

Optimized Effective Potential Method in DFT Part I

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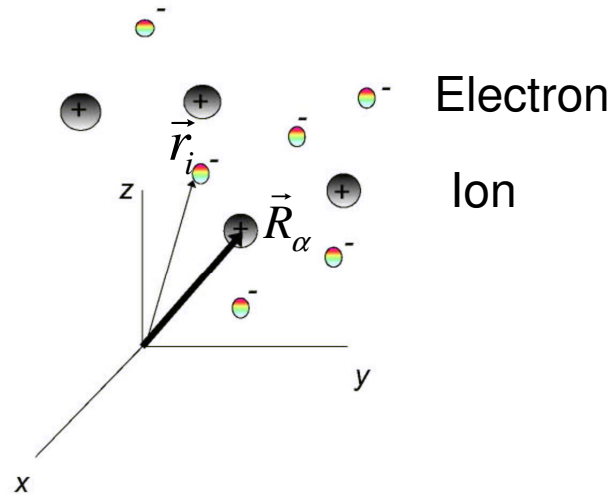
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Outline

- Introduction to the **DFT**
- Approximations in DFT
- Success and Failures of the Approximations
- **OEP** method
- Application of OEP to **Metal clusters**
- Conclusions

Born-Oppenheimer Hamiltonian



$$H_{el} = \sum_{i=1}^N \left(-\frac{1}{2} \vec{\nabla}_i^2 \right) + \frac{1}{2} \sum_{i \neq j=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^N v(\vec{r}_i)$$

$$v(\vec{r}) = - \sum_{\alpha=1}^M \frac{z_{\alpha}}{|\vec{r} - \vec{R}_{\alpha}|}$$

$$\hbar = e^2 = m = 1$$

N and $v(r)$

- For an N -electron system, the external potential, $v(r)$ completely fixes the Hamiltonian; thus N and $v(r)$ determine all properties for the ground state.

Hohenberg-Kohn Theorems of DFT

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)

- Theorem 1:

The external potential $v(\mathbf{r})$ is determined, within a trivial additive constant, by the ground-state electron density $\rho(\mathbf{r})$.

$$\mathbf{V}(\mathbf{r}) \leftrightarrow \rho_0(\mathbf{r}) \rightarrow \mathbf{N}$$
$$\rho_0(\mathbf{r}) \rightarrow \mathbf{V}(\mathbf{r}) \rightarrow \mathbf{H} \rightarrow \Psi_0 \rightarrow \langle \Psi_0 | \mathbf{O} | \Psi_0 \rangle$$

Hohenberg-Kohn Theorems of DFT

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)

Theorem 2.

$$\begin{aligned} E_0 &= \langle \Psi_0 | H | \Psi_0 \rangle \\ &= \int \rho_0(r) v(r) dr + F_{HK}[\rho_0] \equiv E_v[\rho_0] \end{aligned}$$

$$F_{HK}[\rho_0] = \langle \Psi_0 | T + V_{ee} | \Psi_0 \rangle$$

For $\tilde{\rho} \neq \rho_0$,

$$E_0 \equiv E_v[\rho_0] < E_v[\tilde{\rho}] : \text{ a Variational Principle}$$

Euler-Lagrange Equation

For a system with fixed N :

$$K[\rho] \equiv E_v[\rho] - \mu \left\{ \int \rho(r) dr - N \right\}$$

$$\delta K[\rho] / \delta \rho(r) = 0 \quad ; \quad \partial K / \partial N = \mu$$

$$\delta E_v[\rho] / \delta \rho(r) = \mu \quad \rightarrow \rho_0, E_v[\rho_0]$$

$$\tilde{\rho} = \rho_0 + \delta \rho$$

Variations are over all v - representable densities :

$$\tilde{\rho} \rightarrow \tilde{v}(r) \rightarrow \tilde{H} \rightarrow \tilde{\Psi}$$

Problem with variations

NOT all $\tilde{\rho}$ correspond to ground state density of a Hamiltonian!

Levy-Lieb Formulation of DFT

N - representable densities :

$$\rho(r) \geq 0; \quad \int \rho(r) dr = N; \quad \int |\nabla \rho^{1/2}(r)|^2 dr < \infty$$

Levy-Lieb Formulation of DFT

Given the ground - state wave - function Ψ_0 :

How determine $\rho_0(r)$?

Levy-Lieb Formulation of DFT

$$\rho_0(r) = N \int |\Psi_0(r, r_2, \dots, r_N)|^2 dr_2 \dots dr_N$$

Levy-Lieb Formulation of DFT

Now, given the ground - state density $\rho_0(r)$:

How determine Ψ_0 ?

Levy-Lieb Formulation of DFT

Consider the set of ALL anti - symmetric N - particle functions giving the same density $\rho_0(r)$:

$$\{\Psi_{1,\rho_0}, \Psi_{2,\rho_0}, \Psi_{3,\rho_0}, \dots, \Psi_0, \dots\}.$$

How single out Ψ_0 ?

Levy-Lieb Formulation of DFT

According to variational principle for Ψ_0 :

$$E_0 \equiv \langle \Psi_0 | T + V_{ee} + V_{ext} | \Psi_0 \rangle \leq \langle \Psi_{i,\rho_0} | T + V_{ee} + V_{ext} | \Psi_{i,\rho_0} \rangle$$

or

$$\langle \Psi_0 | T + V_{ee} | \Psi_0 \rangle \leq \langle \Psi_{i,\rho_0} | T + V_{ee} | \Psi_{i,\rho_0} \rangle$$

A new variational principle !

Levy-Lieb Formulation of DFT

Among all $\{\Psi_{i,\rho_0}\}$, Ψ_0 minimizes $\langle T + V_{ee} \rangle$.

Therefore :

$$\rho_0 \leftrightarrow \Psi_0$$

Levy-Lieb Formulation of DFT

We had:
$$F_{HK}[\rho_0] \equiv \langle \Psi_0 | T + V_{ee} | \Psi_0 \rangle$$
$$= \min_{\Psi \rightarrow \rho_0} \langle \Psi | T + V_{ee} | \Psi \rangle$$

Now,

$$F[\rho] \equiv \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle$$

Levy-Lieb Formulation of DFT

Variational principle:

$$\begin{aligned} E_0 &= \min_{\Psi} \langle \Psi | T + V_{ee} + V_{ext} | \Psi \rangle \\ &= \min_{\rho} \{ \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} + V_{ext} | \Psi \rangle \} \\ &= \min_{\rho} \{ \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int \rho(r) v(r) dr \} \\ &= \min_{\rho} \{ F[\rho] + \int \rho(r) v(r) dr \} \\ &\equiv \min_{\rho} E_v[\rho] \end{aligned}$$

Density functionals:

We had :

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle \equiv \langle \Psi_{\rho}^{\min} | T + V_{ee} | \Psi_{\rho}^{\min} \rangle.$$

$$T[\rho] \equiv \langle \Psi_{\rho}^{\min} | T | \Psi_{\rho}^{\min} \rangle$$

$$V_{ee}[\rho] \equiv \langle \Psi_{\rho}^{\min} | V_{ee} | \Psi_{\rho}^{\min} \rangle.$$

Kohn-Sham Scheme

W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

Consider a NON - INTERACTING ($V_{ee} = 0$) system under the external potential V_s :

$$F[\rho] \rightarrow \min_{\Psi \rightarrow \rho} \langle \Psi | T | \Psi \rangle \equiv T_s[\rho] \equiv \langle \Phi_{\rho}^{\min} | T | \Phi_{\rho}^{\min} \rangle$$

Φ_{ρ}^{\min} is a non - interacting wave - function :

A single Slater determinant or

a linear combination of a few determinants.

Euler-Lagrange equation for the Kohn-Sham system

$$\frac{\delta T_s[\rho]}{\delta \rho(r)} + v_s(r) = \mu$$

Back to interacting system

Consider the following decomposition :

$$F[\rho] \equiv T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

in which $J[\rho] \equiv \frac{1}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|}$.

Rewrite the Euler - Lagrange Eq :

$$\frac{\delta T_s[\rho]}{\delta \rho(r)} + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} + v(r) = \mu$$

Effective potential

The Euler - Lagrange equations of the interacting and non - interacting systems are consistent if :

$$v_s(r) \equiv v_{eff}(r) \equiv v(r) + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$

Ground-state density of interacting system

$$\left(-\frac{1}{2} \nabla^2 + v_{eff}([\rho]; r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r),$$

$$\rho(r) = \sum_{i=1}^N |\varphi_i(r)|^2$$

$$v_{eff}([\rho]; r) = v(r) + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}.$$

These equations are solved self - consistently.

Ground-state Energy of interacting system

$$\tilde{E}_0 = \sum_{i(\text{occ})} \varepsilon_i - J[\tilde{\rho}_0] + E_{xc}[\tilde{\rho}_0] - \int v_{xc}([\tilde{\rho}_0]; r) \tilde{\rho}_0 dr.$$

Is Kohn-Sham scheme exact?

YES, if :

The ground - state density of the system is both interacting and non - interacting v - representable. Then :

$$\tilde{\rho}_0 = \rho_0$$

Exchange-correlation energy functional

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

$$E_x[\rho] \equiv \left\langle \Phi_{\rho}^{\min} \left| V_{ee} \right| \Phi_{\rho}^{\min} \right\rangle - J[\rho].$$

If Φ_{ρ}^{\min} is a single Slater determinant, then :

$$E_x[\{\varphi_{i\sigma}\}] = -\frac{1}{2} \sum_{i,j=1}^{N_{\sigma}} \int d^3r d^3r' \frac{\varphi_i^*(\vec{r}) \varphi_j^*(\vec{r}') \varphi_j(\vec{r}) \varphi_i(\vec{r}')}{|\vec{r} - \vec{r}'|},$$

$\varphi_j(\vec{r})$: Kohn - Sham orbitals

$$E_c$$

We have:

$$\left\langle \Phi_{\rho}^{\min} \left| T + V_{ee} \right| \Phi_{\rho}^{\min} \right\rangle = T_s[\rho] + J[\rho] + E_x[\rho].$$

On the other hand:

$$E_c[\rho] = F[\rho] - T_s[\rho] - \left\langle \Phi_{\rho}^{\min} \left| V_{ee} \right| \Phi_{\rho}^{\min} \right\rangle.$$

Hence:

$$E_c[\rho] = \left\langle \Psi_{\rho}^{\min} \left| T + V_{ee} \right| \Psi_{\rho}^{\min} \right\rangle - \left\langle \Phi_{\rho}^{\min} \left| T + V_{ee} \right| \Phi_{\rho}^{\min} \right\rangle$$

E_c

$$E_c[\rho] = \langle \Psi_\rho^{\min} | T + V_{ee} | \Psi_\rho^{\min} \rangle - \langle \Phi_\rho^{\min} | T + V_{ee} | \Phi_\rho^{\min} \rangle$$

Since Ψ_ρ^{\min} minimizes $\langle T + V_{ee} \rangle$,

$$E_c[\rho] \leq 0.$$

T_c and V_c

$$\begin{aligned} E_c[\rho] &= \{ \langle \Psi_\rho^{\min} | T | \Psi_\rho^{\min} \rangle - \langle \Phi_\rho^{\min} | T | \Phi_\rho^{\min} \rangle \} \\ &\quad + \{ \langle \Psi_\rho^{\min} | V_{ee} | \Psi_\rho^{\min} \rangle - \langle \Phi_\rho^{\min} | V_{ee} | \Phi_\rho^{\min} \rangle \} \\ &\equiv T_c[\rho] + V_c[\rho] \leq 0. \end{aligned}$$

Inspection gives :

$$T_c[\rho] \geq 0, \quad V_c[\rho] \leq 0.$$

System with $N=1$

$$N = 1 \rightarrow V_{ee} = 0:$$

$$E_x[\rho] = -J[\rho],$$

$$E_c[\rho] = 0,$$

$$\frac{\delta E_x[\rho]}{\delta \rho(r)} = -\frac{\delta J[\rho]}{\delta \rho(r)} = -\int \frac{\rho(r')}{|r-r'|} dr',$$

$$\frac{\delta E_c[\rho]}{\delta \rho(r)} = 0.$$

$$\text{Hence: } \lim_{r \rightarrow \infty} \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} = -\frac{\int \rho(r') dr'}{r} = -\frac{1}{r}.$$

Functional derivative

Given $F[\rho]$:

$$\delta F = \int dr \frac{\delta F[\rho]}{\delta \rho(r)} \delta \rho(r).$$

For number - conserving search :

$$\int \delta \rho(r) dr = 0.$$

Hence :

$$\delta F' \equiv \int dr \left\{ \frac{\delta F[\rho]}{\delta \rho(r)} + \text{const.} \right\} \delta \rho(r) = \delta F.$$

Functional derivatives are defined to within a constant !

Extension of HK Theorem to **non-**number-conserving densities

$$\int \rho(r) dr = N = Z + \omega, \quad 0 \leq \omega \leq 0.$$

For open systems, we do not use a pure state Ψ , but a statistical mixture Γ :

$$\Gamma = \sum_i p_i |\Psi_i\rangle\langle\Psi_i|, \quad \sum_i p_i = 1.$$

$$\begin{aligned} \langle O \rangle_{\Gamma} &= \text{Tr}(\Gamma O) \\ &= \sum_i p_i \langle \Psi_i | O | \Psi_i \rangle \end{aligned}$$

Extension of HK Theorem to non-number-conserving densities

Define :

$$F[\rho] \equiv \min_{\Gamma \rightarrow \rho} \langle T + V_{ee} \rangle_{\Gamma} .$$

Consider :

$$\Gamma = (1 - \omega) |\Psi_Z\rangle\langle\Psi_Z| + \omega |\Psi_{Z+1}\rangle\langle\Psi_{Z+1}| .$$

Easily seen :

$$\rho(r) = (1 - \omega)\rho_Z(r) + \omega\rho_{Z+1}(r),$$

$$N = \int \rho(r) dr = Z + \omega.$$

Here,

$$\rho_Z(r) \equiv Z \int |\Psi_Z(r, r_2, \dots, r_Z)|^2 dr_2 \dots dr_Z .$$

Extension of HK Theorem to **non-**number-conserving densities

$$E_v[\rho] = F[\rho] + \int \rho(r)v(r)dr.$$

$$E = Tr(\Gamma H) = (1 - \omega)E_Z + \omega E_{Z+1},$$

E_Z and E_{Z+1} are the ground - state energies of Z - and $(Z - 1)$ - electron systems, respectively.

Now E is a continuous function of N .

Extension of HK Theorem to non-number-conserving densities

But :

$$\frac{\partial E}{\partial N} = -E_Z + E_{Z+1} = -A_Z.$$

For ensemble composed of $(Z - 1)$ and Z electrons :

$$\frac{\partial E}{\partial N} = -E_{Z-1} + E_Z = -I_Z.$$

$$\mu = \frac{\partial E}{\partial N} = \begin{cases} -I_Z, & Z - 1 < N < Z \\ -A_Z, & Z < N < Z + 1. \end{cases}$$

Extension of HK Theorem to non-number-conserving densities

Resorting to a 3 - atom ensemble with $(Z-1), Z, (Z+1)$ at finite temperature, $1/\beta$, one obtains :

$$\lim_{\beta \rightarrow \infty} \mu = -\frac{1}{2}(I_Z + A_Z) \quad \text{for } N = Z.$$

Derivative discontinuity in Energy

$$\lim_{\omega \rightarrow 0} \left\{ \left[\frac{\delta E[\rho]}{\delta \rho(r)} \right]_{Z+\omega} - \left[\frac{\delta E[\rho]}{\delta \rho(r)} \right]_{Z-\omega} \right\} = I_Z - A_Z > 0.$$

Discontinuity at INTEGER N !

It arises in part from the exchange - correlation energy, and ENTIRELY so if N does not fall on the boundary of an electronic shell or subshell.

Exchange-correlation energy functional

Consider :

$$F_\lambda[\rho] \equiv \min_{\Psi \rightarrow \rho} \langle \Psi | T + \lambda V_{ee} | \Psi \rangle \equiv \langle \Psi_\rho^\lambda | T + \lambda V_{ee} | \Psi_\rho^\lambda \rangle.$$

λ : Strength of ee interaction.

$$\begin{aligned} E_{xc}[\rho] &= (V_{ee}[\rho] - J[\rho]) + (T[\rho] - T_s[\rho]) \\ &= F_{\lambda=1}[\rho] - F_{\lambda=0}[\rho] - J[\rho] \\ &= \int_{\lambda=0}^1 d\lambda \frac{\partial F_\lambda[\rho]}{\partial \lambda} - J[\rho] \\ &= \int_{\lambda=0}^1 d\lambda \langle \Psi_\rho^\lambda | V_{ee} | \Psi_\rho^\lambda \rangle - J[\rho] \end{aligned}$$

Exchange-correlation energy functional

$$E_{xc} = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(r_1) \bar{\rho}_{xc}(r_1, r_2) dr_1 dr_2.$$

$\bar{\rho}_{xc}(r_1, r_2)$: average exchange - correlation hole

$$\bar{\rho}_{xc}(r_1, r_2) \equiv \rho(r_2) \bar{h}(r_1, r_2)$$

$\bar{h}(r_1, r_2) = \bar{h}(r_2, r_1)$: average pair - correlation function

Important sum rule :

$$\int \bar{\rho}_{xc}(r_1, r_2) dr_2 = \int \rho(r_2) \bar{h}(r_1, r_2) = -1$$

Exchange-correlation energy functional

$$\bar{\rho}_{xc}(r_1, r_2) = \rho_x(r_1, r_2) + \bar{\rho}_c(r_1, r_2)$$

$$\int \rho_x(r_1, r_2) dr_2 = -1$$

$$\int \bar{\rho}_c(r_1, r_2) dr_2 = 0$$

$$\bar{\rho}_c(r_1, r_1) \leq 0$$

$$\bar{\rho}_{xc}(r_1, r_2) \geq -\rho(r_2)$$

Uniform scaling properties of functionals

$$\Psi_\gamma(r_1, r_2, \dots, r_N) = \gamma^{3N/2} \Psi(\mathcal{r}_1, \mathcal{r}_2, \dots, \mathcal{r}_N).$$

$$\rho_\gamma(r) = \gamma^3 \rho(\mathcal{r})$$

$$\langle \Psi_\gamma | T | \Psi_\gamma \rangle = \gamma^2 \langle \Psi | T | \Psi \rangle$$

$$E_x[\rho_\gamma] = \gamma E_x[\rho]$$

$$E_c[\rho_\gamma] = \gamma^2 E_c^{1/\gamma}[\rho]$$

$$\lim_{\gamma \rightarrow \infty} E_c[\rho_\gamma] = \text{constant}$$

$$E_c[\rho_\gamma] > \gamma E_c[\rho] \quad \text{for } \gamma > 1$$

$$E_c[\rho_\gamma] < \gamma E_c[\rho] \quad \text{for } \gamma < 1.$$

**Thank You for Your
Attention**

