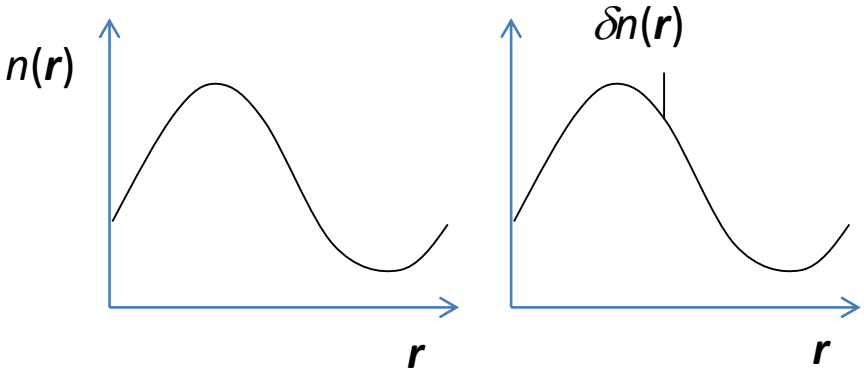
Effective many-body models to search "exact results"

Caution: On the searching path, definition of the Kohn-Sham equation by using functional derivative of the Lieb functional is not always possible. While directional derivative is given for limited directions, not only interpolation but extrapolation of $n(\boldsymbol{r})$ is requested to determine effective potential.

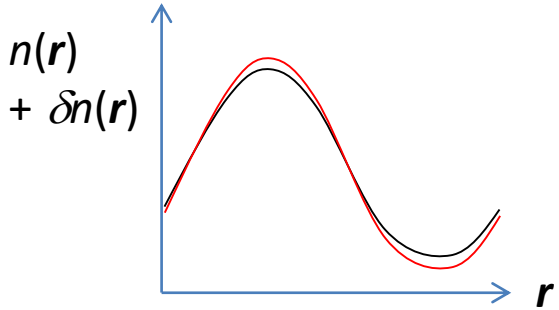
Functional derivative

Variation w.r.t. density

- General variation of $n(\boldsymbol{r})$ includes,

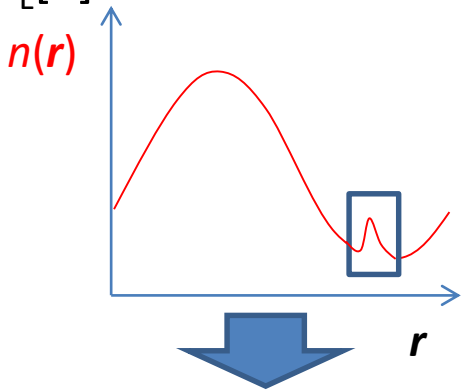


- Variation maintaining N has to be non-local.



Non-linear functional

- Fréchet derivative w.r.t. $\delta n(\boldsymbol{r})$ is accessible for linear functional. But, $F_L[n]$ is not a linear functional.



Since Ψ giving "non-N-rep. $n(\boldsymbol{r})$" is not found, "ensemble v-rep. $n(\boldsymbol{r})$" is requested. The Gâteaux derivative of the Lieb functional has directional dependence on $\delta n(\boldsymbol{r})$ as a function of $\boldsymbol{r}$.

Classification of density

v-representable — A density distribution given by a quantum eigen state in a potential

- $\mathscr{A}(N)$: by an eigen state (a ground state) of an interacting N-body electron system
- $\mathscr{A}(N)'$: by an eigen state (a ground state) of a non-interacting N-body Fermion system

N-representable — by an anti-symmetric wave function of an N-particle system

- $\mathscr{I}(N)$: positive, integrable, thus normalizable to give N, $(\nabla n(\boldsymbol{r})^{1/2})^2$ is also square integrable
- The Harriman-Lieb construction gives a many-body wave function giving $n(\boldsymbol{r})$. Thus existence of the wave functions for constrained minimization is certified.

Ensemble v-representable — Linear combination of two or more v-representable density distributions (Ensemble average as statistical average)

- Defined as an interpolating point of two well-defined end points
- Two end points are v-representable (non-negative, without diverging points)
- A statistical average found on the way of the search is not pure v-representable.

The rigorous DFT method requires "huge amount of calculation steps" far bigger than the statistical quantum mechanics method for N-body problem.

We do not use the Lieb functional.

$$G_T[\Psi'] = \langle \Psi' | \hat{T} | \Psi' \rangle - F_{L,T}[n_{\Psi'}] + F_L[n_{\Psi'}] + \int v_{ext}(\mathbf{r}) n_{\Psi'}(\mathbf{r}) d^3 r.$$

$$G_T[\Psi'] = \langle \Psi' | \hat{T} | \Psi' \rangle + \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 r d^3 r' + E_{xc}[n_{\Psi'}] + \int v_{ext}(\mathbf{r}) n_{\Psi'}(\mathbf{r}) d^3 r.$$

Let's assume that $|\Psi'\rangle$ is a minimizer w.r.t. variation: $\frac{\delta}{\delta \langle \Psi' |} \{ G_T[\Psi'] - E(\langle \Psi' | \Psi' \rangle - 1) \} = 0,$
where density variation is assumed to be given as,

$$n(\mathbf{r}) = \langle \Psi' | \hat{n}(\mathbf{r}) | \Psi' \rangle,$$

$$\delta n(\mathbf{r}) = \{ \langle \Psi' | + \delta \langle \Psi' | \} \hat{n}(\mathbf{r}) \{ | \Psi' \rangle + \delta | \Psi' \rangle \} - n(\mathbf{r})$$: two end points are positive. (Good. But,)

$$= \{ \delta \langle \Psi' | \} \hat{n}(\mathbf{r}) \{ | \Psi' \rangle \} + \{ \langle \Psi' | \} \hat{n}(\mathbf{r}) \{ \delta | \Psi' \rangle \} + \{ \delta \langle \Psi' | \} \hat{n}(\mathbf{r}) \{ \delta | \Psi' \rangle \}.$$

$$\left\{ \hat{T} + \int d^3 r v_{eff}[n, \delta n[\delta \langle \Psi' |]](\mathbf{r}) \hat{n}(\mathbf{r}) \right\} | \Psi' \rangle = E | \Psi' \rangle,$$: known numerical methods are not applicable to solve these equations, since

$$v_{eff}[n, \delta n](\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}),$$: is not a local potential, and

$$\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \frac{\delta}{\delta n(\mathbf{r})} \left\{ F_L[n] - F_{L,T}[n] - \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 r d^3 r' \right\}.$$: the directional derivative has $\delta n[\delta \langle \Psi' |](\mathbf{r})$ dependence.

We offer another way by evading this difficult point of KS equation.

Why do we use DFT?

- Degree of freedom is separated into electrons and nuclei by the Born-Oppenheimer approximation.
  - Electron density characterizes the system!
- Let's determine the free energy (total energy at T=0K) by the electron density.

Hamiltonian

- Born-Oppenheimer approx.

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

- ➢ Classical configuration of nuclei,
- ➢ Determination of static potential.

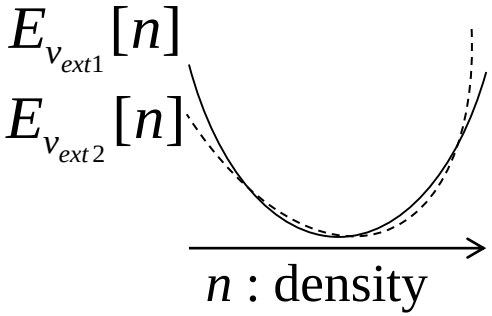
Order parameter

- Funct. deriv. w.r.t. ext. pot.

$$\begin{aligned} & E\left[v_{ext} + \delta v_{ext}\right] - E\left[v_{ext}\right] \\ &= \int d^3r \frac{\delta E\left[v_{ext}\right]}{\delta v_{ext}(\mathbf{r})}\delta v_{ext}(\mathbf{r}) + O\left(\delta^2\right) \\ &= \int d^3r \delta v_{ext}(\mathbf{r}) n(\mathbf{r}) + O\left(\delta^2\right). \end{aligned}$$

Statistical mechanics offers a solution.

- L.D. Landau had predicted relevance of order parameters.
  - Energy of condensed matter is given by “a function of physical variables” i.e. a functional of a function.
    - Landau considered analytic functions at first.
    - Phenomenological, but “exact”, since the idea comes from observation of phenomena.
- Present DFT is interpreted as a realization.
  - Order parameter = Electron density
  - Energy functional = Landau functional



The idea goes back to the original Thomas-Fermi arguments. As such, the history of the quantum statistical mechanics is long.

Derive differential equations

- First, set up a differentiable energy functional.

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

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

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

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

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

This strategy gives us “realistic approaches” of DFT.
We had developed “systematic improvement” of any approximation in DFT.

E_{xc} as quantum fluctuation

- The exchange-correlation energy functional may be written as,

$$E_{xc}[n] = \frac{e^2}{2}\int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} n_{xc}(\mathbf{r},\mathbf{r}')$$

with

$$n_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\int_0^1 [g_n(\mathbf{r},\mathbf{r}',\lambda)-1]d\lambda$$

$$= \int_0^1 [\underbrace{\langle \Psi_\lambda | (\hat{n}(\mathbf{r})-n(\mathbf{r}))(\hat{n}(\mathbf{r}')-n(\mathbf{r}')) | \Psi_\lambda \rangle}_{\text{Quantum Fluctuation!}} / n(\mathbf{r}) - \delta(\mathbf{r}-\mathbf{r}')]d\lambda.$$

- In the local density approximation (LDA), we approximate n_{xc} by that of the homogeneous electron gas as,

$$n_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})\int_0^1 [g^{\text{hom}}{}_n(\mathbf{r},\mathbf{r}',\lambda)-1]d\lambda.$$

'Density-functional theory of atoms and molecules,' by R.G. Parr, & W. Yang, Springer, § 8.5.

Why local density approximation?

LDA exchange-correlation energy can be written as,

$$\bar{E}_{xc}[n] = \frac{e^2}{2}\int d^3r n(\mathbf{r})\int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\bar{n}_{xc}(\mathbf{r},\mathbf{r}') = \int d^3r n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r})).$$

$$\bar{n}_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})\int_0^1 \left[g^{\text{hom}}{}_n(\mathbf{r},\mathbf{r}',\lambda)-1\right]d\lambda.$$

- This LDA exchange-correlation hole satisfies a sum rule. (See next page.)
- The value is given for any $n(\mathbf{r})$.

When we choose LDA, the Kohn-Sham equation reads,

$$\left\{-\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} + v_{eff}(\mathbf{r})\right\}\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}),$$

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

$$n(\mathbf{r}) = \sum_{\sigma}\sum_{\varepsilon_i \le E_F}|\phi_i(\mathbf{r})|^2.$$

For this set of equations, we have computer codes as numerical solvers of quantum mechanical problems for electron systems.

Reasonable accuracy !!!

If you need, you may always make a correction by introducing "multi-reference representation of a model many-body system".

A sum rule in DFT & that in LDA

$$g_n(\mathbf{r},\mathbf{r}',\lambda)=\frac{\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle_{\Psi_\lambda}}{n(\mathbf{r})n(\mathbf{r}')}-\frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}$$

$$=\frac{\langle(\hat{n}(\mathbf{r})-n(\mathbf{r}))(\hat{n}(\mathbf{r}')-n(\mathbf{r}'))\rangle_{\Psi_\lambda}}{n(\mathbf{r})n(\mathbf{r}')}-\frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}+1.$$

$$\int d^3r' n_{xc}(\mathbf{r},\mathbf{r}')=\int d^3r' n(\mathbf{r}')\left\{\int_0^1 g_n(\mathbf{r},\mathbf{r}',\lambda)d\lambda-1\right\}$$

$$=\int d^3r'\left\{\int_0^1\frac{\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle_{\Psi_\lambda}}{n(\mathbf{r})}d\lambda-\frac{n(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}-n(\mathbf{r}')\right\}$$

$$=\int_0^1\frac{1}{n(\mathbf{r})}\left\langle\hat{n}(\mathbf{r})\int d^3r'\hat{n}(\mathbf{r}')\right\rangle_{\Psi_\lambda}d\lambda-\int d^3r'\frac{n(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}-\int d^3r' n(\mathbf{r}')$$

$$=\int_0^1\frac{1}{n(\mathbf{r})}\left\langle\hat{n}(\mathbf{r})\hat{N}\right\rangle_{\Psi_\lambda}d\lambda-1-N$$

$$=N\frac{n(\mathbf{r})}{n(\mathbf{r})}\int_0^1 d\lambda-1-N=N-1-N$$

$$=-1.$$

$$g^{\text{hom}}{}_n(\mathbf{r},\mathbf{r}',\lambda)=\frac{\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle_n^{\text{hom}}}{n(\mathbf{r})n(\mathbf{r}')}-\frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}$$

$$=\frac{\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle_n^{\text{hom}}}{n(\mathbf{r})^2}-\frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})},$$

$$\int d\mathbf{r}' n_{xc}^{LDA}(\mathbf{r},\mathbf{r}')=\int d\mathbf{r}' n(\mathbf{r})\int_0^1\left[g^{\text{hom}}{}_n(\mathbf{r},\mathbf{r}',\lambda)-1\right]d\lambda$$

$$=\int d\mathbf{r}' n(\mathbf{r})\int_0^1\left[\frac{\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle_n^{\text{hom}}}{n(\mathbf{r})^2}-\frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})}-1\right]d\lambda$$

$$=\int_0^1\left[\frac{\langle\hat{n}(\mathbf{r})\int d\mathbf{r}'\hat{n}(\mathbf{r}')\rangle_n^{\text{hom}}}{n(\mathbf{r})}-1-n(\mathbf{r})V\right]d\lambda$$

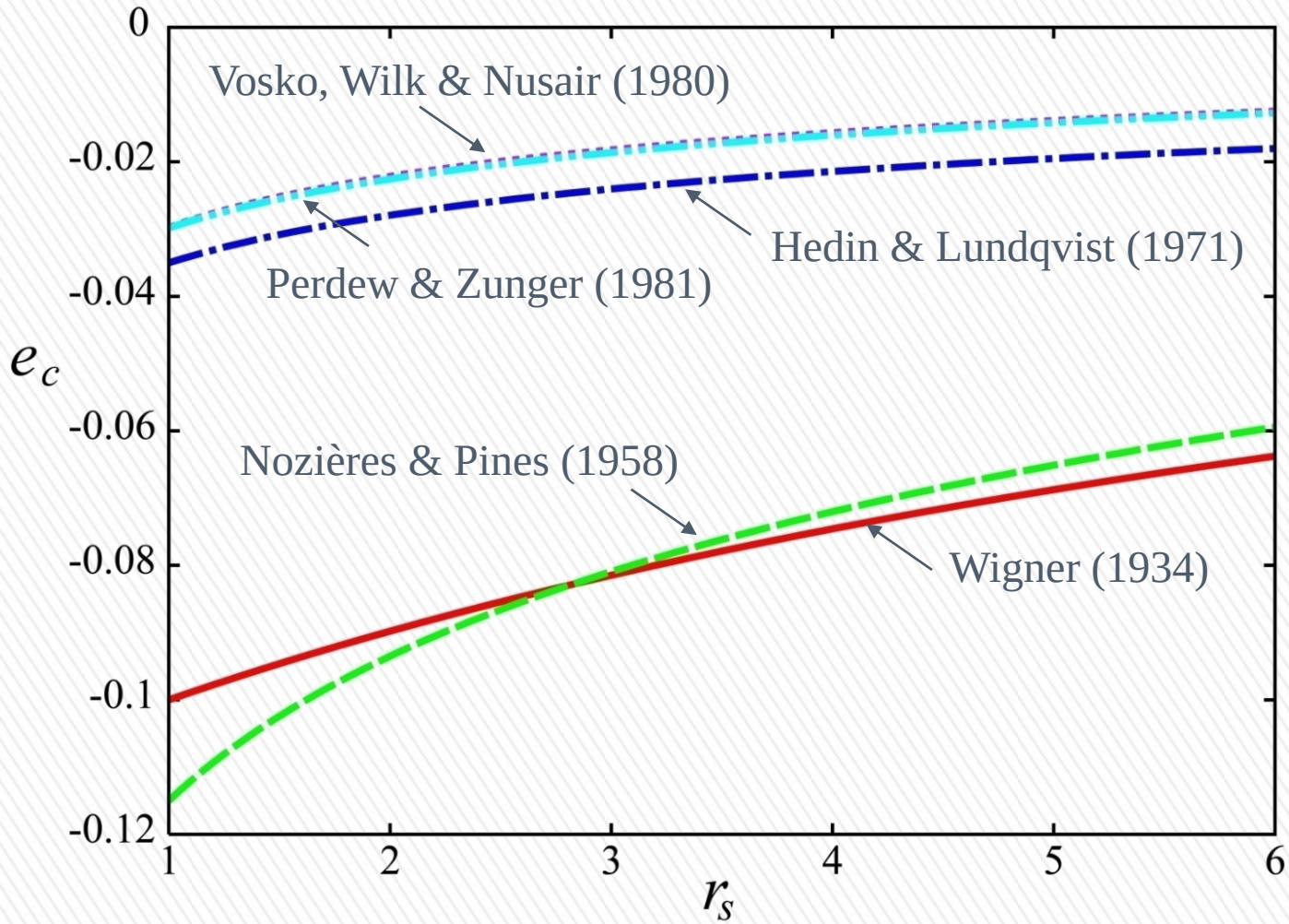
$$=\frac{n(\mathbf{r})^2V}{n(\mathbf{r})}-1-n(\mathbf{r})V$$

$$=-1.$$

Thus, although we have completely different formulae for DFT and LDA, the same sum rule for the exchange-correlation hole is satisfied.

Correlation energy density of 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, $\varepsilon_{xc}(r_s) = \varepsilon_x(r_s) + \varepsilon_c(r_s)$.



How to solve the Kohn–Sham eqs?

$$\left\{-\frac{\hbar^2}{2m}\Delta_{\mathbf{r}}+v_{eff}(\mathbf{r})\right\}\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r}),$$

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

$$n(\mathbf{r})=\sum_{\sigma}\sum_{\varepsilon_i\le E_F}|\phi_i(\mathbf{r})|^2.$$

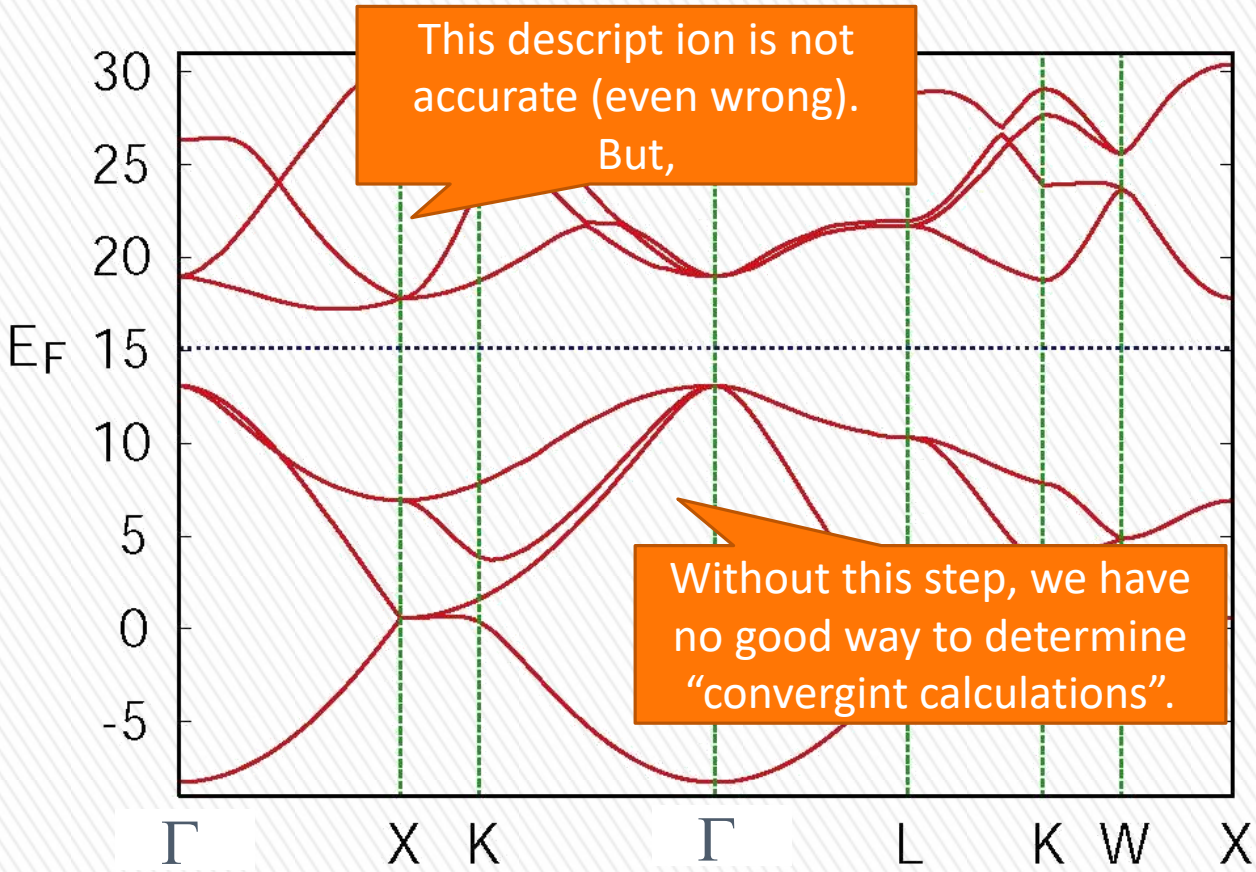
A good point: A complete basis set giving the expansion of the many-body state vector.

We need to find a solution $\{\phi_i(\boldsymbol{r})\}$ satisfying

1. Symmetry of the system (Crystal symmetry, molecular symmetry)
2. Self-consistency

This is a least version for DFT. It is corrected by “quantum charge fluctuation”.

Band structure of cubic diamond



σ^* bands (anti-bonding bands)

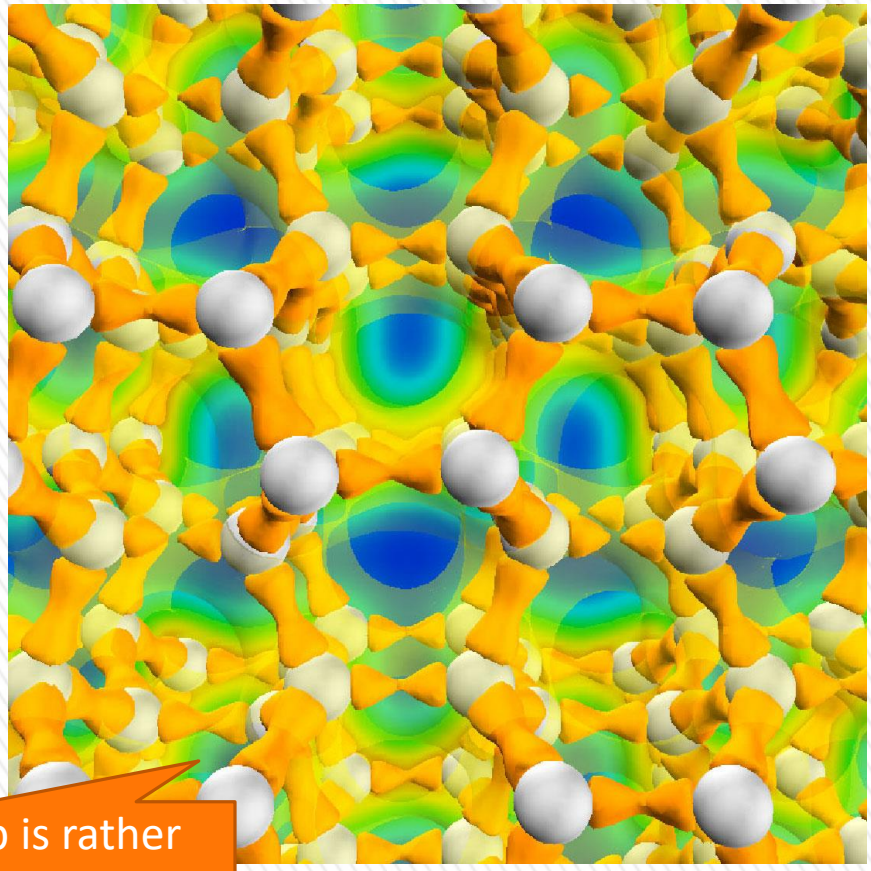
σ bands (bonding bands)

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

LDA by PW91.
Plane-wave expansion with ultra-soft PP.

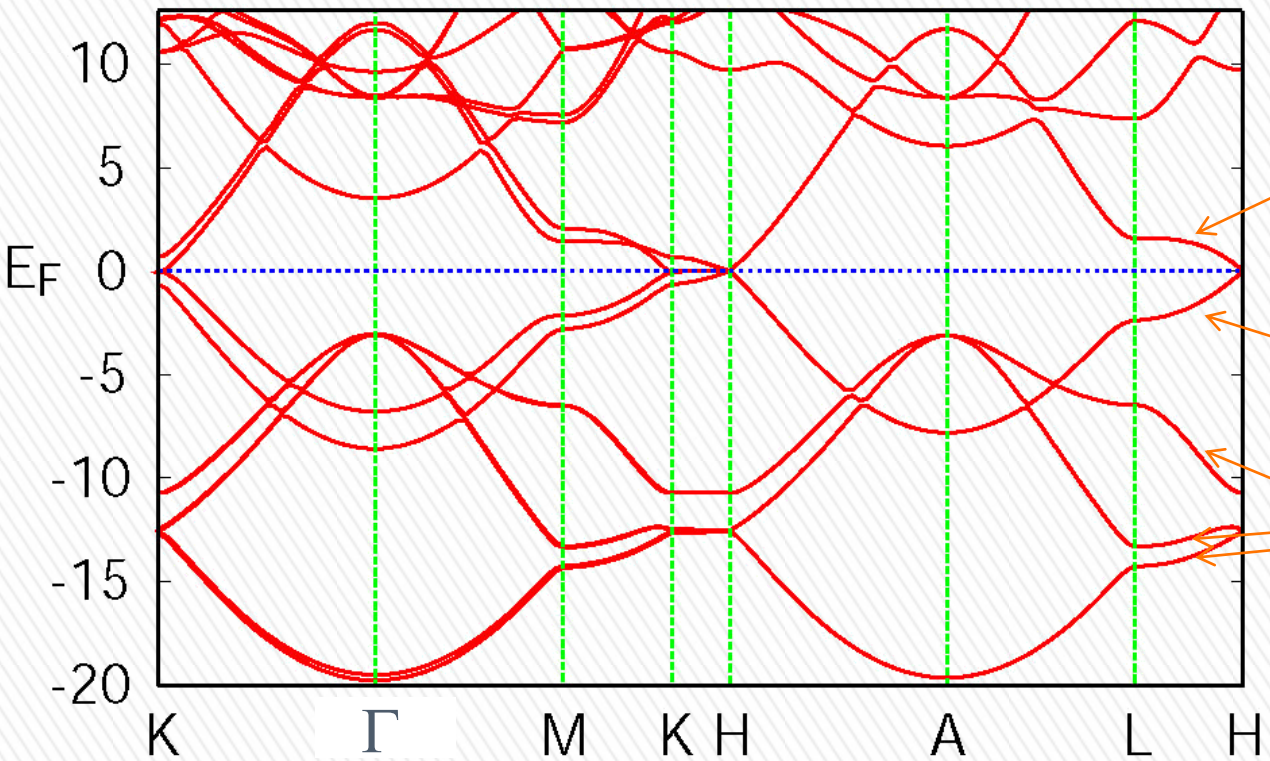
Bonding charge in hex-diamond

- 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.



The density map is rather accurate, because it is determined self-consistently.

Band structure of graphite



σ^* bands (anti-bonding bands)

π^* bands (anti-bonding)

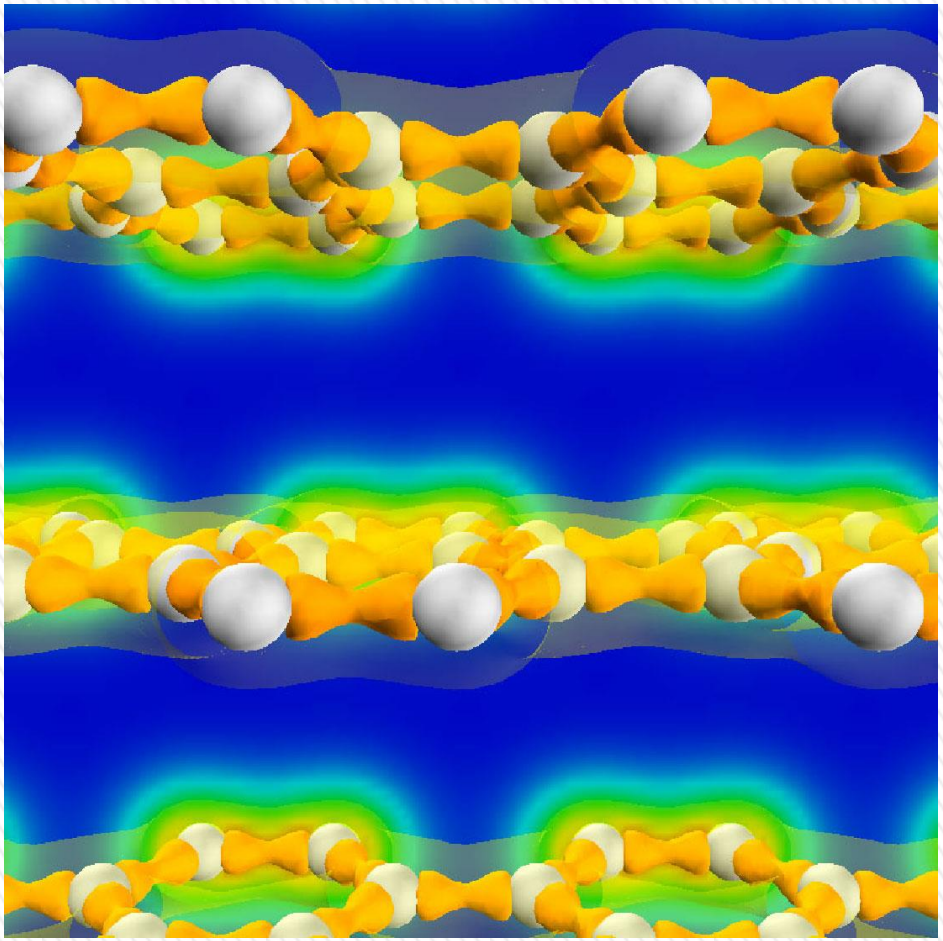
π bands (bonding bands)

σ bands (bonding bands)

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

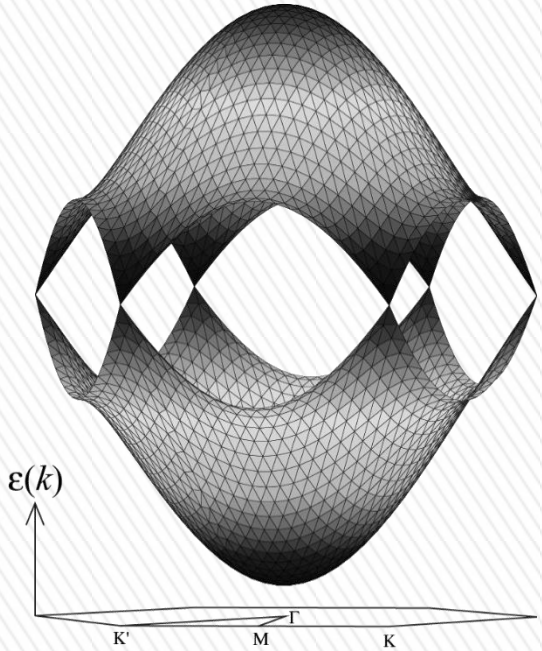
Bonding charge in graphite

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

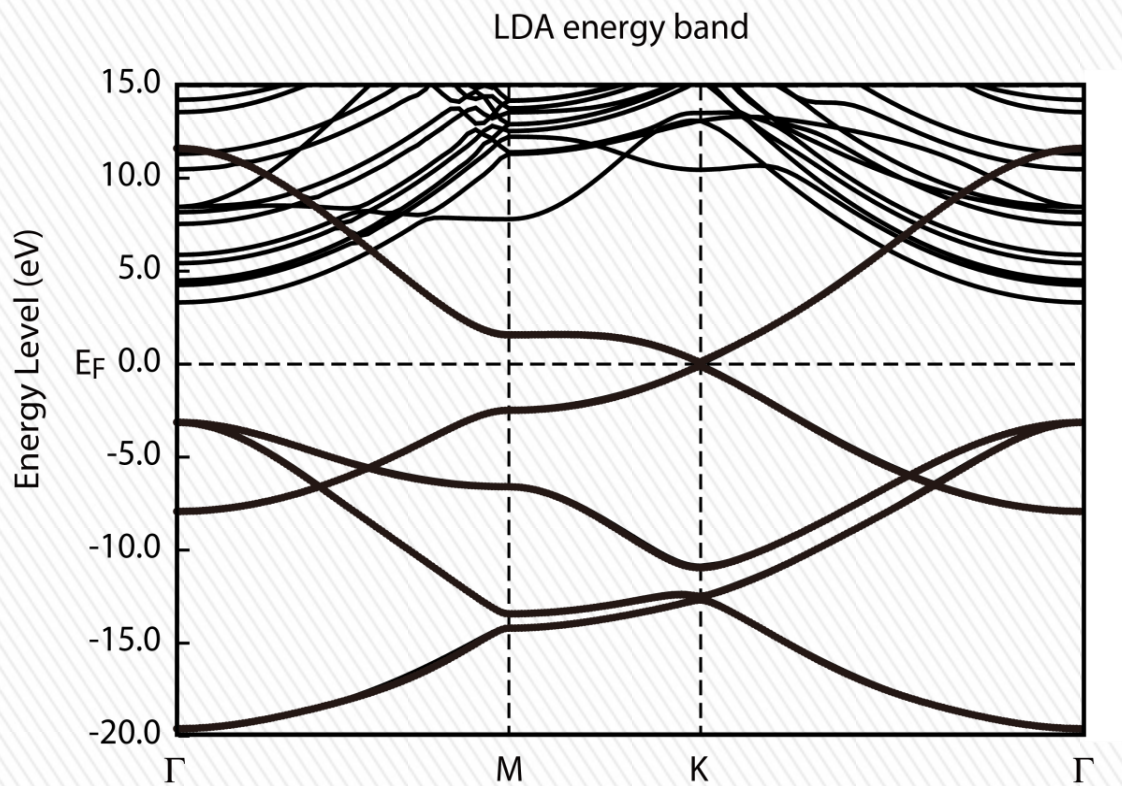


When you see a localized state mediating quantum information process, you may introduce “a solver for correlated electron systems” at any time.

Band structure of Graphene



This is a result by
a tight-binding model.



We want to see “what is seen in the right figure”!!

Idea to use gradient of density

- To overcome limitation of LDA, Kohn & Sham had considered gradient corrections.

- Let's first introduce another order parameter,

$$F[n,\mathbf{j}] = \min_{|a,b\rangle \to (n,\mathbf{j})} \langle a,b | \int H(\mathbf{r}) d\mathbf{r} | a,b \rangle, \; F[n,\mathbf{m}] = \min_{|a,b\rangle \to (n,\mathbf{m})} \langle a,b | \hat{T} + \hat{V}_{\mathrm{ee}} | a,b \rangle.$$

or density for two spins, $n_{\uparrow}(\boldsymbol{r})$, $n_{\downarrow}(\boldsymbol{r})$, or density of multiple species (electrons & nuclei).

- Naively,

$$E_{xc}^{GEA}[n_\uparrow, n_\downarrow] = E_{xc}^{LSDA}[n_\uparrow, n_\downarrow] + \sum_{\sigma,\sigma'} \int d^3r C_{\sigma,\sigma'}(n_\uparrow, n_\downarrow) \frac{\nabla n_\sigma}{n_\sigma^{2/3}} \cdot \frac{\nabla n_{\sigma'}}{n_{\sigma'}^{2/3}}.$$

Generalized gradient approximation

- GEA fails due to violation of sum rules.

- Introduce a GGA exchange-correlation energy functional, whose ex.-corr. hole satisfies desired sum rules.

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow).$$

For the case of exchange hole,

$$\tilde{n}_x^{GGA} = -\frac{1}{2} n(\mathbf{r}) \tilde{y}(\mathbf{r}, \mathbf{u}) \theta(\tilde{y}(\mathbf{r}, \mathbf{u})) \theta(u_x(\mathbf{r}) - u),$$

where $\theta(x)$ is the step function.

'Electronic Structure – Basic Theory and Practical Methods,' by R.M. Martin, Cambridge University Press.

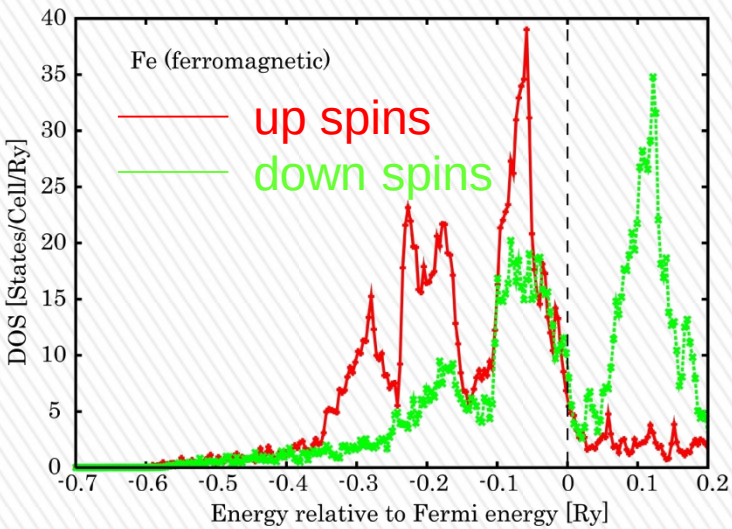
Which do we use, LDA or GGA?

- 3d ferromagnetic metals:

Element	T_c/K	M/μ_B	Configuration
Fe	1043	2.219	$3d^6$
Co	1404	1.715	$3d^7$
Ni	630	0.604	$3d^8$

- LSDA does not reproduce stability of ferromagnetism.
- Spin-GGA reproduces magnetism even quantitatively. (This is practical understanding.)

Internal field considered



Thanks to Akai-KKR

The result suggests existence of ***m***(***r***) in a solution of DFT simulation.

$$\langle \hat{\mathbf{m}}(\mathbf{r}) \rangle, \quad \langle \hat{\mathbf{j}}(\mathbf{r}) \rangle, \quad \text{or}$$

$$\langle \hat{j}_\mu(x) \rangle = \langle \overline{\psi}(x) \gamma_\mu \psi(x) \rangle$$

may be used to determine the internal vector photon field to derive an effective potential problem determining an L^2 basis.

An effective action and the resulting effective Hamiltonian contain all the electron-electron interaction processes in many-body description.

Decision by empirical rules

GGA OK

- Good 3d metals,
- Strong metallic ferromagnets,
- 3d semiconductors,
- Molecules,
- Molecular solids without π-π stacking.

GGA not in use

- Graphite, h-BN, CF,
- Weak ferromagnets,
- Molecular solids with π-π stacking.

For these materials, LDA gives rather reasonable solution.

We may use GGA to obtain a starting (tentative, or initial) solution for consideration of

- Van-der-Waals crystals,
- Materials showing strong-correlation effects.

If both LDA and GGA fails?

We might be able to solve the problem using

- For the van-der-Waals crystals,
  - GGA + van-der-Waals correction,
  - EXX + RPA correlation.
- For the strong-correlation problems,
  - GGA + short-range correlation,
  - EXX + (RPA + vertex corrected) correlation.

Please consult experts!!!

The bulk modulus

$$B_0 = -\frac{Vdp}{dV} = \frac{Vd^2E}{dV^2},$$

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0'-1} + 1\right) - \frac{B_0 V_0}{B_0'-1}.$$

We can compare the methods for c-BN.

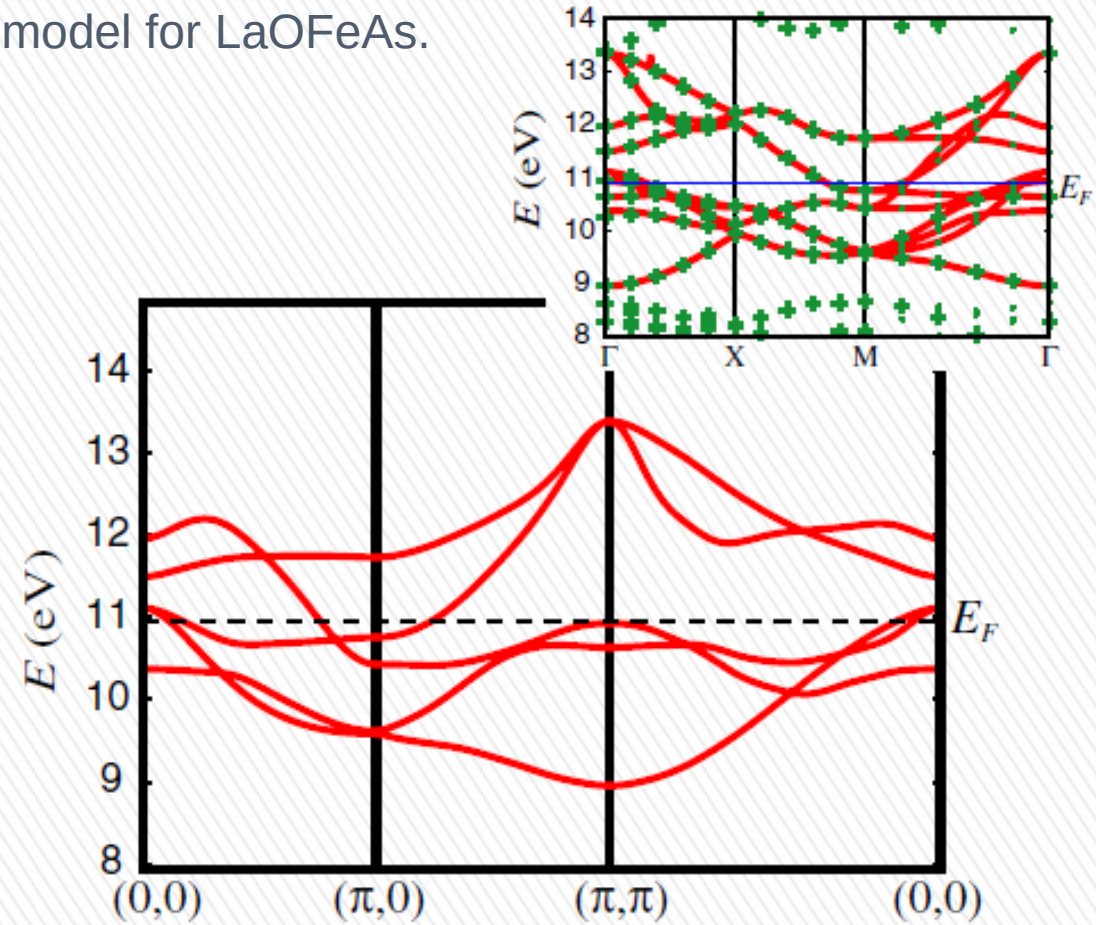
		a	C_L	G	B
This work	PUS	3.6169 ± 0.0005	945 ± 3	410[a]	401[a]
	QE-GGA	3.622	887	384	375
	VASP-GGA	3.626	881	381	372
	QE-LDA	3.569	951	412	402
	VASP-LDA	3.583	940	403	402
Reference (measured)	BS[b]		941	405	400
	BS[c]	3.6157 ± 0.0008	913	399	381
	XRD[d]	3.615 ± 0.002			369 ± 14
	XRD[e]	3.6157 ± 0.0008			387 ± 4
Reference (calculated)	GGA[f]	3.620 ± 0.007[g]	920 ± 38[g]	390 ± 21[g]	385 ± 16[g]
	LDA[h]	3.589 ± 0.012[g]	946 ± 15[g]	408 ± 9[g]	398 ± 12[g]
	hybrid[i]	3.602 ± 0.006[g]			399 ± 7[g]
	MD[j]	3.625 ± 0.023[g]	858 ± 58[g]	360 ± 43[g]	378 ± 2[g]
	Force field[k]		1074	342	618
	Tight binding[l]		1079	341	624
	Tight binding[m]		1310	430	737

- LDA is known to give reasonable estimation.
- People noticed that GGA gives a shifted value.
- Interpretation became possible after BS & PUS have been known.
- Correction of GGA is known to be possible.
- Then, evaluation of TB or force field may be allowed.

Cf. Nagakubo, et al. Appl. Phys. Lett. 102, 241909 (2013).

A tight–binding model by DFT

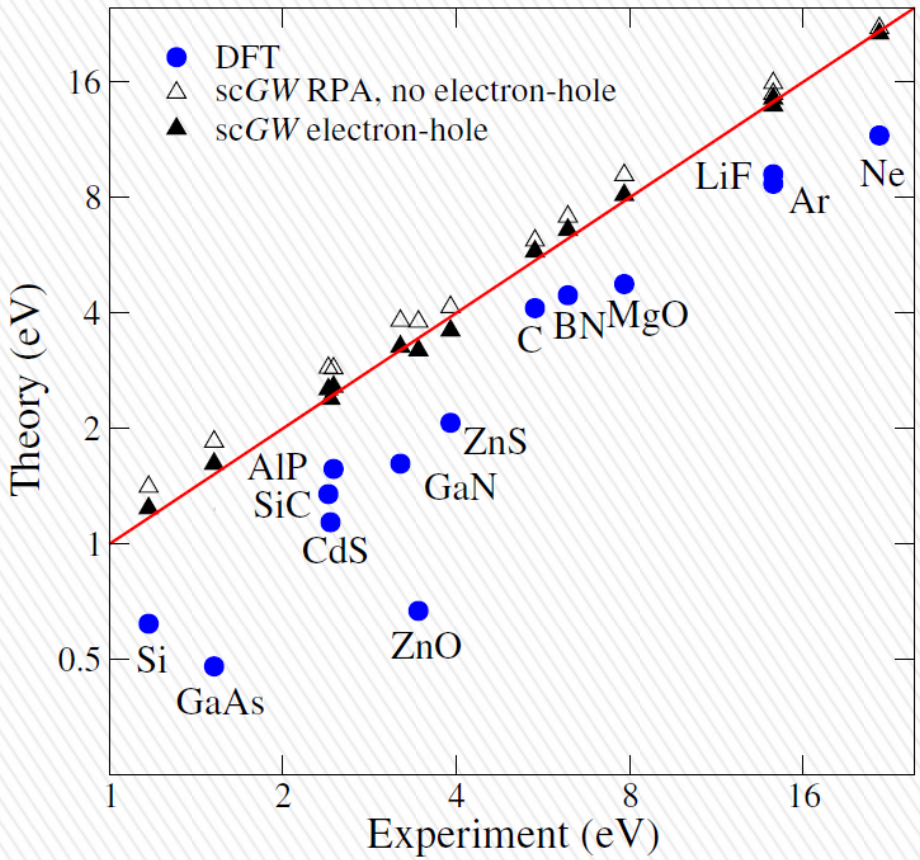
The 5-band model for LaOFeAs.



Ref. K. Kuroki, et al. Phys. Rev. Lett. 101, 087004 (2008).

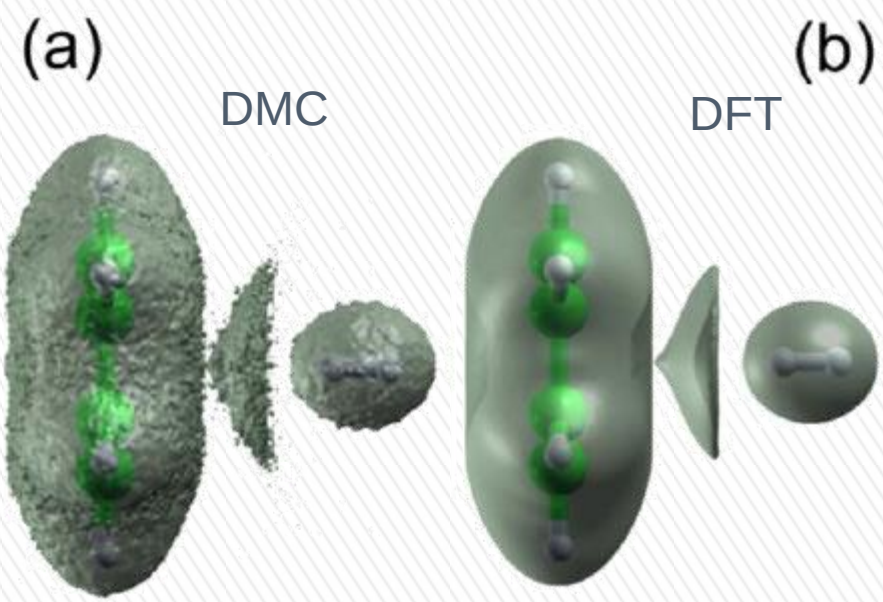
GW+beyond as “a many-body PT”

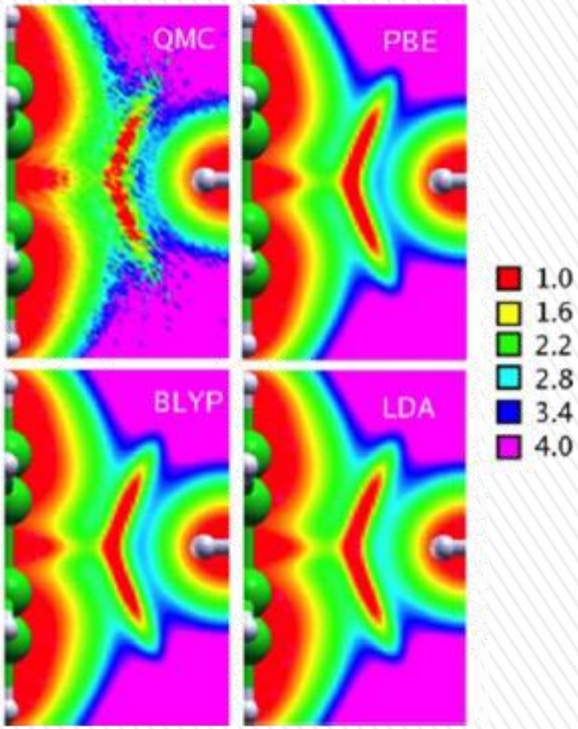
Evaluation of semiconductor gap by self-consistent GW + vertex correction



Ref. M. Shishkin, et al. Phys. Rev. Lett. 99, 246403 (2007).

Diffusion Monte-Carlo method



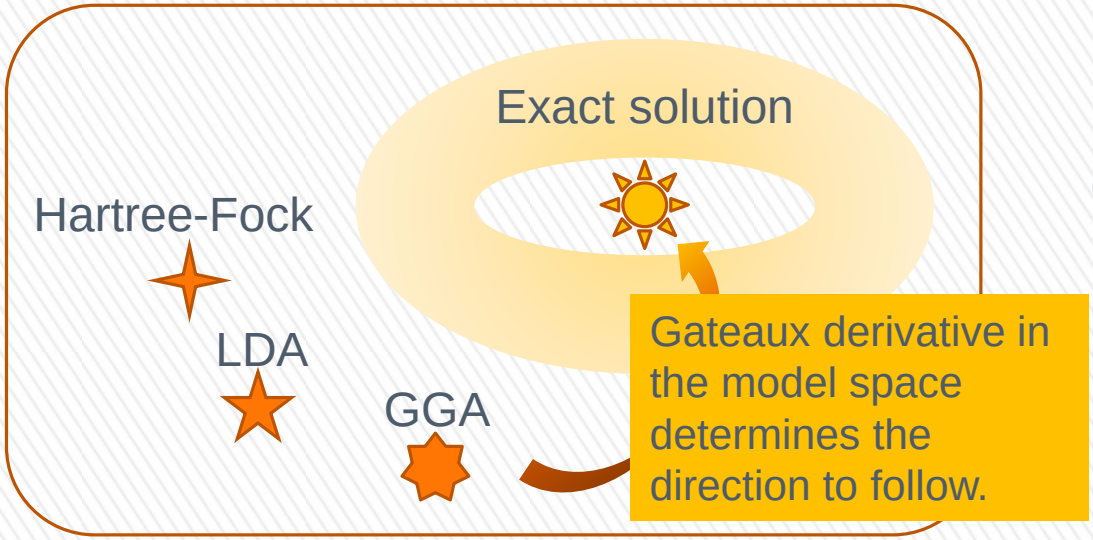


Electronic state and charge distribution of a Hydrogen molecule adsorbed on benzene

Ref. Y. Kanai and J.C. Grossman, Phys. Rev. A 80, 032504 (2009).

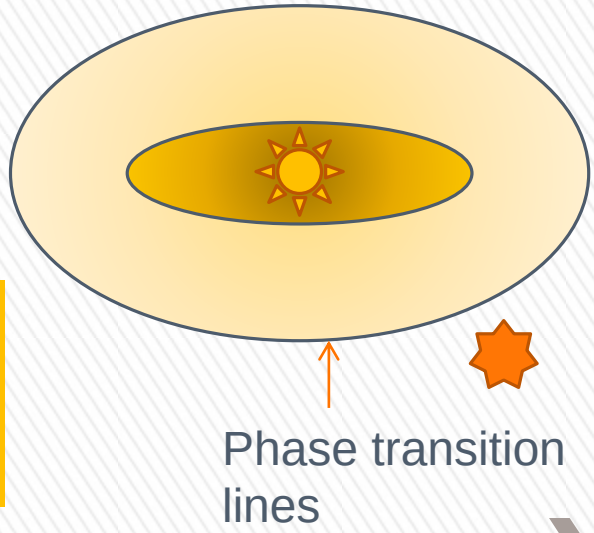
An almighty method

- Space of DFT models
  - Distance : $\left\| n_i - n_{i+1} \right\|.$
  - Variational principle: DFVT by K.K. (2009).



CASE I

CASE II



Q: Why? A: Its because “axiom for materials” tells this strategy.

Super processes

To have an initial state of correlated electron system, we may utilize

The upconversion Hamiltonian

$$\left(H^1 + P_A V_{ee} P_A + H^1_{C,counter} + P_A V_{ee} (1 - P_A) \frac{1}{H^1 + H^1_{C,counter} - E} (1 - P_A) V_{ee} P_A \right) \left| \Psi_A \right\rangle = E \left| \Psi_A \right\rangle.$$

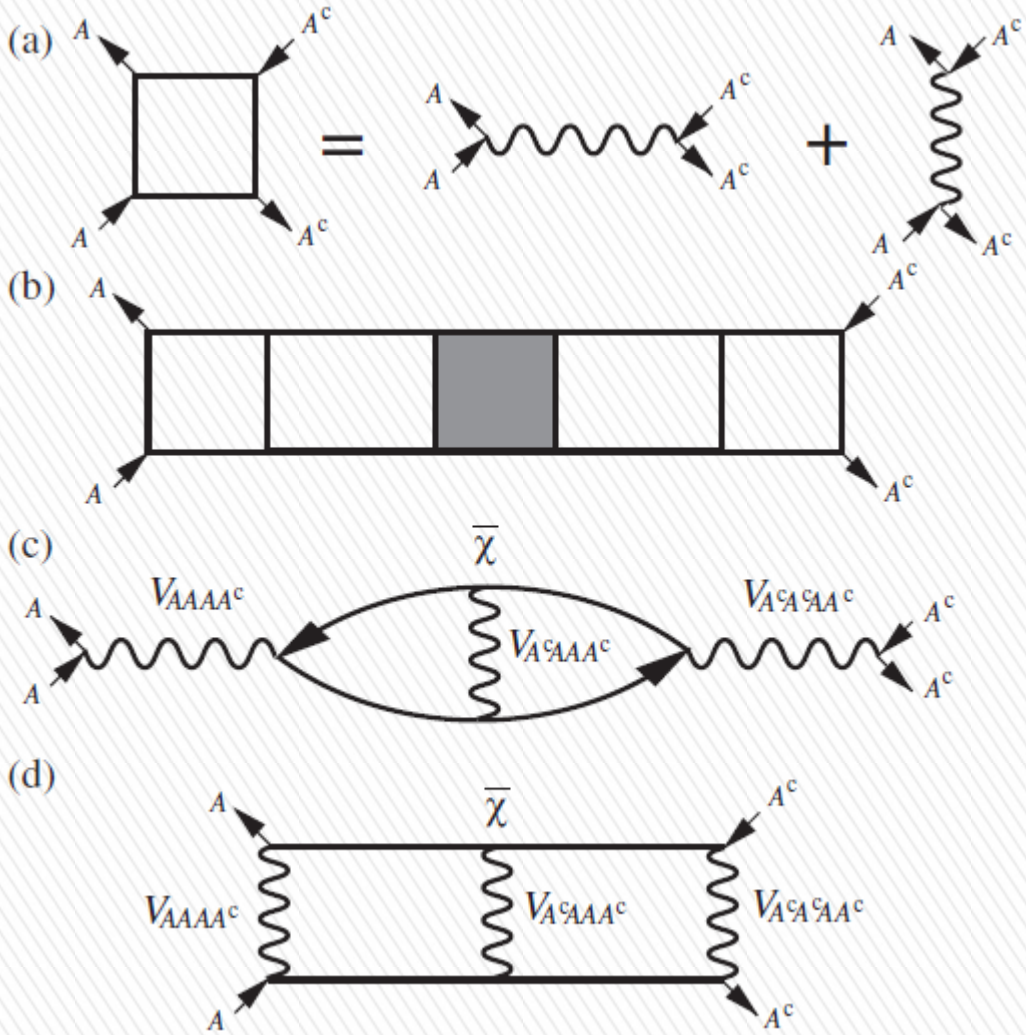
which leads us to the convergent model series in the DFT model space.

Cf. K. Kusakabe, I. Maruyama, "Electronic state calculation method, electronic state calculation device, computer program", PCT filed No. PCT/JP2011/068589, date 2011.8.18.

Problems in static state

Magnetism	Superconductivity	Semi-classical & quantum dynamics		Quantum processes in QED!
The super-exchange process	The super-pair hopping process	The van-der-Waals interaction	…	Two & multi-photon processes

Processes by "Feynman Diagram"



Symmetrized bare interaction

The full super-process for an electron-hole interaction

A polarization bubble diagram with a vertex correction in the above scattering channel

A third-order ladder diagram for the scattering channel

First principles calculation

Why is the KS-DFT not FP?

- When an effective Hamiltonian is derived by renormalization of the phase space of $L^2(R^{3N})$, it is in a form of "a many-body correlation problem", which is tractable in a simulation.
- Its solver is always faster than the encapsulation in $L^2(R^3)$ by the KS scheme.
- This conclusion is a FP.

Why do "first principles" exist?

- There are virtual photons.
- There is no real photon.
- Thus any theory for any system in nature needs to solve a many-body correlation problem.
- There are non-Abelian gauge fields.
- Determination of their source matter fields requires to describe the propagator of the gauge bosons, which is far beyond the U(1) theory.

A comment on U_{eff} and t

Material	U_{bare}	$U_{screened}$	U_{eff}/t
Si	> 10 eV	> 1 eV	～ 0.1
Al	> 10 eV	> 1 eV	～ 0.1
Cuprate super.	> 10 eV	1 ～ 4 eV	2 ～ 6

A narrow band system becomes
'the strongly correlated electron system'

For a metallic system, we have variety of phases including

- An anomalous metallic state for a heavy Fermion system,
- A high-temperature superconducting state of cuprates,

where U_{eff}/t becomes large.

But, a further difficult question is to conclude a Fermi liquid state following the renormalization group algorithm by starting from a DFT basis set.

Dynamical problems

- Properties are to be given by
  - Symmetry,
  - Self-consistency,
  - Time evolution path.

So, dynamics is determined by

  - Initial conditions,
  - Consistency,
  - Conservation laws.
- There, quantum correlation is cut, because we are in the space after the primary observation in our universe.

Cautions:

1. Separation into sub-systems is dangerous without consideration.
2. We have a different heat-bath & environment for a history of the sub-system different from an observed one.

The density functional theory is no more than a method to describe a closed system in equilibrium.
Once the time evolution starts, it means that we need the quantum-statistical mechanics for non-equilibrium systems.

When an initial state is created,

Consider a semiconductor having conduction and valence bands with a band width around 1eV. Assume that the material (each domain of poly-crystal sample) is in a nanometer scale.

Photon irradiation → Local polarization → Electron-hole exc. → Frenkel exciton

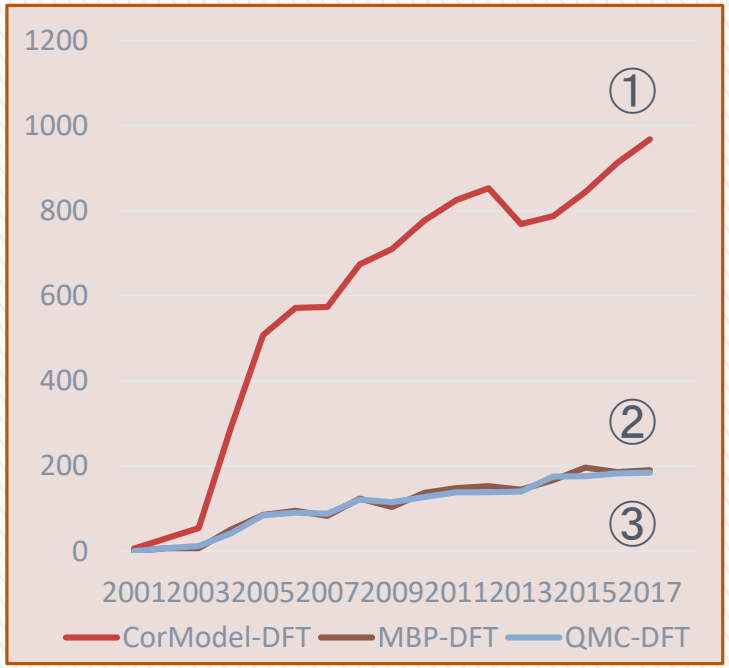
When DFT is applied to the steady initial state of the electron system, the band structure is given by a solution of the Kohn-Sham equation. Wannier orbitals are given by a unitary transformation of the Kohn-Sham Bloch orbitals. Therefore,

Free exciton → Local current → Internal EM field → Atomic force

In this process of theoretical description, we need to generalize DFT from single-referenced to multi-referenced DFT.

The trend in theory of DFT

Growing numbers of APS papers



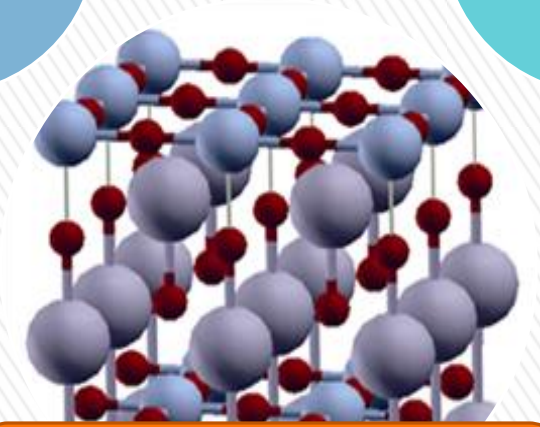
Survey in APS journals

① Correlated electron model & DFT
② Many-body perturbation & DFT
③ Quantum Monte Carlo & DFT

Model calc.

Perturbation
Green's func.

Monte Carlo methods



DFT calculations for Strongly Correlated El. Sys.

Thank you for your attention.