

DFT and Range Separated DFT

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OUTLINE

I. INTRODUCTION: (a) The system of equation defining the density functional approximation (DFA).

II. MOTIVATIONS: To describe with *ab-initio, self-consistent calculations* the *properties of materials*. In search of *a better functional* to describe strongly “correlated” systems within DFT

III. DFT: No doubt a very powerful and successful theory for studying material properties. An overview will be given.

IV. Range Separated DFT: A powerful tool for improving KS-DFT to include many-body effects (long-range correlation).

(a). ACDFT Connection (RPA)

(b). Coupled Cluster Theory

V. CONCLUSION:

Motivations

- ✓ The extreme approximations in standard DFT in obtaining the position dependent exchange-correlation (xc) energy per particle $\varepsilon_{xc}(r)$ for many-electron system.
- ✓ The also very obvious extreme approximations in obtaining the xc potential $V_{xc}(r)$.

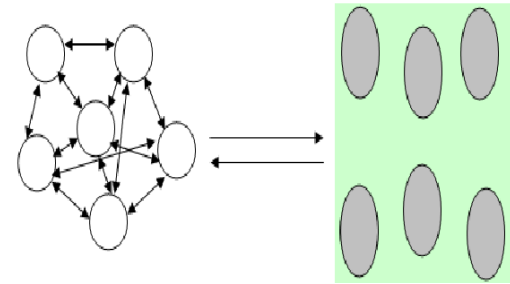
Note: In current implementation in most electronic structure calculations, these two quantities are calculated using LDA functionals and its semi-local variants.

Very Important: While these LDA functionals in DFT obtain correctly many properties of materials self-consistently from ab-initio first principle methods, they fail to yield useful information in the regime of strongly correlated systems.

Fundamentals of HKS-DFT

□ The ground state density is the basic variable.

□ Map many interacting electrons with real potential to non-interaction fictitious particles with effective potential $V_{eff}(r)$.



□ From the mapping above, one gets the so-called KS ansatz:

$$F[n(r)] = T[n(r)] + U[n(r)] + E_{xc}[n(r)]:$$

$$\begin{array}{ccccc}
 & & \xleftarrow{\text{HK}} & n_0(r) & \xleftrightarrow{\text{KS}} & n_0(r) & \xrightarrow{\text{HK}_0} & V_{eff} \\
 & & & \downarrow & & \uparrow & & \downarrow \\
 & & & \Psi_k & \xrightarrow{\quad} & \Psi_0 & & \Phi_0 \xleftarrow{\quad} \Phi_i
 \end{array}$$

□ With all these approximations, one now has a single particle KS equation:

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(r) - \varepsilon_{j\sigma}(r) \right] \phi_{j\sigma}(r) = 0$$

$$\text{where } V_{eff}(r) = V_{ext}(r) + \int d\acute{r} \frac{n(\acute{r})}{|r-\acute{r}|} + \frac{\delta E_{xc}[n_{\uparrow}(r), n_{\downarrow}(r)]}{\delta n_{\sigma}(r)}; \quad n_{\sigma}(r) = \sum_{occ} |\phi_{j\sigma}(r)|^2$$

I. THE SYSTEM OF EQUATIONS

Defining the density functional approximation

EQUATION 1 (Only for the ground state)

$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(n(\vec{r})) \right] |\Phi_n\rangle = \varepsilon_n |\Phi_n\rangle$$

Subject to Equation 2 (Sum over occupied states only)

$$n(r) = \sum_{n=1}^N |\Phi_n(r)|^2 \quad \text{Sum over occupied states only}$$

Kohn and Sham explicitly stated that the system of equations defining LDA has to be solved self-consistently [See Page A1134 of Phys. Rev., Vol. 140, No. 4A, Pages A1133-A1138 (1965)]. Once an LDA potential is selected, the system reduces to the two equations above.

II. DFT Methods Presently Implemented

- ❑ Linear combination of Atomic Orbitals (LCAO) method: BZW method is used and band gap and other related electronic properties are predicted with high accuracy.
- ❑ Linearized Augmented Plane wave (LAPW) method: WIEN2K electronic structure package is used. We have a systematic way of obtaining with high accuracy properties of materials.

Range Separated DFT: (a) ACDFE

- The trick, decomposed the electron-electron (Coulomb) interaction into long-range and short-range components:

$$\frac{1}{r} = V_{ee}^{\mu}(r) + V_{ee}^{\bar{\mu}}(r); \mu \text{ is a parameter controlling the separation}$$

- Treat the short-range component $V_{ee}^{\bar{\mu}}(r)$ with DFT

- Treat the long-range component $V_{ee}^{\mu}(r)$ with any many-body methods. Examples: Several variants of RPA, Configuration interaction, Coupled cluster theory, Second-order perturbation theory, etc.

- The universal functional $F[n(r)] = \min_{\psi} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle$ is also decomposed into:

$$F[n(r)] = F^{\mu}[n(r)] + F^{\bar{\mu}}[n(r)]$$

where \hat{T} is the kinetic energy operator and $\hat{V}_{ee} = \sum_{i < j} 1/r_{ij}$ is the Coulomb interaction operator.

Range Separated DFT Contd: (a) ACFDT

□ Then, the exact ground state energy of an N-electron system, via variational principle (minimization over multi-determinant wave functions ψ) is:

$$\begin{aligned}
 E &= \min_n \left\{ F[n(r)] + \int n(r) \hat{V}_{ne}(r) dr \right\} \\
 &= \min_{\psi} \left\{ \langle \psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{\mu} | \psi \rangle + E_{H_{xc}}^{\bar{\mu}} [n_{\psi}] \right\} \\
 &= \min_{\psi^{\mu} \rightarrow n} \left\{ \langle \psi^{\mu} | \hat{T} + \hat{V}_{ee}^{\mu} | \psi^{\mu} \rangle + F^{\bar{\mu}} [n_{\psi^{\mu}}(r)] + \int n_{\psi^{\mu}}(r) \hat{V}_{ne}(r) dr \right\}
 \end{aligned}$$

where \hat{V}_{ne} is the nuclei-electron interaction, $\hat{V}_{ee}^{\mu} = \frac{1}{2} \iint dr_1 \hat{V}_{ee}^{\mu}(r_{12}) \hat{n}(r_1, r_2)$ is the long-range electron-electron interaction which in real implementation is normally approximated using the error function $\hat{V}_{ee}^{\mu} = \frac{\text{erf}(\mu r)}{r}$, the quantity $\hat{n}(r_1, r_2)$ is the pair density operation, and $E_{H_{xc}}^{\bar{\mu}}$ is the corresponding short-range Hartree-exchange-correlation density functional. Here, ψ^{μ} is given by the Euler-Lagrange equation:

$$\hat{H}^{\mu} \psi^{\mu} \rangle = E^{\mu} \psi^{\mu} \rangle; \text{ where } \hat{H}^{\mu} = \hat{T} + \hat{V}_{ee}^{\mu} + \hat{V}^{\mu}; \hat{V}^{\mu} \text{ is external local potential}$$

(a) The Adiabatic Connection

What is the meaning of ACFDT?

This involves extracting nonlocal ground-state correlations from the linear charge density response function. How?

Generally, the interaction is controlled by μ , and it ranges between 0 and ∞ .

How is the minimization carried out? First, minimization is restricted to single determinant wave functions ϕ (RSH):

$$E_{RSH} = \min_{\phi} \left\{ \left\langle \phi \left| \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{\bar{\mu}} \right| \phi \right\rangle + E_{Hxc}^{\bar{\mu}} [n_{\phi}] \right\}$$

where the minimizing determinant ϕ_0 is given by the Euler-Lagrange equation.

Since E_{RSH} is not exact. Thus, we define $E = E_{RSH} + E_c^{\mu}$. The **adiabatic-connection** is then introduced via the energy expression:

$$E_{\lambda} = \min_{\psi} \left\{ \left\langle \psi \left| \hat{T} + \hat{V}_{ne} + \hat{V}_{Hx,HF}^{\mu} [\phi_0] + \lambda \hat{V}^{\mu} \right| \psi \right\rangle + E_{Hxc}^{\bar{\mu}} [n_{\psi}] \right\}; \quad \begin{array}{l} \lambda \text{ is a coupling} \\ \text{constant} \end{array}$$

where $\hat{V}^{\mu} = \hat{V}_{ee}^{\mu} - \hat{V}_{Hx,HF}^{\mu}$ is the long-range fluctuation perturbation operator. $\hat{V}_{Hx,HF}^{\mu}$ is the sum of the local Hartree part \hat{V}_H^{μ} and nonlocal exchange part $\hat{V}_{x,HF}^{\mu}$.

(a) The Adiabatic Connection Contd

□ Taking a derivative of E_λ gives:

$$E = E_{\lambda=0} + \int_0^1 d\lambda \langle \psi_\lambda^\mu | \hat{V}^\mu | \psi_\lambda^\mu \rangle; \quad E_{\lambda=0} = E_{RSH} - \langle \phi_0 | \hat{V}^\mu | \phi_0 \rangle$$

□ With this, the long-range correlation energy is:

$$E_c^\mu = \frac{1}{2} + \int_0^1 d\lambda \left[\langle \psi_\lambda^\mu | \hat{V}^\mu | \psi_\lambda^\mu \rangle - \langle \phi_0 | \hat{V}^\mu | \phi_0 \rangle \right] = \frac{1}{2} \int_0^1 d\lambda \text{Tr}[\hat{V}^\mu * P_{c,\lambda}^\mu]$$

where $P_{c,\lambda}^\mu$ is the four index correlation contribution of 2-particle density matrix in a one-electron basis, Tr is the trace over the remaining two indices, and * stands for contraction of two indices.

Exact Formal Treatment of the Long-Range $P_{c,\lambda}^{\mu}$

- In terms of space-spin-time coordinates, let $1 = (x_1, t_1)$ and $2 = (x_2, t_2)$. Then, a self-consistent Dyson equation can be defined as:

$$\left(G_{\lambda}^{\mu}\right)^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma_{\lambda}^{\mu}(1,2) - \Delta\Sigma_{\lambda}^{\bar{\mu}}(1,2)$$

where $\Sigma_{\lambda}^{\mu}(1,2) = \Sigma_{Hxc,\lambda}^{\mu}[G_{\lambda}^{\mu}](1,2) - \Sigma_{Hx,\lambda}^{\mu}[G_0](1,2)$ is the long-range self-energy.

- Recall that $P_{c,\lambda}^{\mu} = -\frac{1}{2\pi} \int_{-\infty}^{\infty} du e^{-u0^+} [\chi_{\lambda}^{\mu}(iu) - \chi_{\lambda=0}^{\mu}(iu)] + \Delta_{\lambda}^{\mu}$

where $\chi_{\lambda}^{\mu}(iu)$ is the imaginary 4-point polarizability given by the solution of Bethe-Salpeter-type equation:

$$\left(\chi_{\lambda}^{\mu}\right)^{-1} = \left(\chi_{IP,\lambda}^{\mu}\right)^{-1} - \lambda f_{Hx}^{\mu} - f_{c,\lambda}^{\mu}$$

where $\chi_{IP,\lambda}^{\mu} = -i G_{\lambda}^{\mu} G_{\lambda}^{\mu} = -i G_{\lambda}^{\mu}(1, \hat{2}) G_{\lambda}^{\mu}(2, \hat{1})$ is the independent particle (IP) polarization propagator, λf_{Hx}^{μ} and $f_{c,\lambda}^{\mu}$ are respectively, long-range HF-type Hartree-exchange (known as LR-TDHFT or full RPA) and correlation kernels.

(b). Coupled Cluster

The coupled cluster (CC) Hamiltonian (H) is: $H|\psi\rangle = E|\psi\rangle$ (a)

The CC wavefunction is defined via the exponential ansatz:

$$|\psi\rangle_{CC} = |\psi\rangle_{MBPT} = e^T |\phi_o\rangle \Rightarrow He^T |\phi_o\rangle = Ee^T |\phi_o\rangle; \quad (b)$$

where $T = \sum_N T_N$ is the excitation operator with, $T_N = \left(\frac{1}{n!}\right)^2 \sum_{j\dots abc\dots}^n t_{ij\dots}^{ab\dots} a^\dagger b^\dagger \dots ji\dots$ (c)

Generally, the CC Hamiltonian of Eq. (a) is:

$$H = \sum_{pq} f_{pq} \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{a_p^\dagger a_q^\dagger a_s a_r\} + \langle \phi_o | H | \phi_o \rangle \quad (d)$$

$$= F_N + V_N + \langle \phi_o | H | \phi_o \rangle \Rightarrow H_N = F_N + V_N \quad (e)$$

Then, by similarity transformed normal-ordered Hamiltonian (H_N) via BCH:

$$\begin{aligned} \bar{H} = e^{-T} H e^T \Rightarrow \bar{H} = H_N + [H_N, T_1] + [H_N, T_2] + \frac{1}{2} [[H_N, T_1], T_1] + \frac{1}{2} [[H_N, T_2], T_2] \\ + [[H_N, T_1], T_2] + \dots \end{aligned} \quad (f)$$

Then, by Eq. (e), $[H_N, T] = [F_N, T] + [V_N, T]$

(b). Coupled Cluster

For coupled cluster double (CCD), CCD equation is:

$$E_{CCD} = \langle \phi_o | [H_N, T_2] | \phi_o \rangle \quad (g)$$

and

$$0 = \langle \Phi_{ij}^{ab} | H_N + [H_N, T_2] + \frac{1}{2} [[H_N, T_2], T_2] | \phi_o \rangle \quad (h)$$

Very important tool in CC theory is **Wick's theorem** which on applying to Eqs. (g & h) and taking only connected terms:

$$E_{CCD} = \langle \phi_o | [H_N, T_2]_c | \phi_o \rangle \text{ and } 0 = \langle \Phi_{ij}^{ab} | \left(H_N + H_N T_2 + \frac{1}{2} H_N T_2^2 \right)_c | \phi_o \rangle \quad (i)$$

The CCD correlation energy after lengthy derivation is:

$$E_c^{CCD} = \frac{1}{4} \sum \langle ij || ab \rangle t_{ij}^{ab} = \frac{1}{2} \sum \langle ij | ab \rangle t_{ij}^{ab}$$

t_{ij}^{ab} is obtained basically by solving the CCD equation in spin-orbital basis

What Next?

- ❑ We intend to implement the range separated DFT in NwChem quantum chemistry code.

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**Thank You for
Your Attention**