

# Density Functional Theory (DFT)

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**How to determine the electronic ground state  
in Born-Oppenheimer molecular dynamics (BOMD)?**



# Hohenberg-Kohn Theorem

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Consider a system of  $N$  electrons in an external potential  $v(\mathbf{r})$ .

## Theorem 1

The ground-state density  $\rho(\mathbf{r})$  & the external potential  $\{v(\mathbf{r}) + c\}$  ( $c$  is a constant) are bijective functional, *i.e.*, one-to-one correspondence (see the note on DFT for a proof).

## Theorem 2

Any property of the many-electron ground state  $|\Psi\rangle$ , including the ground-state energy,  $E = \langle\Psi|H|\Psi\rangle$  ( $H$  is the Hamiltonian operator), is a functional of  $\rho(\mathbf{r})$ .

P. Hohenberg & W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.* **136**, B864 ('64)

- See notes on density functional theory

# Functional Derivative Basics

- **Functional derivative:**  $\delta E = \int d\mathbf{r} \frac{\delta E}{\delta f(\mathbf{r})} \delta f(\mathbf{r})$     **functional = function of function:**  $E[f(\mathbf{r})]$

- **Example 1:**  $E[f(\mathbf{r})] = \int d\mathbf{r} (f(\mathbf{r}))^2$

$$E[f(\mathbf{r}) + \delta f(\mathbf{r})] - E[f(\mathbf{r})] = \int d\mathbf{r} \{ [f(\mathbf{r}) + \delta f(\mathbf{r})]^2 - f^2(\mathbf{r}) \} = \int d\mathbf{r} [2f(\mathbf{r})\delta f(\mathbf{r}) + \cancel{\delta f^2(\mathbf{r})}]$$

$$\therefore \frac{\delta E}{\delta f(\mathbf{r})} = 2f(\mathbf{r})$$

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

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

$$= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\overset{\mathbf{r} \leftrightarrow \mathbf{r}'}{\rho(\mathbf{r})\delta\rho(\mathbf{r}') + \rho(\mathbf{r}')\delta\rho(\mathbf{r})} + \cancel{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|}$$

$$= \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta\rho(\mathbf{r})$$

$$\therefore \frac{\delta E}{\delta\rho(\mathbf{r})} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- **See notes on** density functional theory

# Energy Functional

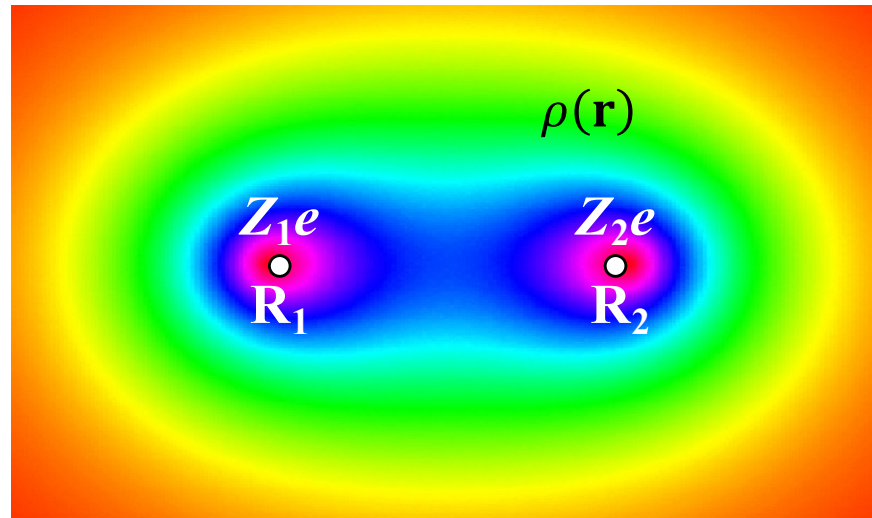
## Definition: Exchange-correlation (xc) functional

$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho(\mathbf{r})]$$

Kinetic energy of  
non-interacting  
electrons

Hartree energy (mean-  
field approximation to  
the electron-electron  
interaction energy)

Exchange-correlation  
energy



# Kohn-Sham Equation

- The many-electron ground state is obtained by solving a set of one-electron Schrödinger equations called Kohn-Sham (KS) equations

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{KS}}(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

KS wave function

KS energy

- KS potential

$$v_{\text{KS}} = v(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n \Theta(\mu - \epsilon_n) |\psi_n(\mathbf{r})|^2$$

exchange-correlation (xc) potential

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}$$

step function chemical potential

$$N = \sum_n \Theta(\mu - \epsilon_n)$$

- See the note on density functional theory for derivation

W. Kohn & L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.* **140**, A1133 ('65)

# Extensions of DFT

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- **Finite-temperature DFT**

N. D. Mermin, “Thermal properties of the inhomogeneous electron gas,” *Phys. Rev.* **137**, A1441 ('65)

- **Current DFT in magnetic fields:  $\rho(\mathbf{r})$  &  $\mathbf{j}(\mathbf{r})$**

M. Ferconi & G. Vignale, “Current density functional theory of quantum dots in magnetic fields,” *Phys. Rev. B* **50**, 14722 ('94)

J. Sun *et al.*, “real-time exciton dynamics with time-dependent density-functional theory,” *Phys. Rev. Lett.* **127**, 077401 ('21)

- **Superconducting-gap DFT:  $\Delta(\mathbf{r}) = \langle \psi_{\uparrow}(\mathbf{r})\psi_{\downarrow}(\mathbf{r}) \rangle$  &  $\rho(\mathbf{r}) = \sum_{\sigma} \langle \psi_{\sigma}^{\dagger}(\mathbf{r})\psi_{\sigma}(\mathbf{r}) \rangle$**

L. N. Oliveira *et al.*, “Density functional theory for superconductors,” *Phys. Rev. Lett.* **60**, 2430 ('88)

- **Ensemble DFT for nearly degenerate & strongly correlated states**

E. K. U. Gross *et al.*, “Density functional theory for ensembles of fractionally occupied states,” *Phys. Rev. A* **37**, 2809 ('88)

M. Filatov, “Spin-restricted ensemble-referenced Kohn–Sham method,” *WIREs Comput. Mol. Sci.* **5**, 146 ('15)

- **For the electronic current operator, see the note on quantum dynamical computation of electronic conductivity**