

Lecture on First-principles Computation (6): Kohn-Sham Density Functional Theory

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Recall: major points in the previous lecture

- Thomas-Fermi-Dirac approximation
- Slater $X\alpha$ method
- Hohenberg-Kohn (KS) theorem II

$$E_{\text{HK}}[n(\mathbf{r}), v_{\text{ext}}] = F_{\text{HK}}[n(\mathbf{r})] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \geq E_0 = E_{\text{HK}}[n_0(\mathbf{r})]$$

$$F_{\text{HK}}[n(\mathbf{r})] = \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle \quad \text{— Universal functional}$$

$$E_0 = \underbrace{\min}_{n(\mathbf{r})} E_{\text{HK}}[n(\mathbf{r}), v_{\text{ext}}]$$

Domain of $n(\mathbf{r})$: **v -representable density**, i.e., corresponding to certain physically realizable $v_{\text{ext}}(\mathbf{r})$.

Hohenberg-Kohn (HK) Theorem

$F_{\text{HK}}[n]$ is a **universal functional**, depending only on the particle density, and valid for all systems with different $v_{\text{ext}}(\mathbf{r})$.

$E[n] = E[n, v_{\text{ext}}]$ depends also on the external potential, and its global minimum corresponds to the ground state of the system.

The HK theorem is not restricted to Coulomb systems

I. Applying the HK theorem to **Coulomb interacting systems**:

$$F_{\text{HK}}[n(\mathbf{r})] = \langle \Psi_0[n(\mathbf{r})] | \hat{T} + \hat{V}_{ee} | \Psi_0[n(\mathbf{r})] \rangle = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})]$$

II. Applying the HK theorem to **non-interacting system**:

$$F_{\text{HK}}[n(\mathbf{r})] = \langle \Phi_0[n(\mathbf{r})] | \hat{T} | \Phi_0[n(\mathbf{r})] \rangle = T_s[n(\mathbf{r})]$$

Levy and Lieb's constrained search method

The existence of a universal functional can be proved in a different way; this is the so-called

Constrained search method (M. Levy; E. Lieb, 1979)

In quantum mechanics, there exists the Rayleigh-Ritz variational principle:

$$E_0 = \underbrace{\min}_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

$\Psi \in \{\text{N-particle antisymmetric wave functions}\}$

In essence, the **Levy & Lieb constrained search method** is the application of the Rayleigh-Ritz variational method **in two successive steps**.

Levy and Lieb's constrained search method

$$E_0 = \underbrace{\min}_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i^N V_{ext}(\mathbf{r}_i)$$

Two-step minimization:

First, fix $n(\mathbf{r})$, minimize $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$ with respect to Ψ that yields $n(\mathbf{r})$

$$\begin{aligned} E_{LL}[n(\mathbf{r})] &= \underbrace{\min}_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r}) \\ &= F_{LL}[n(\mathbf{r})] + \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

Second, minimize $E_{LL}[n(\mathbf{r})]$ with respect to $n(\mathbf{r})$

$$\underbrace{\min}_{n(\mathbf{r})} E_{LL}[n(\mathbf{r})] = E_{LL}[n_0(\mathbf{r})] = E_0$$

Constrained search method: the case of degenerate ground states

$$\hat{H} |\Psi_0^j\rangle = E_0 |\Psi_0^j\rangle, \quad j = 1, \dots, D$$

$$n_0^j(\mathbf{r}) = \langle \Psi_0^j | \hat{n}(\mathbf{r}) | \Psi_0^j \rangle \quad n_0^j(\mathbf{r}) \text{ for different } j \text{ can be the same or different.}$$

- If more than one degenerate ground-state wave functions $|\Psi_0^j\rangle$ yield the same density $\tilde{n}_0(\mathbf{r})$, then

$$E_{\text{LL}}[\tilde{n}_0(\mathbf{r})] = \langle \Psi_0^j | \hat{H} | \Psi_0^j \rangle \quad |\Psi_0^j\rangle \text{ is any of the degenerate ground-state wave functions.}$$

- For degenerate states with different particle densities, then

$$E_{\text{LL}}[n_0^j(\mathbf{r})] = F_{\text{LL}}[n_0^j(\mathbf{r})] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_0^j(\mathbf{r}) = E_0$$

Hohenberg-Kohn functional versus Levy-Lieb functional

$$F_{LL}[n(\mathbf{r})] = \underbrace{\min}_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$F_{HK}[n(\mathbf{r})] = \langle \Psi_0[n(\mathbf{r})] | \hat{T} + \hat{V}_{ee} | \Psi[n(\mathbf{r})] \rangle$$

- Levy-Lieb functional applies to degenerate ground states
- Levy-Lieb functional is defined within a large variational space of electron density, namely, any density that can be obtained from a N -particle anti-symmetric wave function. This is the so-called “ n -representability”.
- Within the domain of “ v -representable” densities, the two functionals yield the same results.

From many-particle system back to single-particle system: the Kohn-Sham method

L.J. Sham



Some thoughts of W. Kohn:

In the winter of 1964, I returned from France to San Diego, where I found my new post-doctoral fellow, Lu Sham. I knew that the Hartree equations described atomic groundstates much better than TF theory. The difference between them lay in the different treatments of the kinetic energy T (See Eqs. (4.10) and (4.13)). I set ourselves the task of extracting the Hartree equations from the HK variational principle for the energy, Eqs. (4.9), (4.7), (4.8), which I knew to be formally *exact* and which therefore had to have the Hartree equations *and* improvements “in them”. In fact it promised a Hartree-like formulation, which – like the HK minimal principle – would be formally exact.

Nobel Lecture, published in 1999

Recalling the Hartree Equation ...

- The Hartree equation:

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$n(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2$$

How to interpret the Hartree equation from the viewpoint of DFT?

Noninteracting Many-particle System from the Viewpoint of DFT

- Noninteracting many-particle system:

$$\left(-\frac{\nabla^2}{2m} + v_{aux}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r}) \quad v_{aux}(\mathbf{r}) \text{ is certain fixed external potential}$$

$$n_0(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2, \quad E_0 = \sum_{l=1}^N \epsilon_l$$

- The Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{aux} = \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2m} + v_{aux}(\mathbf{r}_i) \right)$$

Applying the Hohenberg-Kohn theorem:

$$E[n(\mathbf{r}), v_{aux}] = T_s[n(\mathbf{r})] + \int d^3 r v_{aux}(\mathbf{r}) n(\mathbf{r}) \geq E_0$$

Noninteracting many-particle system from the viewpoint of DFT

$$E[n(\mathbf{r}), v_{aux}] = T_s[n(\mathbf{r})] + \int d^3r v_{aux}(\mathbf{r})n(\mathbf{r}) \geq E_0$$

$$\delta \left\{ E[n(\mathbf{r}), v_{aux}] - \mu \left(\int n(\mathbf{r}) d^3r - N \right) \right\} = 0$$



$$\frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{aux}(\mathbf{r}) - \mu = 0, \quad \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} \text{ is unknown!}$$

The above equation cannot be directly solved, but the solution of the problem is known.

$$\left(-\frac{\nabla^2}{2m} + v_{aux}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

can be viewed as an auxiliary single-particle problem.

$$n_0(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2, \quad E_0 = \sum_{l=1}^N \epsilon_l$$

Energy functional of interacting many-particle system

$$E_{v_{ext}}[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + \int d^3 r v_{ext}(\mathbf{r})n(\mathbf{r}) \geq E_0$$

Re-expressing the functional as:

$$E_{v_{ext}}[n(\mathbf{r})] = T_S[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int d^3 r v_{ext}(\mathbf{r})n(\mathbf{r})$$

$T[n(\mathbf{r})]$: Kinetic energy functional of interacting system;

$T_S[n(\mathbf{r})]$: Kinetic energy functional of noninteracting system;

$E_H[n(\mathbf{r})]$: The Hartree energy functional;

$$E_{xc}[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] - T_S[n(\mathbf{r})] - E_H[n(\mathbf{r})]$$

Exchange-correlation energy functional (everything unknown).

Applying the same strategy to interacting problem ...

$$E_{v_{ext}}[n(\mathbf{r})] = T_S[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int d^3r v_{ext}(\mathbf{r})n(\mathbf{r})$$

$$\delta E_{v_{ext}}[n(\mathbf{r})] = \int \delta n(\mathbf{r}) \left[\frac{\delta T_S[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \underbrace{v_H[n(\mathbf{r})] + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r})}_{v_{eff}(\mathbf{r})} \right]$$

$$\delta \left\{ E_{v_{ext}}[n(\mathbf{r})] - \mu \left(\int n(\mathbf{r}) d^3r - N \right) \right\} = 0$$



$$\frac{\delta T_S[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{eff}(\mathbf{r}) - \mu = 0$$

Suppose $v_{eff}(\mathbf{r})$ is known, one can obtain the ground-state electron density of the original many-body problem via an auxiliary single-particle problem.

The Kohn-Sham equation (1965)

$$\left(-\frac{\nabla^2}{2m} + v_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

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

$$n(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2$$

To be solved
self-consistently

$$n(\mathbf{r}) \rightarrow n_0(\mathbf{r})$$

$$E_0 = -\frac{1}{2m} \sum_{l=1}^N \langle \phi_l | \nabla^2 | \phi_l \rangle + E_H[n_0(\mathbf{r})] + E_{xc}[n_0(\mathbf{r})] + \int d^3 r v_{ext}(\mathbf{r}) n_0(\mathbf{r})$$


In contrast to the Hartree case, by solving the **Kohn-Sham equation**, **one can in principle obtain the exact ground-state energy and density of interacting systems**, if $E_{xc}[n(\mathbf{r})]$ is known **exactly**.

The underlying assumption of the Kohn-Sham method: non-interacting v -representability

$$\frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{eff}[n(\mathbf{r})] - \mu = 0$$

$$V_{eff}[n(\mathbf{r})] = V_H[n(\mathbf{r})] + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r})$$

Kohn-Sham ansatz:


$$n(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2$$

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \phi_l(\mathbf{r}) = \epsilon_l \phi_l(\mathbf{r})$$

The ground-state density of any interacting system can be reproduced by a non-interacting system.

The physical meaning of Kohn-Sham (KS) orbitals (a highly debated topic)

KS orbitals and orbital energies are determined (implicitly) by the electron density:

$$\epsilon_l = \epsilon_l[n_0(\mathbf{r})]; \psi_l = \psi_l[n_0(\mathbf{r})]$$

- **KS orbitals are auxiliary variables, and have no strict physical meaning (except for HOMO).** They are introduced to reproduce the particle density of interacting systems

$$n(\mathbf{r}) = \sum_{l=1}^N |\phi_l(\mathbf{r})|^2$$

- The energy of highest occupied molecular orbital (HOMO) ϵ_N corresponds to the first ionization energy of the system – the Janak theorem (1978).

$$I = E_0(N - 1) - E_0(N) = -\epsilon_N$$

Features of the Kohn-Sham method

- The KS scheme is one particular implementation of DFT (and not the unique one). The key is to map the interacting many-body system to independent-particle system; By solving self-consistently the independent-particle problem, one obtains the particle density and ground-state energy of the physical, interacting problem.
- Comparison to the Hartree-Fock method:

The Hartree-Fock (HF) equations are obtained by minimizing the energy; solving the HF equation one obtains the “best” energy under the single-determinant constraint. HF is an approximation intrinsically. The KS equations are obtained by mapping; solving the KS equation one obtains the best particle density. The KS method is an exact method in principle.
- In practical calculations $E_{xc}[n(\mathbf{r})]$ and $v_{xc}[n(\mathbf{r})]$ must be approximated.

$E_{xc}[n(\mathbf{r})]$ and $V_{xc}[n(\mathbf{r})]$

$$v_{eff}(\mathbf{r}) = v_{ext}[n(\mathbf{r})] + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

$$V_{xc}[n(\mathbf{r})] = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Exact form $E_{xc}[n(\mathbf{r})]$ of is not known, and will not be known. In practice the approximation for $E_{xc}[n(\mathbf{r})]$ determines the quality of KS-DFT calculations. Looking for accurate and generally applicable $E_{xc}[n(\mathbf{r})]$ is a key issue in KS-DFT.

References

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Homework

Discuss and compare the following methods/approximations, and describe your own understanding of these approaches.

1. the Hartree approximation
2. the Hartree-Fock approximation
3. Thomas-Fermi-Dirac method
4. Slater $X\alpha$ method
5. Kohn-Sham method