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

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

And we know when to separate ions

from electrons: $\underline{\Psi}(\{\vec{R}_I\}, \{\vec{r}_k\}) \approx \sum_{\nu} \Lambda_{\nu}(\{\vec{R}_I\}) \bar{\Phi}_{\nu}(\{\vec{r}_k, \vec{r}_k\})$

$$H^e \bar{\Phi}_{\nu}(\{\vec{R}_I\}, \{\vec{r}_k\}) =$$

$$(T^e + V^{e-ion} + V^{e-e}) \bar{\Phi}_{\nu}(\{\vec{R}_I\}, \{\vec{r}_k\})$$

Chapter 2.3 "Jellium"



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

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

$$\bar{\Phi}_{\nu}(\{\vec{r}_k, \sigma_k\}) = \bar{\Phi}_{\nu}(\{\vec{r}_k\}) \cdot \chi(\{\sigma_k\})$$

$$H^e = T^e = \sum_{\mathbf{k}} \frac{\hbar^2}{2m} \cdot \nabla_{\mathbf{k}}^2$$

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

$$\epsilon_j(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (\lambda_{\text{de Broglie}} = \frac{2\pi}{k})$$

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

Base region: Volume $V_g \equiv$ box (L_x, L_y, L_z)

Periodic Boundary Conditions (Born-von Karman)

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

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

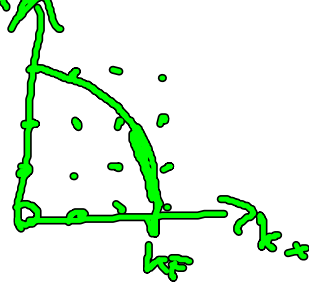
each \mathbf{k} point
has "volume"

$$\frac{(2\pi)^3}{V_g}$$

Jellium, N electrons

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

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



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

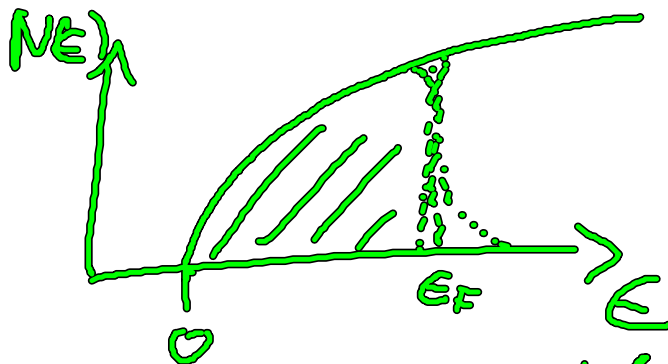
$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3}$$

often $\frac{4}{3}\pi r_s^3 = \frac{V_0}{N} = \frac{1}{n(r)}$

↑
"Density parameter"

Definition: "Density of States" $N(\epsilon)d\epsilon$
 "# of states between $\epsilon, \epsilon+d\epsilon$ "

Exercise → 3D result $N^{3D}(\epsilon) = \frac{m\sqrt{2}}{\pi^2\hbar^3} \sqrt{2m\epsilon}$
 $\epsilon \geq 0$



DOS at Fermi level

$$\frac{N(\epsilon_F)}{V_0} = \frac{m}{\pi^2\hbar^3} \sqrt{2m \frac{\hbar^2}{2m} k_F^2}$$

$\sim k_F$

Chapter 3 Electron-Electron Interaction

Electronic Hamiltonian

$$H^e = \sum_{\mathbf{k} \in \Lambda} \sum_{\sigma} -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_{\mathbf{k}}}^2 + \sum_{\mathbf{k} \in \Lambda} v(\mathbf{r}_{\mathbf{k}})$$

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

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

How to tackle H^e ? (in general)

1. Try to find a good mean-field theory! (following)
2. "The first order": Write down Φ_0 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) parameterised form for $\Phi_0(\{\underline{r}_k\})$

use variational principle: $\frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \text{min.}$
for the ground state

Hartree approximation (1928)

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

Then $H^e = \sum_{k \in \mathbb{N}} h(\underline{r}_k)$

separable.
Oh joy.

More rigorously:

Generally: Use variational principle

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

not = for Hartree

$$\begin{aligned} \underline{\Phi}_v(\{\underline{r}_k\}) &\Rightarrow \underline{\Phi}^{\text{Hartree}}(\dots) \\ &= \varphi_{01}(\underline{r}_1) \cdot \varphi_{02}(\underline{r}_2) \cdot \dots \cdot \varphi_{0n}(\underline{r}_n) \end{aligned}$$

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

spin function: separated off!

But do not forget (i.e. 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 $\langle \underline{\Phi}^{\text{Hartree}} | \underline{\Phi}^{\text{Hartree}} \rangle = 1$

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

$$\langle \underline{\Phi}^{\text{Hartree}} | H^e | \underline{\Phi}^{\text{Hartree}} \rangle = \sum_{\text{Hartree}} E^{\text{Hartree}} [\varphi_{01}, \varphi_{01}, \dots, \varphi_{01}, \varphi_{02}, \dots, \varphi_{0n}]$$

$$\begin{aligned}
&= \int d^3r_1 d^3r_2 \dots d^3r_N \left\{ \varphi_{01}^* \varphi_{02}^* \dots \varphi_{0N}^* (\underline{r}) \left[-\sum_{k=1}^N \frac{\hbar^2}{2m} \nabla_{\underline{r}_k}^2 + V(\underline{r}_k) \right] \right. \\
&\quad \left. \varphi_{01}(\underline{r}_1) \varphi_{02}(\underline{r}_2) \dots \varphi_{0N}(\underline{r}_N) \right\} \\
&+ \int d^3r_1 d^3r_2 \dots d^3r_N \left\{ \varphi_{01}^*(\underline{r}_1) \dots \varphi_{0N}^*(\underline{r}_N) \left[\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k,k'=1 \\ k \neq k'}}^N \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} \right] \right. \\
&\quad \left. \varphi_{01}(\underline{r}_1) \dots \varphi_{0N}(\underline{r}_N) \right\} \\
&= \sum_{k=1}^N \int d^3r_k \varphi_{0k}^*(\underline{r}_k) \left(-\frac{\hbar^2}{2m} \nabla_{\underline{r}_k}^2 + V(\underline{r}_k) \right) \varphi_{0k}(\underline{r}_k) \\
&+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k,k'=1 \\ k \neq k'}}^{NN} \int d^3r_k d^3r_{k'} \varphi_{0k}^*(\underline{r}_k) \varphi_{0k'}^*(\underline{r}_{k'}) \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} \cdot \\
&\quad \varphi_{0k}(\underline{r}_k) \varphi_{0k'}(\underline{r}_{k'})
\end{aligned}$$

Minimize a function

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

$$\begin{aligned}
\overrightarrow{\varphi_{0i}^* + \delta\varphi_{0i}^*} \delta Q &= Q(\varphi_{01}, \dots, \varphi_{0N}, \varphi_{01}^*, \dots, \varphi_{0i}^* + \delta\varphi_{0i}^*, \dots, \varphi_{0N}^*) \\
&\quad - Q(\varphi_{01}, \dots, \varphi_{0N}, \varphi_{01}^*, \dots, \varphi_{0N}^*) \\
&= 0
\end{aligned}$$

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

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

$$\rightarrow Q(\dots \varphi_{0i} + \delta \varphi_{0i} \dots) - Q(\dots \varphi_{0i} \dots) =$$

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

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

But $Q[\dots]$ needs constraint that $\langle \varphi_{0i} | \varphi_{0i} \rangle = 1$

$$Q[\dots] = E^{\text{Hartree}}[\varphi_{01}, \dots, \varphi_{0N}, \varphi_{01}^*, \dots, \varphi_{0N}^*] - \sum_{k=1}^N (\epsilon_{0k} (1 - \langle \varphi_{0k} | \varphi_{0k} \rangle)) = \underline{\text{min.}}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \right] \varphi_{0i}(\underline{r})$$

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

$$\underbrace{\int d\underline{r}_k \varphi_{0k}^*(\underline{r}_k) \frac{1}{|\underline{r}_k - \underline{r}|} \varphi_{0k}(\underline{r}_k)}$$

contains $\varphi_{0k}^* \varphi_{0k} \rightarrow$ a density

Rewrite $\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) + V^{\text{Hartree}}(\underline{r}) + V_{0i}^{\text{SC}}(\underline{r}) \right]$

$$\varphi_{0i}(\underline{r}) = \epsilon_{0i} \varphi_{0i}(\underline{r})$$

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

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

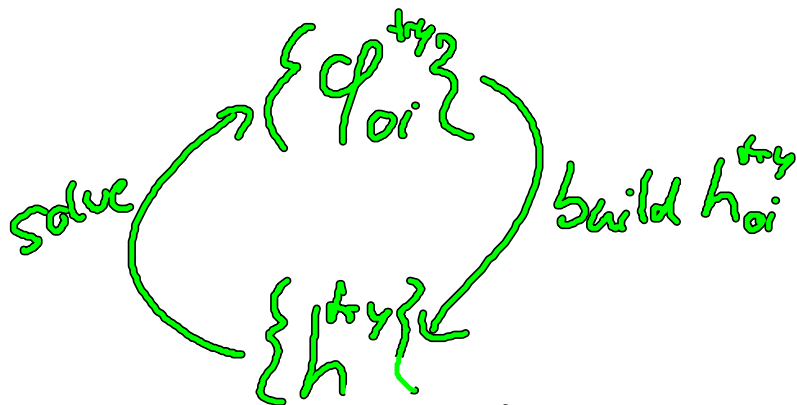
$$= \sum_{k=1}^N |\varphi_{0k}(\underline{r})|^2$$

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

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



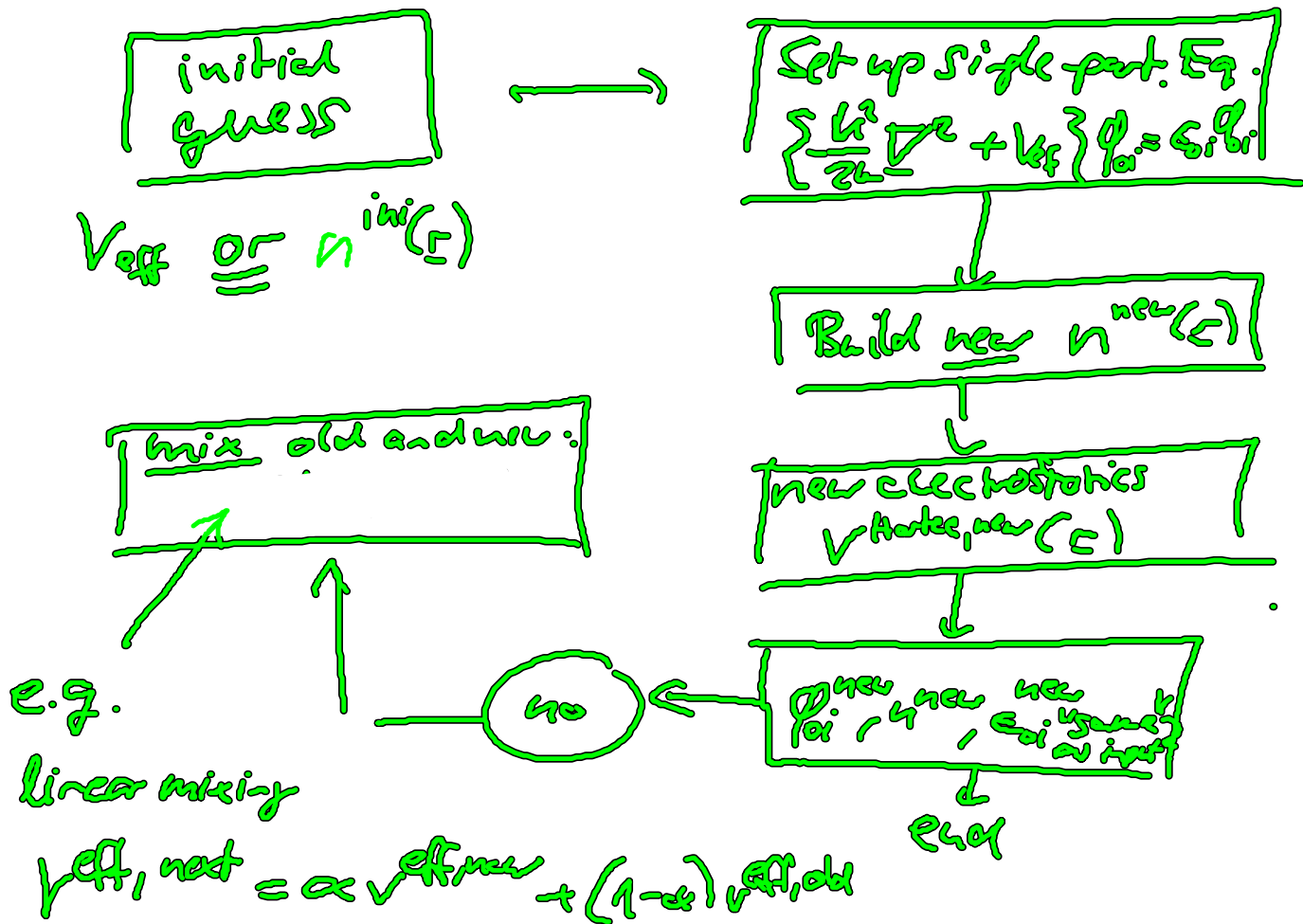
DEPENDS ON
THE SOLUTIONS $\varphi_{0i}(\underline{r})$
THEMSELVES!
NON-LINEAR!



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

"self-consistency"

self-consistent field method



Exercise: Variational principle for
Hartree-Fock

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