The 15th CMD Workshop Basic Theory of the first-principles electronic structure calculation

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- A brief review of the quantum mechanics
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The electron wave: a wave of probability

de Broglie found that the electron is a wave!

Planck-Einstein $E = hv = \hbar w$, $w = 2\pi v$. $\hbar = h/(2\pi)$. $p = \frac{h}{\lambda} = \hbar k, \qquad k = 2\pi / \lambda.$ de Broglie Interference fringe Electron gun Schematic picture of (emitter) an electron $\bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$ Electron bi-prism Wavefunction $\psi(x,t) = \exp(i(kx - wt)) = \exp(i(px - Et)/\hbar).$

Let's find an equation for the wave function. Later interpretation will come.

Designing the wave equation Wave packet: $\psi(x,t) = \int_{-\infty}^{\infty} f(p) \exp(i(px - E(p) \cdot t)/\hbar) dp$, $i\hbar \frac{\partial}{\partial t} \psi(x,t) = \int_{-\infty}^{\infty} Ef(p) \exp(i(px - E(p) \cdot t)/\hbar) dp$,

: the time derivative gives the energy.

$$\left(\frac{\hbar}{i}\right)^2 \frac{\partial^2}{\partial x^2} \psi(x,t) = \int_{-\infty}^{\infty} p^2 f(p) \exp(i(px - E(p)t)/\hbar) dp,$$

: the position derivative gives the momentum.

Thus, if
$$E(p) - \frac{p^2}{2m} = 0$$
 is satisfied, then,
 $\left(i\hbar \frac{\partial}{\partial t} - \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) \psi(x,t) = 0.$



The Schrödinger equation for a free particle.

The Schrödinger equation for a particle

Here,

Thus, an electron acting as a classical particle in some condition is a wave which follows the next equation of motion.

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\mathbf{r}, t).$$

we assume a dispersion relation, $E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}.$

If an external potential exists and the energy is given as, $E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + v(\mathbf{r})$, we should utilize

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r},t) + v(\mathbf{r})\psi(\mathbf{r},t).$$

Electron-electron interaction & electron spin



: The Coulomb interaction (repulsion)

Spin is a small magnetic moment on electron. But, possible states are only two states specified by the spin variable σ_i . (Note that electron is a point particle.)

 $\Phi(\cdots, \boldsymbol{r}_i, \boldsymbol{\sigma}_i, \cdots)$

The Schrödinger equation for an electron system

Finally, we have the next differential equation:

The Schrödinger equation for N electrons is given as follows.

$$\begin{split} \mathcal{H}\Phi &= \mathop{\scriptscriptstyle \Sigma}_{i} \mathcal{H}(\mathbf{r}_{i})\Phi + \mathop{\scriptscriptstyle \Sigma}_{i < j} \mathcal{V}(\mathbf{r}_{i},\mathbf{r}_{j})\Phi = E\Phi \\ \mathcal{H}(\mathbf{r}) &= -\frac{\hbar^{2}}{2m}\Delta + v(\mathbf{r}) \ , \\ \mathcal{V}(\mathbf{r}_{i},\mathbf{r}_{j}) &= \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \, . \end{split}$$

The wave function $\Phi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \cdots, \mathbf{r}_N, \sigma_N)$ is determined in a phase space of coordinates \mathbf{r}_i and spin variables σ_i .

Each electron has a spin $\mathbf{S} = \frac{\hbar}{2}\vec{\sigma}$ and a magnetic moment $\mu = -g\mu_B \mathbf{S}$ with a g-factor g = 2.0023 in vaccume.

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Concept of the variational principle

• The energy expectation value of any state is larger or equals to the ground-state energy.



This concept holds for any system described by the quantum mechanics (QM).

Another variational principle

- When we can divide a set of wave functions into subsets by
 - Symmetry
 - □ An order parameter

we can have another variational principle.



The lowest state in p_x-waves

The lowest state in $d_{3z^2-r^2}$ -wave

The single particle density $n(\mathbf{r})$ as an order parameter of an electron system

Levy's energy density functional $F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$

- This functional has a minimum.
- It represents that the phase space of many-body wave function is classified by the single-particle density.

Minimization search is done both in *n* explicitly and ψ .

The lowest solution is given by $n_2(\mathbf{r})$ for the potential $v_{\text{ext1}}(\mathbf{r})$, but $n_1(\mathbf{r})$ for $v_{\text{ext2}}(\mathbf{r})$.

The Kohn-Sham theory

- By the density-functional theory, we can utilize the single-particle density n(r) instead of $\Phi(x_1, x_2, x_3, \cdots)$.
- Once n(r) is made as a major variable, we can construct a theory to connect
 - □ The original many-body problem
 - An effective single-particle problem

The Kohn-Sham Minimization process

$$E_{0} = \langle \Psi_{GS} | \hat{T} + \hat{V}_{ee} | \Psi_{GS} \rangle + \int n_{GS}(\mathbf{r}) v_{ext}(\mathbf{r}) d^{3}r$$

$$= \min_{n} \left\{ \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^{3}r \right\}$$

$$= \min_{n} \left\{ \min_{\Psi' \to n(\mathbf{r})} \langle \Psi' | \hat{T} | \Psi' \rangle + F[n] - F_{T}[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^{3}r \right\}$$

$$= \min_{n} \left\{ \min_{\Psi' \to n(\mathbf{r})} \left\{ \langle \Psi' | \hat{T} | \Psi' \rangle + F[n_{\Psi'}] - F_{T}[n_{\Psi'}] + \int n_{\Psi'}(\mathbf{r}) v_{ext}(\mathbf{r}) d^{3}r \right\} \right\}$$

$$= \min_{\Psi'} \left\{ \langle \Psi' | \hat{T} | \Psi' \rangle + \frac{e^{2}}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^{3}r d^{3}r' + F[n_{\Psi'}] - \frac{e^{2}}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^{3}r d^{3}r' + F[n_{\Psi'}] \right\}$$

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

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

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

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

$$(3)$$

The GS energy is given by minimization of the wavefunction functional. ¹³

The local density approximation I.

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 **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.

$$\begin{split} \delta E_{xc}[\rho(\mathbf{r})] &= \int \mathrm{d}\mathbf{r} \, \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) \\ &= \int \mathrm{d}\mathbf{r} \, \frac{\partial \varepsilon_{xc}(\rho) \rho}{\partial \rho} \bigg|_{\rho = \rho(\mathbf{r})} \delta \rho(\mathbf{r}) \end{split}$$

Thus v_{xc} is given by,

$$v_{xc}(\mathbf{r}) = rac{\partialarepsilon_{xc}(
ho)
ho}{\partial
ho}igg|_{
ho=
ho(\mathbf{r})}$$

Correlation energy density for LDA

Exchange-Correlation hole for atoms

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

$$=\int_0^1 \left[\left\langle \Psi_{\lambda} \left| \left(\hat{n}(\boldsymbol{r}) - n(\boldsymbol{r}) \right) \left(\hat{n}(\boldsymbol{r}') - n(\boldsymbol{r}') \right) \right| \Psi_{\lambda} \right\rangle / n(\boldsymbol{r}) - \delta(\boldsymbol{r} - \boldsymbol{r}') \right] d\lambda.$$

Fluctuation!

 In LDA, we approximate nxc by that of the homogeneous electron gas as,

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

Sum rule on the LDA exchange-correlation

$$g(\mathbf{r},\mathbf{r}',\lambda) = \frac{\langle (\hat{n}(\mathbf{r}) - n(\mathbf{r}))(\hat{n}(\mathbf{r}') - n(\mathbf{r}')) \rangle}{n(\mathbf{r})n(\mathbf{r}')} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} + 1 = \frac{\langle \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') \rangle}{n(\mathbf{r})n(\mathbf{r}')} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})}$$
$$g^{\hom_{n}}(\mathbf{r},\mathbf{r}',\lambda) = \frac{\langle \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') \rangle_{n}^{\hom_{n}}}{n(\mathbf{r})n(\mathbf{r}')} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} = \frac{\langle \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') \rangle_{n}^{\hom_{n}}}{n(\mathbf{r})^{2}} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})}$$

Let V be the volume of the system. Then, we have,

$$\int d\mathbf{r}' n_{xc}^{LDA}(\mathbf{r},\mathbf{r}') = \int d\mathbf{r}' n(\mathbf{r}) \int_{0}^{1} \left[g^{\text{hom}}_{n}(\mathbf{r},\mathbf{r}',\lambda) - 1 \right] d\lambda$$

$$= \int d\mathbf{r}' n(\mathbf{r}) \int_{0}^{1} \left[\frac{\langle \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') \rangle_{n}^{\text{hom}}}{n(\mathbf{r})^{2}} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} - 1 \right] d\lambda = \int_{0}^{1} \left[\frac{\langle \hat{n}(\mathbf{r}) \int d\mathbf{r}' \hat{n}(\mathbf{r}') \rangle_{n}^{\text{hom}}}{n(\mathbf{r})} - 1 - n(\mathbf{r}) V \right] d\lambda$$

$$= \int_{0}^{1} \left[\frac{n(\mathbf{r}) V \langle \hat{n}(\mathbf{r}) \rangle_{n}^{\text{hom}}}{n(\mathbf{r})} - 1 - n(\mathbf{r}) V \right] d\lambda = -1.$$

Thus, LDA satisfies the sum rule.

Exchange-correlation hole in H

Gunnarsson, Jonson & Lundqvist, PRB 20 (1979) 3136.

FIG. 4. Exchange-correlation hole $n_{\rm XC}$ (\mathbf{r}, \mathbf{r}') (Eq. 15) for a hydrogen atom. The full curve shows the exact hole, while the dashed curves depict the hole in the LD approximation [Eq. (16)] for various positions of the electron (0,1, and 2 a.u. from the proton), using the dielectric function of Singwi *et al* (Ref. 37). The *x*-axis gives the distance from the nucleus.

FIG. 6. Spherical average of the hydrogen XC hole [Eq. (16)] times r'' for r=1 and 2 a.u. as a function of r''. The full curves give the exact results and the dashed curves are calculated in the LD approximation.

If one looks at spherical average of the XC hole, the LDA result is close to the exact one.

 $E_{\rm xc}[n]$ is proportional to an integral of the XC hole. Thus the total energy and its parameter derivatives, i.e. atomic forces, internal stress.

Exchange hole for a neon atom

FIG. 5. Exchange hole $n_x(\bar{t}, \bar{t}')$ for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r.

FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times r'' for (a) r = 0.09 a. u. and (b) r = 0.4 a.u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

Gunnarsson, Jonson & Lundqvist, PRB 20 (1979) 3136.

Determination equation at the stationary point

By making a derivative of $\overline{G}_T[\Psi] - E(\langle \Psi | \Psi \rangle - 1)$ with respect to $\langle \Psi |$, and by equating it to be zero, we have a secular equation,

$$\left[\hat{T} + \int v_{\text{eff}}(\mathbf{r})\hat{n}(\mathbf{r})d^3r\right]|\Psi\rangle = E|\Psi\rangle .$$
(4)

Here the effective single particle potential $v_{\text{eff}}(\mathbf{r})$ is given by,

$$v_{\rm eff}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} + v_{\rm ext}(\mathbf{r}) .$$
 (5)

The charge density $n(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \sum_{\sigma} \langle \Psi | \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma}(\mathbf{r}) | \Psi \rangle.$$
 (6)

The Kohn-Sham equation

We solve the one-body problem given by v_{eff} as,

$$\left\{-\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r})\right\}\phi_l(\mathbf{r}) = \varepsilon_l\phi_l(\mathbf{r}),\tag{7}$$

If we construct a set of creation and annihilation operators $d_{l,\sigma}^{\dagger}$, $d_{l,\sigma}$ associated with $\phi_l(\mathbf{r})$, the effective problem is found to be given by,

$$\sum_{l,\sigma} \varepsilon_l d_{l,\sigma}^{\dagger} d_{l,\sigma} |\Psi\rangle = E |\Psi\rangle.$$
(8)

Why the density functional theory is so promising?

- The basic assumption:
 - Speed of particles in steady states in your hands: nuclei < electrons < photons
 - Electrons in a classical electro-magnetic (EM) field is quantum mechanical.

Separation of degrees of freedom in the many-body system is introduced!

Density of electrons as the order parameter
 & the source of the EM field. (static screening)

Self-consistent determination of the electron density is essential to distinguish the electron system in various conditions.

Band structure of cubic diamond

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.

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.

The spin-density functional theory

To introduce spin density as a basic variable in DFT, we have to modify the theory.

- Current-DFT formulation
 - Extension of Levy's functional to relativistic version (Rajagopal-Callaway, and other works)
- DFT with arbitral basic variables
 - Extension of Levy's constrained search (Higuchi-Higuchi)

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

 $E_{\rm xc}[n,m]$ is obtained by e.g. fitting the numerical data of QMC for a spin polarized electron gas. \rightarrow LSDA, spin-GGA Solvers for DFT are immediately applied for the spin-DFT calculations.

GEA, GGA and meta-GGA

• Gradient expansion approximation : GEA

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

Generalized gradient approximation : GGA

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

Meta Generalized gradient approximation : meta-GGA

GEA exchange hole

$$\begin{split} \tilde{n}_x^{GEA}(\mathbf{r}, \mathbf{r} + \mathbf{u}) &= -n(\mathbf{r})\tilde{y}(\mathbf{r}, \mathbf{u})/2, \\ \tilde{y}(\mathbf{r}, \mathbf{u}) &= J(z) + 4L(z)\hat{\mathbf{u}} \cdot \mathbf{s}/3 - 16M(z)(\hat{\mathbf{u}} \cdot \mathbf{s})^2/27 - 16N(z)s^2/3, \\ \mathbf{s}(\mathbf{r}) &= \nabla n(\mathbf{r})/(2k_F(\mathbf{r})n(\mathbf{r})), \\ k_F(\mathbf{r}) &= \left(3\pi^2 n(\mathbf{r})\right)^{1/3}, \\ k_F(\mathbf{r}) &= 2k_F(\mathbf{r})u, \\ \hat{\mathbf{u}} &= \mathbf{u}/u. \end{split}$$

Here \tilde{n}_{xc}^{GEA} means an expression in which an expression proportional to $|\nabla n|^2$ and another to $\nabla^2 n$ are integrated by parts to reduce the order of derivatives.

Difficulty in the gradient expansion approximation

Cf. K. Burke, J.P. Perdew and Y. Wang In electronic Density Functional Theory edt. Dobson et al. (1998).

- The gradient expansion approximation (GEA) fails due to
 - □ Impossibe to full fill next equality and an inequality.

 $n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) \leq 0,$: negativity of exchange hole

$$\int d^3 u n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -1, \quad : \text{ sum rule for exchange hole}$$
$$\int d^3 u n_c(\mathbf{r}, \mathbf{r} + \mathbf{u}) = 0. \quad : \text{ sum rule for correlation hole}$$

Here, $n_x(\mathbf{r}, \mathbf{r} + \mathbf{u})$ and $n_c(\mathbf{r}, \mathbf{r} + \mathbf{u})$ are the exchange hole and the correlation hole, which follows $n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) + n_c(\mathbf{r}, \mathbf{r} + \mathbf{u})$ and,

$$n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = \int_{0}^{1} d\lambda n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \qquad \begin{array}{l} \text{Coupling constant is proportional to } \lambda \\ \text{keeping } \rho(\mathbf{r}). \end{array}$$
$$= \int_{0}^{1} d\lambda \left[\frac{\langle \Psi_{\lambda} | (\hat{n}(\mathbf{r}) - n(\mathbf{r})) (\hat{n}(\mathbf{r} + \mathbf{u}) - n(\mathbf{r} + \mathbf{u})) | \Psi_{\lambda} \rangle}{n(\mathbf{r})} - \delta(\mathbf{u}) \right].$$

GGA given by cutoff procedure to GEA

In GGA, starting from GEA, cuttoff procedure is introduced to keep

negativity of exchange hole sum rule for exchange hole sum rule for correlation hole

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.

For the case of correlation hole, similar expressions with a cutoff in a reduced separation on the Thomas-Fermi length scale, when it is integrated.

Transition metal elements

- Characteristics of 3d transition metals
 - Spins in an atom or in an ion align by Hund's coupling
 - The Hund rule tells that if there is degeneracy w.r.t. *L* & S,
 - $\Box \quad \text{The maximum } S \text{ appears.}$
 - $\Box \quad \text{The maximum allowed } L \text{ for given } S \text{ appears.}$
 - d-orbitals have characters below.
 - They are rather localized around the nucleus.
 - They form narrow bands.

To explain ferromagnetism in 3d transition metals, we have to consider at least by an itinerant electron picture, since

Element	T _c /K	M/μ_B	Configuration
Fe	1043	2.219	3d ⁶
Со	1404	1.715	3d ⁷
Ni	630	0.604	3d ⁸

DFT-GGA calculation of Fe

T. Asada & K. Terakura, PRB 46 (1992) 13599.

GGA calculations of tetragonal manganites

FIG. 1. (a) The phase diagram of $La_{1-x}Sr_xMnO_3$ in the plane of c/a and doping x obtained from total energy calculations as demonstrated in (b). The solid lines give the phase boundaries obtained from calculations with experimental volumes, while the dashed lines correspond to the case with experimental volumes expanded by about 9%. (b) The calculated total energies for different phases of $La_{1-x}Sr_xMnO_3$ as a function of the c/a ratio with fixed doping x = 0.5. c/a is varied with the corresponding experimental volume fixed.

FIG. 3 (color). The calculated charge density distribution for the energy window of 0.6 eV width just below the Fermi level for the different magnetic structures corresponding to all the marks (\times) in the phase diagram of Fig. 1. The different spin components (up and down) are drawn as different colors. The Mn atom site at the corners of the cubes, while O atom (green spheres) site at the edge centers.

Fang, Solovyev & Terakura, PRL 84 (2000) 3169.

GGA may reproduce the orbital ordered (OO) magnetic phases. Metal-insulator transition with OO may also be found.

Catalytic reaction on Pd surface

 Three way catalyst
 NO_x reduction NO_x \rightarrow 1/2N₂+x/2O₂
 CO oxidation CO+1/2O₂ \rightarrow CO₂
 CH_x oxidation CH_x+(1+x/2)O₂ \rightarrow CO₂+x/2H₂O

Segregation of Pd nano-particles and solid-solution of Pd in the perovskite

Oxidation and reduction processes on Pd oxide film is a key to understand the phenomenon.

Bridge site structure

Total energy : -968.8677(Ry)Total force : $6.1 \times 10^{-5}(Ry/a.u.)$

Reaction of NO_x & CO

$$x (PdO)_4/Pd+NO_x \rightarrow N_2 + x (PdO)_4O/Pd$$

 $\Delta = 2x E_{PdO} + 2 E_{NOx} - 2x E_{PdO+O} - E_{N_2}$
 $(PdO)_4O/Pd+CO \rightarrow CO_2 + (PdO)_4/Pd$
 $\Delta = E_{PdO+O} + E_{CO} - E_{PdO} - E_{CO_2}$

PdO : (PdO)₄/Pd

Oxygen	NO ₂	NO reduction	N ₂ O	CO oxydation
sites	reduction	energy(Ry)	reduction	energy(Ry)
	energy(Ry)		energy(Ry)	
bridge	0.2888	0.2086	0.096	0.204
hollow	0.2872	0.2078	0.092	0.208

A first-principles simulation of NT-FET

- Using the ESM Method
 - We can obtain electronic structure of nanotube modeling the channel of FET

Simulation by Yoshihisa Minamigawa, et al.

Summary on the field effect doping

Case	Induced electrons / Carbon • V
Exp. (nanotube film)	7.28×10^{-4}
Calc. (7,0) tubes with 10Å spacing	1.2×10^{-3}
Calc. (7,0) tubes with 5.3 Å spacing	8.2×10^{-4}
Calc. a tube film (double layer)	3.6×10^{-5}
Calc. a tube film (double layer)	6.7×10^{-4}

This result shows that feasibility of the simulation.

The electric field is screened almost completely by a single layer of tubes. The field effect doping is done in the top layer of the tube film.

But, since the LDA error is not improved in the present approach, the given Kohn-Sham state is not accurate enough to reproduce the chemical potential shift across the band gap, E(N+1)-E(N), for infinitely long CNT, which has to be accurately evaluated by DFT.

Difficulty in GGA

- Impossible to reproduce cohesion of layered materials, graphite, hex-BN and CF.
 - Due to two dimensionality.
 - Due to Van-der Waals nature (even worse for one-dimensional materials including metallic nanotubes)
- Impossible to reproduce magnetism of weak ferromagnets including ZrZn₂, meta-magnetic paramagnets including YCo₂ in the Laves phase.
 - Due to strong tendency to stabilize ferromagnetism.
- Interestingly, L(S)DA reproduces qualitative features of these problematic materials.
- Much accurate calculations (DMC for 2DEG, DMC with backflow effects etc for EG) are required as references.

Various methods to overcome difficulty of DFT-LDA, DFT-GGA

- Excitation spectrum is not properly described by DFT-LDA, DFT-GGA.
 - This is partly because DFT is only for the ground state. However, sometimes, DFT-LDA & DFT-GGA incorrectly conclude a metal rather than gapped excitations (Mott's insulator).

- For excitations: GW, GW+T, EXX+RPA (perturbative methods.)
- For Mott's insulator: LDA+U, LDA++ (a model description introduced in DFT.)
- A new theory on the model space.

