Density Functional Theory: Fundamentals and Recent Developments

Weitao Yang
Duke University

Theory
Biological
Nano
Material

Funding
ACS
NIH
Lam Research

Los Alamos Computational Condensed Matter Summer School
LANL, June 15, 2026

Outline

1. Fundamental Principles of DFT

2. Kohn-Sham Equations and Density Functional Approximations

3. Fractional Perspectives: Insight and Corrections of Systematic Errors in Density Functional Approximation

4. Excited State Theory

The Schrodinger Equation for N electrons

$$\hat{H}\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N) = E\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)$$

$$\mathbf{x} = \mathbf{r}, s$$

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

$$\hat{V}_{ee} = \sum_{i<j}^N \frac{1}{r_{ij}}$$

$$\hat{T} = \sum_i^N -\frac{1}{2}\nabla^2$$

$$v_{ext}(\mathbf{r}) = -\sum_A -\frac{Z_A}{r_{Ai}}$$

Wavefunction--the curse of dimensionality

$$H\Psi = E\Psi$$

# of electrons	wavefunction	amount of data
1	$\Psi(\mathbf{r}_1)$	10^3
2	$\Psi(\mathbf{r}_1, \mathbf{r}_2)$	10^6
…	…	…
N	$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)$	10^{3N}

- The amount of data contained in wavefunction grows exponentially with the number of electrons! $N \sim 1 - 10000$

- The problem is caused by the exponential increase in volume associated with adding extra dimensions to a (mathematical) space.

The curse of dimensionality in QM

The problem is caused by the exponential increase in volume associated with adding extra dimensions to a (mathematical) space.

Exponential growth of information

N, positions and types of atoms $\Leftrightarrow$ N, $v(\mathbf{r})$

$\Downarrow$ $\Updownarrow$

H

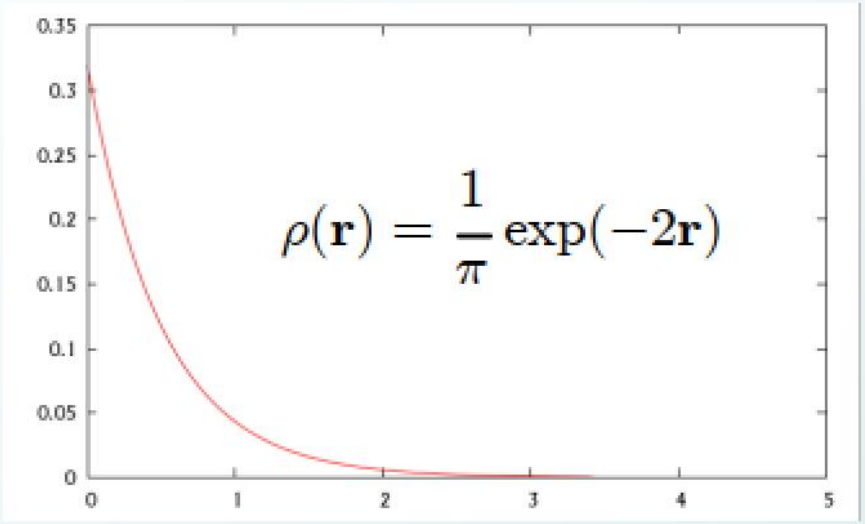
$\Downarrow$

10^{3N} in $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$?

1. $v(\mathbf{r})$ is the electrostatic potential from the nuclei
2. $v(\mathbf{r}) = \sum_{A}^{Atoms} -\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$

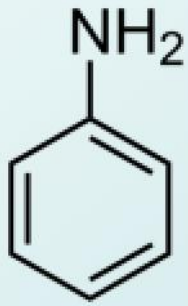
Electron density $\rho(\mathbf{r})$, 3-dimentional only

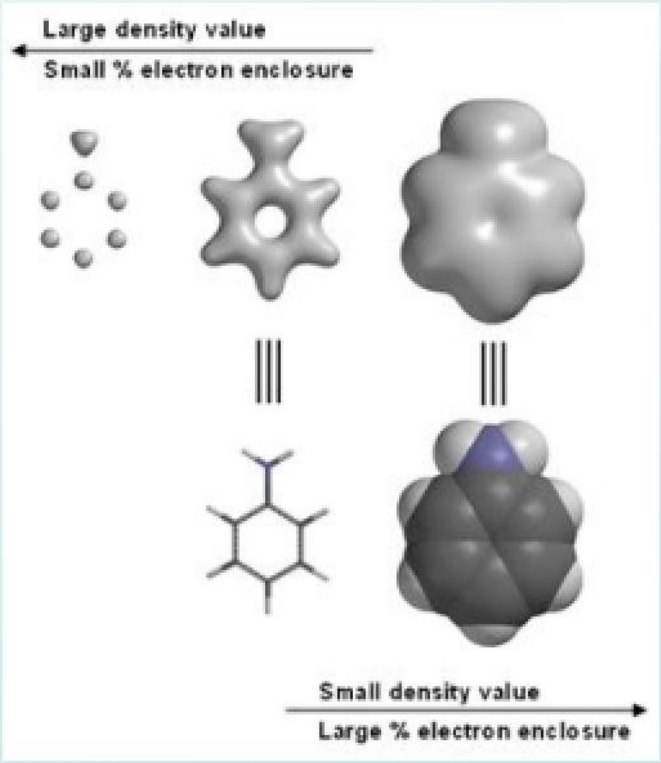
Electron density for the hydrogen atom



Distance from the nucleus

Electron density for aniline

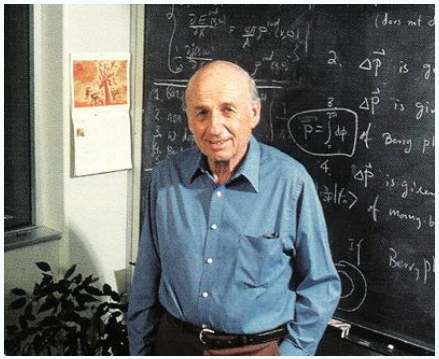




- **Electron density** $\rho(\mathbf{r})$ is the measure of the probability of an electron being present at a specific location.

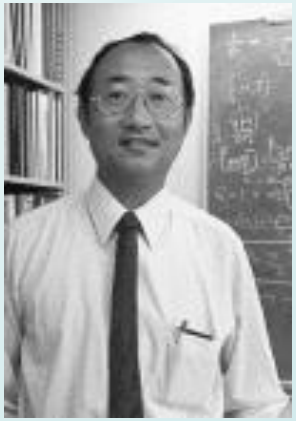
- Experimental observables in X-ray diffraction for structural determination of small and large molecules

Density Functional Theory



Walter Kohn

Pierre C. Hohenberg



Lu J. Sham

The Nobel Prize in Chemistry 1998

Density functional theory (DFT) (1964, 1965)

1 $\rho(\mathbf{r}) \Longleftrightarrow N, v(\mathbf{r}) \Longleftrightarrow \Psi$

2. $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ Just the sum of molecular orbital densities

DFT: Exchange-correlation energy

$$E = E[\rho(\mathbf{r})]$$

E = Kinetic energy + potential energy
+ Coulomb interaction energy
+ $E_{xc}[\rho(\mathbf{r})]$

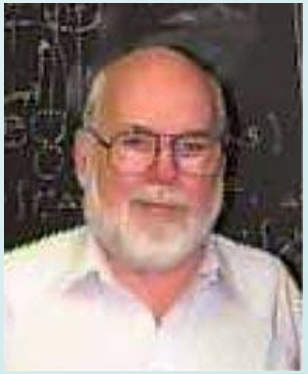
$E_{xc}[\rho(\mathbf{r})]$

- Exchange-correlation energy
- The only unknown piece in the energy
- About 10% of E

Approximations in exchange-correlation energy

$$E_{xc}[\rho(\mathbf{r})]$$

- 1965: Kohn and Sham, Local Density Approximation (LDA)
- 1980s-1990s: Axel Becke, Robert Parr, John Perdew


- Generalized Gradient Approximation (GGA)
- Hybrid Functionals (B3LYP, PBE0)

Density Functional Theory

- Structure of matter: atom, molecule, nano, condensed matter
- Chemical and biological functions
- Electronic
- Vibrational
- Magnetic
- Optical (TD-DFT)

A deeper look at the Hamiltonian

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

Only $\sum_i^N v_{ext}(\mathbf{r}_i)$ depends on atoms and molecules

$$\sum_i^N v_{ext}(\mathbf{r}_i) = \int d\mathbf{r} v_{ext}(\mathbf{r}) \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\int d\mathbf{r} f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_0) = f(\mathbf{r}_0)$$

Introducing the electron density

$$\langle \Psi | \sum_i^N v_{ext}(\mathbf{r}_i) | \Psi \rangle = \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \sum_i^N v_{ext}(\mathbf{r}_i)$$

$$= \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \int d\mathbf{r} v_{ext}(\mathbf{r}) \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$$

$$= \int d\mathbf{r} v_{ext}(\mathbf{r}) \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$$

$$= \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) = \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$$

Introducing the electron density

$$
\begin{aligned}
\rho(\mathbf{r}) &= \int d\mathbf{x}^N \left|\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)\right|^2 \sum_i^N \delta(\mathbf{r}-\mathbf{r}_i) \\
&= \langle\Psi| \sum_i^N \delta(\mathbf{r}-\mathbf{r}_i) |\Psi\rangle \\
&= N \langle\Psi| \delta(\mathbf{r}-\mathbf{r}_1) |\Psi\rangle \\
&= N \int d\mathbf{x}^N \left|\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)\right|^2 \delta(\mathbf{r}-\mathbf{r}_1) \\
&= N \int ds_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N \left|\Psi(\mathbf{r}s_1,\mathbf{x}_2,\ldots\mathbf{x}_N)\right|^2
\end{aligned}
$$

the electron density $\rho(\mathbf{r})$

1. The electron density at r in physical space
2. The probability of finding an electron at r
3. A function of three variables

$$\rho(\mathbf{r}) \geq 0$$

$$\int d\mathbf{r}\rho(\mathbf{r}) = N$$

For a determinant wave function

$$|\Phi_0\rangle = |\chi_1 \chi_2 \cdots \chi_i \chi_j \cdots \chi_N\rangle$$

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle \Phi_0 | \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_0 \rangle \\
&= \sum_i^N \langle \Phi_0 | \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_0 \rangle \\
&= \sum_i^N \int d\mathbf{x}_i \, |\chi_i(\mathbf{x}_i)|^2 \, \delta(\mathbf{r} - \mathbf{r}_i) \\
&= \sum_i^N \int d\mathbf{x}_i \, |\chi_i(\mathbf{x}_i)|^2 \, \delta(\mathbf{r} - \mathbf{r}_i) \\
&= \sum_i^N \int d\mathbf{r}_i \sum_{s_i} |\phi_i(\mathbf{r}_i)\sigma(s_i)|^2 \, \delta(\mathbf{r} - \mathbf{r}_i) \\
&= \sum_i^N |\phi_i(\mathbf{r})|^2
\end{aligned}$$

Hohenberg-Kohn Theorems

Given N and an external potential $v(\mathbf{r})$, its ground state electron density $\rho(\mathbf{r})$ and non-degenerate state wavefunction Ψ_v.

$$H_v = \hat{T}\left(\{\mathbf{r}_i\}\right) + \hat{V}_{ee}\left(\{\mathbf{r}_i\}\right) + V(\{\mathbf{r}_i\},\{\mathbf{R}_i\})$$

$$V(\{\mathbf{r}_i\},\{\mathbf{R}_i\}) = \sum_i^N v\left(\mathbf{r}_i\right)$$

$$H_v\Psi_v = \mathrm{E_v}\Psi_v$$

Assume there is another external potential $w(\mathbf{r})$ having the **same electron density $\rho(\mathbf{r})$**, with a non-degenerate state wavefunction Ψ_w.

$$H_w\Psi_w = \mathrm{E_w}\Psi_w$$

Then based on the variational principle, we should have the ground state energy

$$\begin{aligned} \mathrm{E_v} &< \langle \Psi_w | H_v | \Psi_w \rangle \\ &= \langle \Psi_w | H_w | \Psi_w \rangle + \langle \Psi_w | V - W | \Psi_w \rangle \\ &= \mathrm{E_w} + \int \mathrm{d}\mathbf{r} \big(v(\mathbf{r}) - w(\mathbf{r}) \big) \rho(\mathbf{r}) \end{aligned}$$

and

$$\mathrm{E_w} \quad < \mathrm{E_v} + \int \mathrm{d}\mathbf{r} \big(w(\mathbf{r}) - v(\mathbf{r}) \big) \rho(\mathbf{r})$$

But this leads to a contradiction:

$$\mathrm{E_w} + \mathrm{E_v} < \mathrm{E_w} + \mathrm{E_v}$$

Therefore, $w(\mathbf{r}) = v(\mathbf{r})$. The mapping from ground state density $\rho(\mathbf{r})$ to potential $v(\mathbf{r})$ is unique!

For a trial density $\rho(\mathbf{r})$ from a ground state of potential $w(\mathbf{r})$, the HK functional is defined as

$$E[\rho] = \langle \Psi_w | H_v | \Psi_w \rangle$$
$$= \langle \Psi_w | \hat{T}(\{\mathbf{r}_i\}) + \hat{V}_{ee}(\{\mathbf{r}_i\}) | \Psi_w \rangle + \int \mathrm{d}\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r})$$
$$= F[\rho] + \int \mathrm{d}\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r})$$

The ground state energy for potential $\mathrm{v}(\mathbf{r})$ is

$$\mathrm{E_v} = \min_{\rho(\mathbf{r})} \left(F[\rho] + \int \mathrm{d}\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) \right)$$
$$= \min_{\rho(\mathbf{r})} E_v[\rho]$$

Issues with the HK approach

$$\mathrm{E_v} = \min_{\rho(\mathbf{r})} \left(F[\rho] + \int \mathrm{d}\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) \right)$$
$$= \min_{\rho(\mathbf{r})} E_v[\rho]$$

Since we are interested in ground-state solutions, the restrictions of the variational domain to v –representable densities, $\mathcal{D}_v$, may not appear to be an issue.

However, in the HK DFT, there is a ***v*-representability** problem: restricting the trial density ρ to the v-representable set, $\mathcal{D}_v$, is a concern when one considers the minimization, because it is difficult to force the allowed variations of the trial densities to be v-representable.

The condition for a density to be in $\mathcal{D}_v$is not known in terms of a density itself.

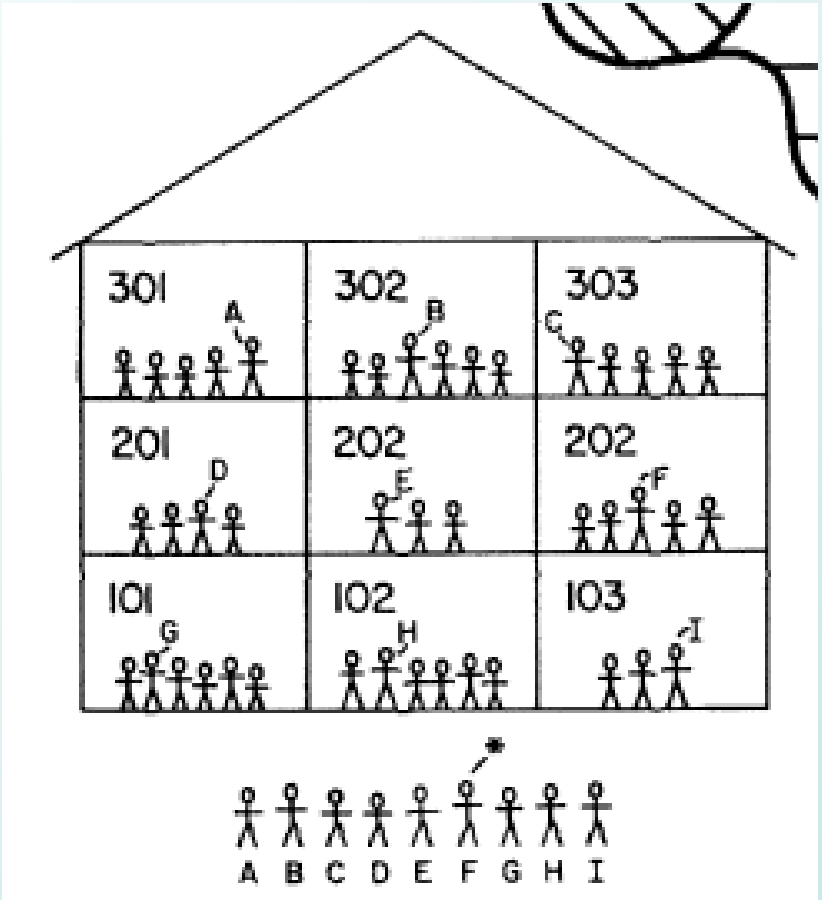
$$
\begin{aligned}
E^0 &= \min_{\Psi} \langle \Psi | \, H \, | \Psi \rangle \\
&= \min_{\Psi} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \langle \Psi | \sum_{i}^{N} v_{ext}(\mathbf{r}_i) \, | \Psi \rangle \right\} \\
&= \min_{\Psi} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\}
\end{aligned}
$$

Most QM methods use the wavefunction as the computational variable and work on its optimization.

An alternative route

Goal: Looking for the max height, and the tallest kid in a school.

1) We can first look for the tallest kid in each class
2) then compare the result from each class



An alternative route

Goal: Looking for the max height, and the tallest kid in a school.

1) We can first look for the tallest kid in each class
2) then compare the result from each class

$h(K_i)$ is the height of kid K_i

$$
\begin{aligned}
max \quad height &= \max_i \{h(K_i)\} \\
&= \max_J \max_{K_i \in class(J)} \{h(K_i)\} \\
&= \max_J H(J)
\end{aligned}
$$

$H(J) = \max_{K_i \in class(J)} \{h(K_i)\}$, the max height of class J

An alternative route

$$
\begin{aligned}
max \quad height &= \max_{i} \{h(K_i)\} \\
&= \max_{J} \max_{K_i \in class(J)} \{h(K_i)\} \\
&= \max_{J} H(J)
\end{aligned}
$$

i is the original variable

J is the reduced variable

$H(J) = \max_{K_i \in class(J)} \{h(K_i)\}$ is a constrained search

The constrained-search formulation of DFT

$$
\begin{aligned}
E^0 &= \min_{\Psi} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \min_{\Psi \to \rho(\mathbf{r})} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \left\{ \min_{\Psi \to \rho(\mathbf{r})} \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \left\{ F[\rho(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} E_v[\rho(\mathbf{r})]
\end{aligned}
$$

Levy, 1979

The constrained search

A. We have a new $F[\rho(\mathbf{r})] = \min_{\Psi \to \rho(\mathbf{r})} \langle \Psi | T + V_{ee} | \Psi \rangle$

1. A functional of density; given a density, it gives a number.
2. A universal functional of density, independent of atoms, or molecules.

B. The ground state energy is the minimum

$$\begin{aligned} E^0 &= \min_{\rho(\mathbf{r})} E_v[\rho(\mathbf{r})] \\ &= \min_{\rho(\mathbf{r})} \left\{ F[\rho(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \end{aligned}$$

C. $\rho(\mathbf{r})$ is the new reduced variable

Functions and Functionals

- **A function of one variable is a mapping from a number to a number**
- **A function of multi-variables is a mapping from muny numbers to a number**
- **A functional is a mapping from a function to a number.**

$I \leftarrow f(x)$		$I = \int_a^b dx f(x)$
$E \leftarrow \Psi(x)$		$E[\Psi] = \langle \Psi \mid H \mid \Psi \rangle$
$E \leftarrow \rho(\mathbf{r})$		$E[\rho] = ?$

Functional is the continuous version of function of infinitively many variables.

Functional derivatives

$$
\begin{aligned}
dy(t) &= \lim_{\epsilon \to 0} \frac{\left[y(t + \epsilon dt) - y(t) \right]}{\epsilon} \\
&= \frac{y(t) + \epsilon y'(t) dt - y(t)}{\epsilon} \\
&= y'(t) dt \\
&= \lim_{\epsilon \to 0} \frac{dy(t + \epsilon t)}{d\epsilon}
\end{aligned}
$$

$$
dy(t_1, t_2, \ldots) = \sum_i \frac{\partial y(t_1, t_2 \ldots)}{\partial t_i} dt_i
$$

$$
\begin{aligned}
\delta F[f(x)] &= \lim_{\epsilon \to 0} \frac{\left[F[f(x) + \epsilon \delta f(x)] \right] - F[f(x)]}{\epsilon} \\
&= \int dx \frac{\delta F}{\delta f(x)} \delta f(x) \\
&= \lim_{\epsilon \to 0} \frac{dF[f(x) + \epsilon \delta f(x)]}{d\epsilon}
\end{aligned}
$$

Functional derivatives

$$\delta F[f(x)] = \int dx \frac{\delta F}{\delta f(x)} \delta f(x)$$

The meaning of functional derivative: let $\delta f(x) = \delta(x - x_0)$, then

$$\delta F[f(x)] = \int dx \frac{\delta F}{\delta f(x)} \delta(x - x_0) = \frac{\delta F}{\delta f(x_0)}$$

How to take functional derivatives

$$F[f(x)] = \int dx g(f(x))$$

$$\begin{aligned}
\delta F[f(x)] &= \lim_{\epsilon \to 0} \frac{d}{d\epsilon} \int dx g(f(x) + \epsilon \delta f(x)) \\
&= \lim_{\epsilon \to 0} \frac{d}{d\epsilon} \int dx \left\{ g(f(x)) + \frac{dg(f(x))}{df} \epsilon \delta f(x) \right\} \\
&= \int dx \left\{ \frac{dg(f(x))}{df} \delta f(x) \right\}
\end{aligned}$$

$$\frac{\delta F}{\delta f(x)} = \frac{dg(f(x))}{df}$$

$$T_{TF}[\rho] = C_F \int d\mathbf{r} \rho(\mathbf{r})^{\frac{5}{3}}$$

$$\frac{\delta T_{TF}[\rho]}{\delta \rho(\mathbf{r})} = \frac{5}{3} C_F \rho(r)^{\frac{2}{3}}$$

How to take functional derivatives

$$F[f(x)] = \int dx g(f(x), f'(x))$$

$$\begin{aligned}
\delta F[f(x)] &= \lim_{\epsilon \to 0} \frac{d}{d\epsilon} \int dx g(f(x) + \epsilon \delta f(x), f'(x) + \epsilon \delta f'(x)) \\
&= \lim_{\epsilon \to 0} \frac{d}{d\epsilon} \int dx \left\{ g(f(x)) + \frac{\partial g}{\partial f} \epsilon \delta f(x) + \frac{\partial g}{\partial f'} \epsilon \delta f'(x) \right\} \\
&= \int dx \left\{ \frac{\partial g}{\partial f} \delta f(x) \right\} + \int dx \frac{\partial g}{\partial f'} \delta f'(x) \\
&= \int dx \left\{ \frac{\partial g}{\partial f} \delta f(x) \right\} + \int \frac{\partial g}{\partial f'} d(\delta f(x)) \\
&= \int dx \left\{ \frac{\partial g}{\partial f} \delta f(x) \right\} - \int dx \left(\frac{d}{dx} \frac{\partial g}{\partial f'} \right) \delta f(x) + \frac{\partial g}{\partial f'} \delta f(x) \Big|_{boundary}
\end{aligned}$$

$$\frac{\delta F}{\delta f(x)} = \frac{dg(f(x))}{df} - \frac{d}{dx} \frac{\partial g}{\partial f'}$$

The Thomas Fermi Approximation for T

1. **Divide the space into many small cubes**
2. **Approximate the electrons in each cubes as independent particles in a box (Fermions)**
3. **T= Sum of the contributions from all the cubes**

Eigenstate energies for particle in a cubic box

$$\epsilon = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ml^2}R_\epsilon^2$$

With quantum numbers $n_x, n_y, n_z = 1, 2, 3, ...$

Each state can have two electrons (spin up and spin down).

The Thomas Fermi Approximation for T

The number of states (with $energy < \epsilon$) $\Phi(\epsilon)$

$$\Phi(\epsilon) = \frac{1}{8}\frac{4\pi R_\epsilon^3}{3} = \frac{\pi}{6}(\frac{8ml^2}{h^2}\epsilon)^{\frac{3}{2}}$$

Density of states

$$g(\epsilon) = \frac{d\Phi(\epsilon)}{d\epsilon} = \frac{\pi}{4}(\frac{8ml^2}{h^2})^{\frac{3}{2}}\epsilon$$

Two electrons occupy each state. The kinetic energy is

$$t = 2\int_0^{\epsilon_F} \epsilon g(\epsilon)d\epsilon = \frac{8\pi}{5}(\frac{2m}{h^2})^{\frac{3}{2}}l^3\epsilon_F^{\frac{5}{2}}$$

$$N = 2\int_0^{\epsilon_F} g(\epsilon)d\epsilon = \frac{8\pi}{3}(\frac{2m}{h^2})^{\frac{3}{2}}l^3\epsilon_F^{\frac{3}{2}}$$

The Thomas Fermi Approximation for T

To express t as a function of density

$$t = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} l^3 (\frac{N}{l^3})^{\frac{5}{3}}$$

$$\frac{N}{l^3} \to \rho$$

$$l^3 \to d\mathbf{r}$$

$$T_{TF}[\rho] = \sum t = C_F \int d\mathbf{r} \rho(\mathbf{r})^{\frac{5}{3}}$$

$$C_F = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$$

---Local density approximation for T

A Homework Problem

Find the TF kinetic energy for a 2-d system.

The Thomas Fermi energy functional

For the Vee functional, use the classical electron-electron interaction energy

$$J[\rho] = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

The Thomas-Fermi total energy functional is

$$E_{TF}[\rho] = C_F \int d\mathbf{r}\rho(\mathbf{r})^{\frac{5}{3}} + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

The minimization of $E_{TF}[\rho]$ leads to the Euler-Lagrange equation, with μ for the constraint of $\int d\mathbf{r}\rho(\mathbf{r}) = N$.

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T_{TF}[\rho]}{\delta\rho(\mathbf{r})} + v_J(\mathbf{r}) + v_{ext}(\mathbf{r})$$

or

$$\frac{5}{3}C_F\rho(r)^{\frac{2}{3}} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{ext}(\mathbf{r}) = \mu$$

Comments on TF theory: Orbital-Free DFT

•Beautiful and simple theory, with density as the basic variable

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_{TF}[\rho]}{\delta \rho(\mathbf{r})} + v_J(\mathbf{r}) + v_{ext}(\mathbf{r})$$

$$\frac{5}{3} C_F \rho(r)^{\frac{2}{3}} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}) = \mu$$

•**Linear Scaling! O(N)**

BUT,

•the energy is NOT a bound to the exact energy

•no shell structure for atoms, no oscillation

•no bounding for molecules

•Main problem is in the local approximation for T

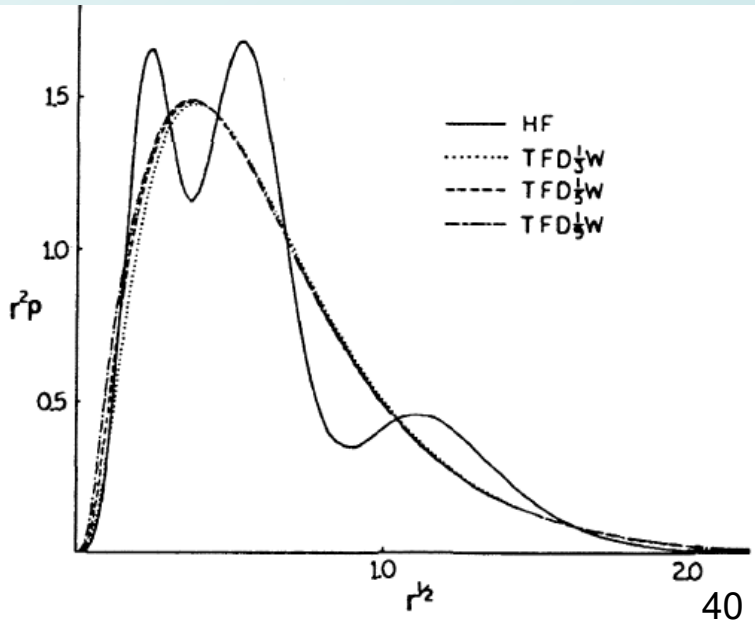


Figure 6.3 Electron density for argon from various models (after Yang 1986.)

Kohn-Sham theory, going beyond the Thomas-Fermi Approximation

Use a non-interacting electron system, —Kohn-Sham reference system, to calculate the electron density and kinetic energy

$$|\Phi_s\rangle = |\chi_1\chi_2\cdots\chi_i\chi_j\cdots\chi_N\rangle$$

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

$$T_s[\rho] = \langle\Phi_s| \sum_i^N -\frac{1}{2}\nabla_i^2 |\Phi_s\rangle$$

$$= \sum_i^N \int d\mathbf{r}_i \phi_i^*(\mathbf{r}_i) \left(-\frac{1}{2}\nabla_i^2\right) \phi_i(\mathbf{r}_i)$$

$$= \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle$$

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad T_s[\rho] = \sum_i^N \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle$$

- $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ is the true electron density, but $T_s[\rho]$ is not $T[\rho]$. However, $T_s[\rho]$ is a very good approximation to $T_s[\rho]$

- The essence of KS theory is to solve $T_s[\rho]$ exactly in terms of orbitals

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad T_s[\rho] = \sum_i^N \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle$$

Introduce the exchange correlation energy functional

$$\begin{aligned} F[\rho] &= T[\rho] + V_{ee}[\rho] \\ &= T_s[\rho] + J[\rho] + E_{xc}[\rho] \end{aligned}$$

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

$$J[\rho] = \tfrac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Kohn-Sham Equations

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad T_s[\rho] = \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle$$

In terms of the orbitals, the KS total energy functional is now

$$E_v[\rho] = \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

The g.s. energy is the minimum of the functional w.r.t. all possible densities. The minimum can be attained by searching all possible orbitals

$$W[\phi_i] = E_v[\phi_i] - \sum_i^N \varepsilon_i \{< \phi_i|\phi_i > -1\}$$

$$\frac{\delta W[\phi_i]}{\delta \phi_i(\mathbf{r})} = 0$$

The orbitals $\{|\phi_i\rangle\}$ are the eigenstates of an one-electron local potential $v_s(\mathbf{r})$ if we have explicit density functional for $E_{xc}[\rho]$ (KS equations)

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)|\phi_i\rangle = \varepsilon_i\,|\phi_i\rangle\,,$$

or a nonlocal potential $v_s^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')$, if we have orbital functionals for $E_{xc}[\phi_i]$ (generalized KS equations)

$$\left(-\frac{1}{2}\nabla^2 + v_s^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')\right)|\phi_i\rangle = \varepsilon_i^{\mathrm{GKS}}\,|\phi_i\rangle\,.$$

One electron Equations

Kohn-Sham (KS)

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)|\phi_i\rangle = \varepsilon_i|\phi_i\rangle$$

$$v_s(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} + v_J(\mathbf{r}) + v_{ext}(\mathbf{r})$$

Generalized Kohn-Sham (GKS)

$$\left(-\frac{1}{2}\nabla^2 + v_s^{\mathrm{NL}}(\mathbf{r},\,\mathbf{r}')\right)|\phi_i\rangle = \varepsilon_i^{\mathrm{GKS}}|\phi_i\rangle$$

$$v_s^{\mathrm{NL}}(\mathbf{r},\,\mathbf{r}') = \frac{\delta E_{xc}[\delta\rho_s(\mathbf{r}',\mathbf{r})]}{\delta\rho_s(\mathbf{r}',\mathbf{r})} + \left[v_J(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\delta(\mathbf{r}'-\mathbf{r})$$

Computational Scaling

In finite basis sets, KS and GKS equations turn into matrix eigenvalue problem. **The scaling is N^3**.

Feastures of Kohn-Sham theory

1. With N orbitals, the kinetic energy is treated rigorously. In comparison with the Thomas-Fermi theory in terms of density, it is a trade of computational difficulty for accuracy.

2. The KS or GKS equations are in the similar form as the Hartree-Fock equations and can be solved with similar efforts.

3. KS or GKS changes a N interacting electron problem into an N non-interacting electrons in an effective potential.

4. The E_xc is not known, explicitly. It is about 10% of the energy for atoms.

The Local Density Approximation (Kohn-Sham, 1964)

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))$$

$\varepsilon_{xc}(\rho(\mathbf{r}))$ is the XC energy per particle of a homogeneous electron gas of density ρ. It is a function of ρ.

Dirac exchange energy functional

$$E_x^{LDA}[\rho] = -C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r}$$

Functional derivatives

$y(t)$	dt	$dy(t) = y'(t)dt$
$y(t_1, t_2)$	$dt_1 dt_2$	$dy(t_1, t_2) = y'_1(t_1, t_2)dt_1 + y'_2(t_1, t_2)dt_2$
$y(t_1, t_2, ..t_n)$	$dt_1 dt_2 ... dt_n$	$dy(t_1, t_2..t_n) = \sum_{i=1}^{n} y'_i(t_1, t_2...t_n)dt_i$
...		
$F[f(\mathbf{x})]$	$\delta f(x)$	$\delta F = \int dx \frac{\delta F}{\delta f(x)} \delta f(x)$

Functional Derivatives: Continuous extension of multivariable derivatives

Beyond the Local Density Approximation

LDA	$E_{xc} = \int d\mathbf{r}\, f(\rho)$	VWN, PW,
GGA	$E_{xc} = \int d\mathbf{r}\, f(\rho, \nabla\rho)$	BLYP, PW96, PBE
Hybrid	$E_{xc} = c_1 E_x^{HF} + c_2 E_{xc}^{GGA}$	B3LYP, PBE0
range-separated		....

$$E_{\mathrm{x}}^{\mathrm{B88}} = -\sum_{\sigma=\alpha,\beta}\int \rho_{\sigma}{}^{4/3}\left[\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} + \frac{\beta x_{\sigma}{}^{2}}{1 + 6\beta x_{\sigma}\sinh^{-1} x_{\sigma}}\right]\mathrm{dr}$$

$$E_{\mathrm{x}}^{\mathrm{PBE}} = -\int \rho^{4/3}\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} + \frac{\mu s^{2}}{1 + \mu s^{2}/\kappa}\right]\mathrm{dr}$$

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{ij\sigma}\int\int \frac{\phi^{*}_{i\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,\phi^{*}_{j\sigma}(\mathbf{r}')\,\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{dr}\,\mathrm{dr}'$$

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = 0.2E_{\mathrm{x}}^{\mathrm{HF}} + 0.8E_{\mathrm{x}}^{\mathrm{LDA}} + 0.72\Delta E_{\mathrm{x}}^{\mathrm{B88}} + 0.81E_{\mathrm{c}}^{\mathrm{LYP}} + 0.19E_{\mathrm{c}}^{\mathrm{VWN}}$$

$$\frac{1}{r_{ij}} \equiv \underbrace{\frac{\operatorname{erf}(\mu r_{ij})}{r_{ij}}}_{\text{long range}} + \underbrace{\frac{\operatorname{erfc}(\mu r_{ij})}{r_{ij}}}_{\text{short range}}$$

and long-range Hartree−Fock is given by

$$E_{\mathrm{x}}^{\mathrm{lr-HF}} = -\frac{1}{2}\sum_{ij\sigma}\iint \frac{\phi^*_{i\sigma}(\mathbf{r}_1)\,\phi_{j\sigma}(\mathbf{r}_1)\,\operatorname{erf}(\mu r_{12})\,\phi^*_{j\sigma}(\mathbf{r}_2)\,\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \tag{15}$$

The corresponding form of the long-range LDA exchange energy can be calculated from the explicit form of the LDA exchange-hole, to give[86]

$$E_{\mathrm{x}}^{\mathrm{lr-LDA}} = \frac{1}{2}\sum_{\sigma}\int \rho_\sigma^{4/3} K_\sigma^{\mathrm{LDA}}\left(\frac{8}{3}a_\sigma\left[\sqrt{\pi}\,\operatorname{erf}\left(\frac{1}{2a_\sigma}\right) + 2a_\sigma(b_\sigma - c_\sigma)\right]\right)\mathrm{d}\mathbf{r} \tag{16}$$

Atomization energies for a few selected molecules, mH

Mol.	Exp.	LSDA	PBE	UHF	MP2	B3LYP
H_2	174.5	180.3	166.7	133.9	165.7	—
Li_2	39.3	37.9	31.7	4.8	25.5	33.5
Be_2	4.8	20.6	15.6	11.2	−1.6	—
N_2	364.0	427.1	387.6	183.3	368.1	365.6
F_2	62.1	124.6	85.1	−15.9	111.6	57.7
LiH	92.4	96.9	85.2	52.6	86.1	92.9
OH	169.6	197.9	175.0	108.4	165.7	172.3
HF	225.7	259.1	226.3	154.6	227.9	222.1
H_2O	370.0	424.9	373.2	245.4	366.5	368.1
NH_3	473.9	537.5	480.8	318.7	462.1	478.4
CH_4	668.2	737.2	669.0	522.7	661.3	670.4
CO	413.2	476.3	428.4	277.3	423.9	408.3
NO	243.7	316.2	273.9	84.5	242.2	248.0
Cl_2	92.4	132.1	103.7	—	—	87.8

Mean Absolute Errors (MAE) Thermochemistry(G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

	post-B3LYP				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78
GGA and Meta-GGA					
BLYP	6.64	7.37	0.0205	1.46	0.79
HCTH	5.59	4.15	0.0119	2.22	0.48
HCTH407	5.72	4.69	0.0107	1.05	0.50
PBE	15.99	8.29	0.0148	1.24	0.63
BP86	15.71	8.49	0.0158	1.39	0.66
BPBE	7.55	6.81	0.0155	1.67	0.53
OLYP	5.22	5.36	0.0142	2.21	0.53
OPBE	8.86	5.21	0.0121	2.55	0.31
TPSS	7.85	8.03	0.0123	1.16	0.44
M06-L	5.87	3.82	0.0056	0.58	0.40

Mean Absolute Errors (MAE) Thermochemistry(G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

	post-B3LYP				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78
					Hybrid Functionals
TPSSh	6.03	6.45	0.0082	0.98	0.30
B3LYP	4.28	4.50	0.0097	1.01	0.37
PBE0	6.37	4.11	0.0089	0.76	0.21
B97−1	3.90	3.88	0.0093	0.75	0.28
B97−2	4.31	2.79	0.0087	0.97	0.19
B97−3	3.70	2.22	0.0087	0.92	0.26
M06	4.78	2.03	0.0088	0.47	0.39
M06-2X	3.34	1.37	0.0110	0.34	0.35
M06-HF	6.26	3.14	0.0167	0.88	0.73
HF	132.38	15.12	0.0277	3.15	1.01
HFLYP	35.39	9.18	0.0423	1.13	1.36

Mean Absolute Errors (MAE) Thermochemistry(G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

	post-B3LYP				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78
					Range-Separated Functionals
CAMB3LYP	4.04	2.51	0.0119	0.69	0.23
LCBLYP	16.91	3.73	0.0169	0.90	0.31
rCAMB3LYP	5.50	2.76	0.0225	0.78	0.37
LC-PBE	16.69	3.07	0.0245	0.75	0.53
HSE	4.37	3.43	0.0082	0.77	0.21