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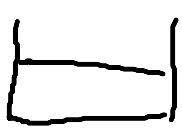
Recap: We'd like to predict, from quantum mechanics alone, the properties of real matter!

So far: $H\Psi = E\Psi$ for electrons and nuclei
($\equiv$ ions + valence electrons)

And we know when to separate ions from electrons: $\Psi(\{\vec{R}_I\},\{\underline{r}_k\}) = \sum_\nu \Lambda_\nu(\{\underline{R}\})\,\Phi_\nu(\{\underline{R}\},\{\vec{r}_k\})$

$$H^e\,\Phi_\nu(\{\vec{R}_I\},\{\underline{r}_k\}) =$$
$$(T^e + V^{e-ion} + V^{e-e})\,\Phi(\{\vec{R}_I\},\{\vec{r}_k\})$$

Chapter 2.3 "Jellium"



$V^{e-ion} = \text{const}$

$V^{e-e} = \text{const.}$

$$\Phi_\nu(\{\vec{r}_k,\sigma_k\}) = \Phi_\nu(\{\underline{r}_k\})\cdot\chi(\{\sigma_k\})$$

$$H^e = T^e = \sum_{k=1}^{N} -\frac{\hbar^2}{2m} \cdot \underline{\nabla}^2_{r_k}$$

$$-\frac{\hbar^2}{2m} \underline{\nabla}^2 \varphi_j(\underline{r}) = \epsilon_j \varphi_j(\underline{r}) \Rightarrow \varphi_j(\underline{r}) = e^{i\underline{k}\underline{r}}$$

$$\epsilon_1(\underline{k}) = \frac{\hbar^2 k^2}{2m} \qquad \left(\lambda_{\text{de Broglie}} \doteq \frac{2\pi}{k} \right)$$

Quantum number(s) : $\underline{k} = (k_x, k_y, k_z)$

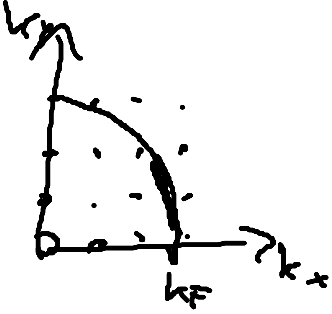
Base region: Volume $V_g \overset{\text{e.g.}}{\equiv}$ box (L_x, L_y, L_z)

Periodic Boundary Conditions (Born-von Karman)

$$\varphi(\underline{r}) = \varphi(\underline{r} + \underline{e}_x \cdot L_x) = \varphi(\underline{r} + \underline{e}_y L_y) =$$

$\underline{k}$ now discrete : $= \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right)$ n_i integers

each k point has "volume" $\frac{(2\pi)^3}{V_g}$



Jellium, N electrons

$$N = 2 \cdot \frac{4}{3}\pi k_F^3 \Big/ \frac{(2\pi)^3}{V_g}$$

$$= \frac{k_F^3}{3\pi^2} \cdot V_g$$

$$n(\underline{r}) = \frac{N}{V_g} = \frac{1}{(3\pi^2)} k_F^3$$

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \left(3\pi^2 n(\underline{r})\right)^{2/3}$$

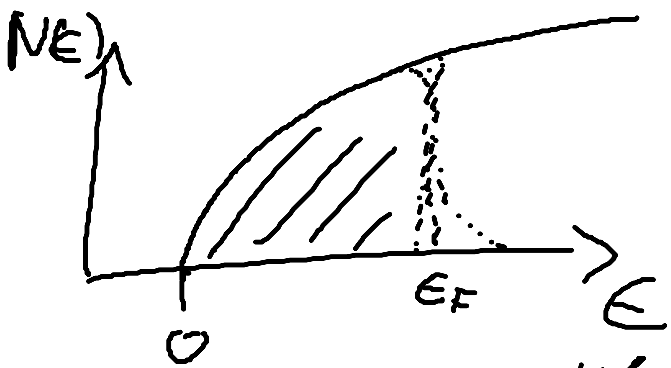
often $$\frac{4}{3}\pi r_s^3 = \frac{V_g}{N} = \frac{1}{n(\underline{r})}$$

"Density parameter"

Definition: "Density of States" $N(\epsilon)\,d\epsilon$

"# of states between ϵ, $\epsilon + d\epsilon$"

$\boxed{\text{Exercises}}$ → 3D result $$N^{3D}(\epsilon) = \frac{m V_g}{\pi^2 \hbar^3}\sqrt{2m\epsilon} \qquad \epsilon \geq 0$$



DOS at Fermi level $$\frac{N(\epsilon_F)}{V_g} = \frac{m}{\pi^2\hbar^3}\sqrt{2m\frac{\hbar^2}{2m}k_F^2}$$

$\sim k_F$

Chapter 3 Electron-Electron Interaction

Electronic Hamiltonian
$$H^e = \sum_{k=1}^{N} -\frac{\hbar^2}{2m}\nabla^2_{\underline{r}_k} + \sum_{k=1}^{N} v(\underline{r}_k)$$

$$+\sum_{\substack{k\,k' \\ k\neq k'}}^{N\,N} \frac{1}{2}\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\underline{r}_k-\underline{r}_{k'}|} \qquad \text{UGH.}$$

Wouldn't it be nice if $V^{e-e} \approx \sum_k^N v^{e-e}(\underline{r}_k)$

How to tackle H^e? (in general)

1. Try to find a good mean-field theory! (following)
2. "The front door": Write down Φ_ν as good as we can

3. Green function techniques
   usually: Series expansion starting from effective single-particle solution
   e.g. first series term: "GW" approximation for excited states (among others)

4. Quantum Monte Carlo
   → write (good) parameterized form for $\Phi_\nu(\{\underline{r}_n\})$
   use variational principle: $\frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \text{min.}$ for the ground state

Hartree approximation (1928)

What if $V^{e-e}(\{\underline{r}_k\}) \underset{N}{\approx} \sum_{k=1}^{N} v^{\text{Hartree}}(\underline{r}_k)$

Then $H^e = \sum_{k=1} h(\underline{r}_k)$ separable.

Oh joy.

More rigorously:

Generally: Use variational principle

$$\frac{\langle \underline{\Phi} | H^e | \underline{\Phi} \rangle}{\langle \underline{\Phi} | \underline{\Phi} \rangle} \geq E_0^e$$

$\uparrow$ not $=$ for Hartree

$$\underline{\Phi}_\nu(\{\underline{r}_k\}) \Rightarrow \underline{\Phi}^{\text{Hartree}}(\ldots)$$
$$= \varphi_{01}(\underline{r}_1) \cdot \varphi_{02}(\underline{r}_2) \cdots \varphi_{0N}(\underline{r}_N)$$

Actually $\underline{\Phi}_\nu \equiv \underline{\Phi}_\nu(\{\underline{r}_k\}) \cdot \chi_\sigma(\{\sigma_k\})$.

spin function: separated off!

But do not forget (in Hartree-Fock)

Minimize:
$$\frac{\langle \underline{\Phi}^{\text{Hartree}} | H^e | \underline{\Phi}^{\text{Hartree}} \rangle}{\langle \underline{\Phi}^{\text{Hartree}} | \underline{\Phi}^{\text{Hartree}} \rangle}$$

But $\langle \underline{\Phi}^{\text{Hartree}} | \underline{\Phi}^{\text{Hartree}} \rangle = 1$

$$\longrightarrow \langle \varphi_{0i} | \varphi_{0i} \rangle = 1$$

$$\langle \underline{\Phi}^{\text{Hartree}} | H^e | \underline{\Phi}^{\text{Hartree}} \rangle = E^{\text{Hartree}}[\varphi_{01}, \varphi_{02}, \ldots \varphi_{0N}, \varphi_{01}^*, \varphi_{02}^*, \ldots \varphi_{0N}^*]$$

$$= \int d^3r_1\, d^3r_2 \dots d^3r_N \left\{ \varphi_{01}^*(\underline{r}_1)\varphi_{02}^*(\underline{r}_2)\dots\varphi_{0N}^*(\underline{r}_N) \left[-\sum_{k=1}^{N} \frac{\hbar^2}{2m} \underline{\nabla}_{r_k} + V(\underline{r}_k) \right] \varphi_{01}(\underline{r}_1)\varphi_{02}(\underline{r}_2)\dots\varphi_{0N}(\underline{r}_N) \right\}$$

$$+ \int d^3r_1\, d^3r_2 \dots d^3r_N \left\{ \varphi_{01}^*(\underline{r}_1)\dots\varphi_{0N}^*(\underline{r}_N) \left[\frac{1}{2}\frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k k' \\ k\neq k'}}^{NN} \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} \right] \varphi_{01}(\underline{r}_1)\dots\varphi_{0N}(\underline{r}_N) \right\}$$

$$= \sum_{k=1}^{N} \int d^3r_k\, \varphi_{0k}^*(\underline{r}_k) \left(-\frac{\hbar^2}{2m}\underline{\nabla}_{r_k} + V(\underline{r}_k) \right) \varphi_{0k}(\underline{r}_k)$$

$$+ \frac{1}{2}\frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k k' \\ k\neq k'}}^{NN} \int d^3r_k\, d^3r_{k'}\, \varphi_{0k}^*(\underline{r}_k)\varphi_{0k'}^*(\underline{r}_{k'}) \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} \varphi_{0k}(\underline{r}_k)\varphi_{0k'}(\underline{r}_{k'})$$

Minimize a functional

$$Q(\varphi_{01}, \dots, \varphi_{0N}, \varphi_{01}^*, \dots \varphi_{0N}^*)$$

$$\varphi_{0i}^* \to \varphi_{0i}^* + \delta\varphi_{0i}^* \quad \delta Q = Q(\varphi_{01}, \dots \varphi_{0N}, \varphi_{01}^*, \dots, \varphi_{0i}^* + \delta\varphi_{0i}^*, \dots, \varphi_{0N}^*)$$

$$- Q(\varphi_{01}, \dots, \varphi_{0N}, \varphi_{01}^*, \dots \varphi_{0N}^*)$$

$$= 0$$

$$\left\langle \varphi_{0i} + \delta\varphi_{0i} \right| -\frac{\hbar^2}{2m}\underline{\nabla}^2 + V(\underline{r}) \left| \varphi_{0i} \right\rangle$$

$$+ \sum_{\substack{k=1 \\ k\neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \left\langle (\varphi_{0i} + \delta\varphi_{0i})\varphi_{0k} \right| \frac{1}{|\underline{r}_i - \underline{r}_k|} \left| \varphi_{0i}\varphi_{0k} \right\rangle$$

$\rightarrow \quad Q(\ldots \varphi_{oi} + \delta\varphi_{oi} \ldots) - Q(\ldots \varphi_{oi} \ldots) =$

$$= \langle \delta\varphi_{oi} | -\frac{\hbar}{2m} \underline{\nabla} + V(\underline{r}) | \varphi_{oi} \rangle$$

$$+ \sum_{\substack{k=1 \\ k \neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \delta\varphi_{oi} \varphi_{ok} | \frac{1}{|\underline{r}_i - \underline{r}_k|} | \varphi_{oi} \varphi_{ok} \rangle - \epsilon_{oi} \langle \delta\varphi_{oi} | \varphi_{oi} \rangle$$

$$= 0$$

But $Q[\ldots]$ needs contraint that $\langle \varphi_{oi} | \varphi_{oi} \rangle = 1$.

$$Q[\ldots] = E^{\text{Hartree}}[\varphi_{o1}, \ldots, \varphi_{oN}, \varphi_{o1}^*, \ldots, \varphi_{oN}^*]$$

$$- \sum_{k=1}^{N} \left(\epsilon_{ok} \left(1 - \langle \varphi_{ok} | \varphi_{ok} \rangle \right) \right) = \underline{\min}.$$

$$\left[-\frac{\hbar^2}{2m} \underline{\nabla}^2 + v(\underline{r}) \right] \varphi_{oi}(\underline{r})$$

$$+ \sum_{\substack{k=1 \\ k \neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \underbrace{\langle \varphi_{ok} | \frac{1}{|\underline{r}_k - \underline{r}|} | \varphi_{ok} \rangle}_{\int d^3r_k \, \varphi_{ok}^*(\underline{r}_k) \frac{1}{|\underline{r}_k - \underline{r}|} \varphi_{ok}(\underline{r}_k)} \varphi_{oi}(\underline{r}) = \epsilon_{oi} \varphi_{oi}(\underline{r})$$

contains $\varphi_{ok}^* \varphi_{ok} \longrightarrow$ a density

Rewrite $\left[-\frac{\hbar^2}{2m} \nabla^2 + v(\underline{r}) + v^{\text{Hartree}}(\underline{r}) + v_{oi}^{SIC}(\underline{r}) \right]$

$$\varphi_{oi}(\underline{r}) = \epsilon_{oi} \varphi_{oi}(\underline{r})$$

$$V^{\text{Hartree}}(\underline{r}) = \frac{e^2}{4\pi\epsilon_0}\int d^3r' \frac{n(\underline{r}')}{|\underline{r}-\underline{r}'|}$$

Where $n(\underline{r}) = \langle \underline{\Phi} | \sum_{k=1}^{N} \delta(\underline{r}-\underline{r}_k) | \underline{\Phi} \rangle$ __general__!

$$= \sum_{k=1}^{N} |\varphi_{0k}(\underline{r})|^2$$

$$V^{\text{SIC}}(\underline{r}) = -\frac{e^2}{4\pi\epsilon_0}\int d^3r' \frac{|\varphi_{0i}(\underline{r}')|^2}{|\underline{r}-\underline{r}'|}$$

$$\hat{h}^{\text{Hartree}} = \left\{ -\frac{\hbar^2}{2m}\underline{\nabla}^2 + V_{\text{eff}} \right\}$$

$\Uparrow$

DEPENDS ON
THE SOLUTIONS $\varphi_{0i}(\underline{r})$
themselves!
NON-LINEAR!

$$\begin{tikzcd} \{\varphi_{0i}^{\text{try}}\} \arrow[d, bend left=60, "\text{build } h_{0i}^{\text{try}}"] \\ \{h^{\text{try}}\} \arrow[u, bend left=60, "\text{solve}"] \end{tikzcd}$$

until $\{\varphi_{0i}^{\text{in}}\} = \{\varphi_{0i}^{\text{out}}\}$

"self-consistency"

Self-consistent field method

initial guess → Set up single-part. Eq.

$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}\right\}\varphi_{0i} = \varepsilon_{0i}\varphi_{0i}$

V_{eff} or $n^{ini}(\underline{r})$

↓

Build new $n^{new}(\underline{r})$

↓

new electrostatics $V^{Hartree,new}(\underline{r})$

↓

$\varphi_{0i}^{new}, n^{new}, \varepsilon_{0i}^{new}$ "same" as input?

no → mix old and new

↓

end

e.g. linear mixing

$V^{eff,next} = \alpha V^{eff,new} + (1-\alpha) V^{eff,old}$

Exercise: Variational principle for Hartree-Fock

$$E^{HF} = T[\{\varphi_{0i}\}] + E^{e-io}[\{\varphi_{0i}\}] + E^{Hartree}[\{\varphi_{0i}\}] + E^{x}[\{\varphi_{0i}\}]$$