Density Functional Theory (DFT)

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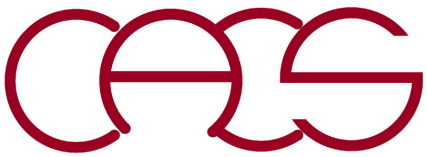
How to determine the electronic ground state in Born-Oppenheimer molecular dynamics (BOMD)?



Hohenberg-Kohn Theorem

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

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

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

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

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

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

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

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

- **See notes on** functional derivative

Energy Functional

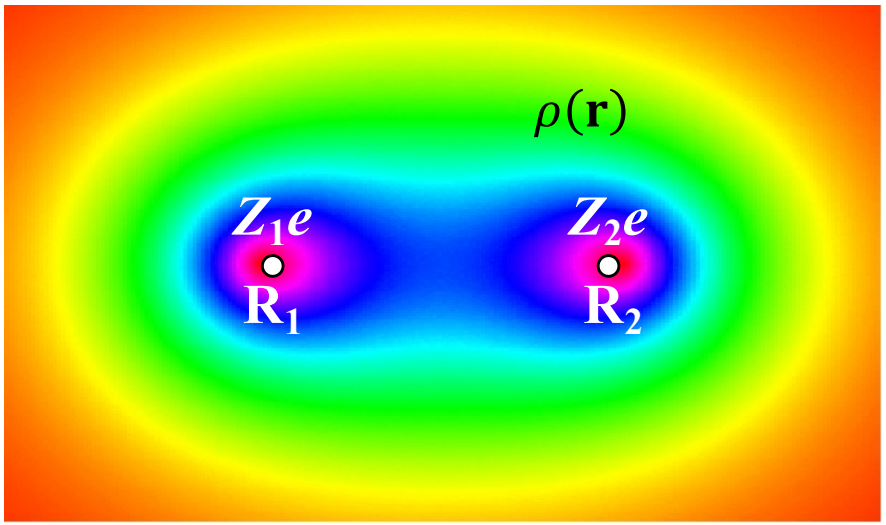
Definition: Exchange-correlation (xc) functional

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

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**

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

KS wave function — KS energy

- **KS potential**

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

exchange-correlation (xc) potential

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

step function — chemical potential

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

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

- **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

- **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) Exchange-correlation vector potential, $\mathbf{A}_{\mathrm{xc}}$

  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)

  See the note on DFT for superconductors

- **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)

  See notes on energy balance sheet and ensemble local-field dynamics

- **For the electronic current operator, see the note on**

  quantum dynamical computation of electronic conductivity