

Title: Explorations in Condensed Matter-2

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Abstract:

Review

Hartree-Fock

$$H = -\frac{1}{2} \int \psi_{i\sigma}^* \nabla^2 \psi_{i\sigma} + \int \psi_{i\sigma}^* \psi_{i\sigma} v_{ee}(\mathbf{r}-\mathbf{r}') \underbrace{\psi_{i\sigma}(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}')}_{\psi_{i\sigma}^2} + \int \psi_{i\sigma}^* v(\mathbf{r}) \psi_{i\sigma}$$

Rewriting of QM (electrons)

QM, ground state energy, minimize functional

$$E[\psi] = \langle \psi | H | \psi \rangle = \int d^3r \psi^* H \psi$$

Rewriting of QM (electrons)

QM, ground state energy, minimize functional

$$E[\psi] = \langle \psi | \hat{H} | \psi \rangle = \int_{\mathbb{R}^3} d\mathbf{r} \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r})$$

$\psi = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ N electrons

→ variational principle
 $E_0 \leq E[\Psi] \quad \forall \Psi \in \mathcal{H}$

Define $n(\vec{r}) = \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \langle \Psi | \hat{U}_r^+ \hat{U}_r | \Psi \rangle$

→ variational principle
 $E_0 \leq E[\Psi] \quad \forall \Psi \in \mathcal{H}$

Define $n(\vec{r}) = \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle \stackrel{\text{if}}{=} \langle \Psi | \hat{\psi}_{\vec{r}}^\dagger \hat{\psi}_{\vec{r}} | \Psi \rangle$

Principle of DFT \exists functional $E[n]$ \min of $E[n] = E_0$ g.s. energy

→ variational principle
 $E_0 \leq E[\Psi] \quad \forall \Psi \in \mathcal{H}$

Define $n(\vec{r}) = \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle \stackrel{\text{if}}{=} \langle \Psi | \hat{\psi}_{\vec{r}}^\dagger \hat{\psi}_{\vec{r}} | \Psi \rangle$

Principle of DFT \exists functional $E[n]$ (• assuming non-degen. ground state)

- min of $E[n] = E_0$ g.s. energy
- min occurs for $E[n_0] = E_0$
 \vec{r}
g.s. density

→ variational principle
 $E_0 \leq E[\Psi] \quad \forall \Psi \in \mathcal{H}$

Define $n(\vec{r}) = \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle \stackrel{\text{if}}{=} \sum_i \langle \Psi | \hat{q}_{i\vec{r}}^\dagger \hat{q}_{i\vec{r}} | \Psi \rangle$

Principle of \exists functional $E[n]$ (assuming non-degen. ground state)

- min of $E[n] = E_0$ g.s. energy
- min occurs for $E[n_0] = E_0$
 \vec{n}_0 g.s. density

function of a function
 $n_1(\vec{r}) \rightarrow E_1$
 $n_2(\vec{r}) \rightarrow E_2$

Consider single electron (von Weizsäcker functional) (1d) $\psi = \psi(x)$
Assume ψ real, non-negative everywhere

$$\begin{aligned}
 \langle 4 | \hat{T} | 4 \rangle &= \int_x \langle 4 | x \rangle \langle x | \hat{T} | 4 \rangle = \int_x 4^*(x) \left[-\frac{1}{2} \frac{d^2}{dx^2} 4(x) \right] \quad \psi(x) = \sqrt{n(x)} \\
 &= \int_x n^{-1/2} \left(n' \right)^2 - \frac{1}{4} n^{-1/2} n'' \\
 &= \int
 \end{aligned}$$

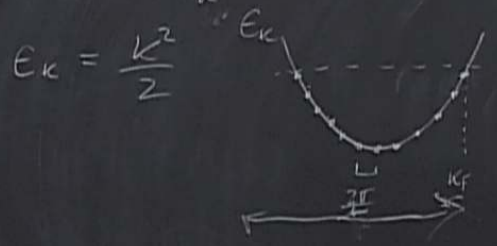
$$\begin{aligned}
 &= \int_x \langle \psi | x \rangle \langle x | \hat{T} | \psi \rangle = \int_x \psi^*(x) \left[-\frac{1}{2} \nabla_x^2 \psi(x) \right] \psi(x) = \sqrt{n(x)} \\
 &= \int_x n^{1/2} \left(\frac{1}{8} n^{-3/2} (n')^2 - \frac{1}{4} n^{1/2} n'' \right) \underline{E_x} \\
 &= \int_{-\infty}^{\infty} dx \left(\frac{1}{8} \frac{(n')^2}{n} - \frac{1}{4} n'' \right) \quad n' \Big|_{-\infty}^{\infty} \quad n' \rightarrow 0 \text{ at } \pm \infty \\
 &= \int \frac{1}{8} \frac{(n'(x))^2}{n(x)} dx \quad \text{Kinetic energy functional } T(n(x), n'(x)) \\
 &E^{vw}[n] = T(n(x), n'(x)) \\
 &= \frac{1}{8} \int_x \frac{(n'(x))^2}{n(x)} dx + \int n(x) \quad \text{always a density fun}
 \end{aligned}$$

$$\rightarrow = \int_{-\infty}^{\infty} \frac{1}{2} \frac{(n'(x))^2}{n(x)} dx$$

Kinetic energy functional $T(n(x), n'(x))$

$n' \Big|_{-\infty}^{\infty} = 0$ at $\pm \infty$

$$\hat{H} = \hat{T} = \sum_k \epsilon_k \hat{\psi}_k^\dagger \hat{\psi}_k ; \quad k = \frac{2\pi n}{L} \quad n \text{ integer} \quad \text{ring of size } L$$



$$= N \Rightarrow k_F = \frac{\pi N}{L} = \pi n$$

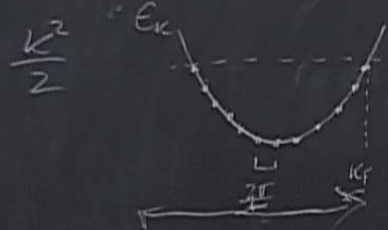
$$\int_{-k_F}^{k_F} \frac{dk}{2\pi} \frac{k^2}{2} = \frac{1}{6 \cdot 2\pi} \left(k^3 \Big|_{-k_F}^{k_F} \right) = \frac{1}{6\pi} k_F^3 = \frac{1}{6\pi} (\pi n)^3 = \frac{\pi^2}{6} n^3$$

$$= \int \frac{1}{8} \frac{(n'(x))^2}{n(x)} dx$$

Kinetic energy functional $T(n(x), n'(x))$

$n' \Big|_{-\infty}^{\infty} = 0$ at $\pm \infty$

$= \sum_k E_k \psi_k^+ \psi_k$; $k = \frac{2\pi n}{L}$ n integer ring of size L



size of Fermi sea $\left\{ \frac{2k_F}{L} \right\} = N \Rightarrow k_F = \frac{\pi N}{L} = \pi n$

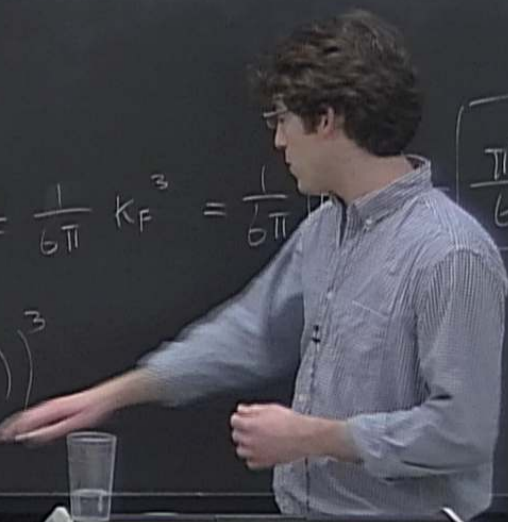
spacing $\left\{ \frac{2\pi}{L} \right\}$

$$T = \frac{1}{L} \sum_{k=-k_F}^{k_F} \frac{k^2}{2} \stackrel{L \rightarrow \infty}{=} \int_{-k_F}^{k_F} \frac{dk}{2\pi} \frac{k^2}{2} = \frac{1}{6 \cdot 2\pi} \left(k^3 \Big|_{-k_F}^{k_F} \right) = \frac{1}{6\pi} k_F^3 = \frac{1}{6\pi} \left(\frac{\pi n}{L} \right)^3 L^3$$

with $k = -k_F$

$$t(n) = \frac{\pi^2}{6} n^3; \quad T(n) = \int dx \frac{\pi^2}{6} (n(x))^3$$

$$\frac{\pi^2}{6} n^3$$



$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$
 \rightarrow variational
 $E_0 \leq E[\Psi]$

von Weizsäcker \rightarrow valid for single electron

Thomas-Fermi \rightarrow valid: uniform, non-interacting; density (n.I.)

$$E[n] = T_{\text{ext}}[n] + V_{\text{ext}}[n] + \underbrace{\int_V v_{\text{ee}}(r) n(r) dr}_{\text{TF}} + \int_V \frac{\hbar^2}{2m} (\nabla n)^2 + \int_V v_{\text{ee}}(r, r') n(r') n(r) + \int_V v(r) n(r)$$



$$E[n] = T(n) + V_{ee}(n) + V[n] \stackrel{TF}{=} \int_x \frac{\hbar^2}{2m} (n(x))'{}^2 + \int_x \int_{x'} v_{ee}(x-x') n(x) n(x') + \int_x v(x) n(x)$$

Hohenberg and Kohn [Phys. Rev. 136, B864 (1964)]

but density functionals are rigorous footing

consider class of H 's

$$H_{\nu} = \underbrace{\hat{T}}_{\text{fixed}} + \underbrace{\hat{V}_{ee}}_{\text{fixed}} + \sum_{j=1}^N v(\hat{r}_j)$$

↑ "control knob"

valid uniform, non-interacting; high density (K.I.)

$$E[n] = T(n) + \underbrace{V_{cc}(n)}_{\int v(\vec{r})n(\vec{r})} + \underbrace{V[n]}_{\int_x \frac{\hbar^2}{2} (n(x))' ^2} + \int_x \int_{x'} v_{cc}(x-x') n(x) n(x') + \int_x v(x) n(x)$$

Hohenberg and Kohn [Phys. Rev. 136, B864 (1964)]
 put density functionals on rigorous footing

Consider class of H 's

$$H_v = \underbrace{\hat{T}}_{\text{fixed}} + \underbrace{\hat{V}_{cc}}_{\text{fixed}} + \int v(\vec{r}) \hat{n}(\vec{r})$$

↑ "control knob"

Typically $\hat{T} = -\frac{1}{2} \sum_{j=1}^N \nabla_j^2$
 $\hat{V}_{cc} = \frac{1}{2} \sum_{i,j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$

HK showed:
 two H 's $H_v, H_{v'}$ (H, H')
 • assuming each has non-degen. ground state
 • ground states ψ, ψ' same density
 $\Rightarrow v, v'$ differ by const shift
 $v' = v + C$