3 Electron-Electron Interaction

3.1 Hartree Approximation

$$\Phi^e = \Phi^{\text{Hartree}}(\{\vec{r}_i\}) = \varphi_{o_1}(\vec{r}_1)\,\varphi_{o_2}(\vec{r}_2)\cdots\varphi_{o_N}(\vec{r}_N)$$

what are the best functions $\varphi_{o_i}(\vec{r})$

"best": $\langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle \equiv$ minimum

$$\langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle = \int \varphi^*_{o_1}(\vec{r}_1)\cdots\varphi^*_{o_N}(\vec{r}_N)$$

$$\left[\sum_{k=1}^{N} \frac{-\hbar^2}{2m}\nabla^2_{r_k} + v(\vec{r}_k)\right]\varphi_{o_1}(\vec{r}_1)\cdots\varphi_{o_N}(\vec{r}_N)\,d^3r_1\cdots d^3r_N$$

$$+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\int \varphi^*_{o_1}(\vec{r}_1)\cdots\varphi^*_{o_N}(\vec{r}_N)\sum_{\substack{k,k'=1\\ k\neq k'}}^{N}\frac{1}{|\vec{r}_k-\vec{r}_{k'}|}\varphi_{o_1}(\vec{r}_1)\cdots$$

$$\cdots\varphi_{o_N}(\vec{r}_N)\,d^3r_1\cdots d^3r_N$$

$$= \sum_{k=1}^{N}\int \varphi^*_{o_k}(\vec{r}_k)\left[\frac{-\hbar^2}{2m}\nabla^2_{r_k} + v(\vec{r}_k)\right]\varphi_{o_k}(\vec{r}_k)\,d^3r_k$$

$$+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{k,k'\\ k\neq k'}}\iint \varphi^*_{o_k}(\vec{r}_k)\,\varphi^*_{o_{k'}}(\vec{r}_{k'})$$

$$+\left[\frac{\vec{\quad}}{\vec{r}_k - \vec{r}_{k'}}\right] \varphi_{o_k}(\vec{r}_k)\,\varphi_{o_{k'}}(\vec{r}_{k'})\,d^3\vec{r}_k\,d^3\vec{r}_{k'}$$

$\equiv$ energy functional

$\equiv \tilde{E}^{\text{Hartree}}\left[\varphi_{o_1}, \varphi_{o_2} \cdots \varphi_{o_N}; \varphi_{o_1}^* \varphi_{o_2}^* \cdots \varphi_{o_N}^*\right]$

$\equiv$ side remark

function: number(s) $\longrightarrow$ number

$\varphi(\vec{r})$

e.g. $\sin(x)$

functional: function(s) $\longrightarrow$ number

$\tilde{E}^{\text{Hartree}}$

find the function $\varphi_{o_i}(\vec{r})$ that minimize $\tilde{E}^{\text{Hartree}}$

$$\langle \varphi_{o_i} | \varphi_{o_i} \rangle = 1$$

$\Rightarrow$ new functional

$$Q[\varphi_{o_1} \cdots \varphi_{o_N} \cdots \varphi_{o_N}^*] \equiv E^{Hartree}$$

$$- \sum_{\kappa=1}^{N} \epsilon_{o_\kappa} \left(1 - \langle \varphi_{o_\kappa} | \varphi_{o_\kappa} \rangle \right)$$

$\equiv$ minimum ← should zero

← Lagrange parameter

Min. $\equiv$ change any φ_{o_κ} by $\delta\varphi_{o_\kappa} \equiv$ arbitrary function

$\rightarrow \delta Q \equiv$ zero

$$\delta Q = Q[\varphi_{o_1}^* \cdots \varphi_{o_\kappa}^* + \delta\varphi_{o_\kappa}, \cdots \varphi_{o_N}^*, \varphi_{o_1} \cdots \varphi_{o_N}]$$

$$- Q[\varphi_{o_1}^* \cdots \varphi_{o_\kappa}^* \cdots \varphi_{o_N}^*, \varphi_{o_1} \cdots \varphi_{o_N}]$$

$$\langle \delta\varphi_{o_i} \left| \frac{-\hbar^2}{2m} \nabla^2 + v(r) \right| \varphi_{o_i} \rangle \leftarrow$$

$$- \sum_{\substack{\kappa=1 \\ \kappa \neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \delta\varphi_{o_i} \varphi_{o_\kappa} \left| \frac{1}{|\vec{r}_\kappa - \vec{r}_i|} \right| \cdots$$

$$\times \varphi_{o_i} \varphi_{o_\kappa} \rangle = \epsilon_{o_i} \langle \delta\varphi_{o_i} | \varphi_{o_\kappa} \rangle$$

This must hold for any $\delta\varphi_{o_i}$ & $\delta\varphi_{o_i}^*$ for all $i = 1 \cdots N$.

$$\Rightarrow \left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) + \sum_{\substack{\kappa=1 \\ \kappa \neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \varphi_{o_\kappa} \left| \frac{1}{|\vec{r}_\kappa - \vec{r}_i|} \right| \varphi_{o_i} \rangle \right]$$

$$\hat{h}\,\varphi_{o_i}(\vec{r}) = \epsilon_{o_i}\,\varphi_{o_i}(\vec{r})$$ Hartree eqn.

$$= \left[\frac{-\hbar^2}{2m}\nabla^2 + v^{eff}(\vec{r})\right]\varphi_{o_i}(\vec{r}) = \epsilon_{o_i}(\vec{r})\,\varphi_{o_i}(\vec{r})$$

$$v^{eff}(\vec{r}) = v(\vec{r}) + v^{Hartree}(\vec{r}) + v^{SIC}_{o_i}(\vec{r})$$

$$v^{Hartree}(\vec{r}) = \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d^3\vec{r}'$$

$$v^{SIC}_{o_i} = -\frac{e^2}{4\pi\epsilon_0}\int \frac{|\varphi_{o_i}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\,d^3\vec{r}'$$

SIC self interaction correction

$$n(\vec{r}) = \langle\phi|\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)|\phi\rangle$$

$$\Uparrow \phi^{Hartree} \qquad = \sum_{k=1}^{N}|\varphi_{o_k}(r)|^2$$

Looks like single particle eqn.

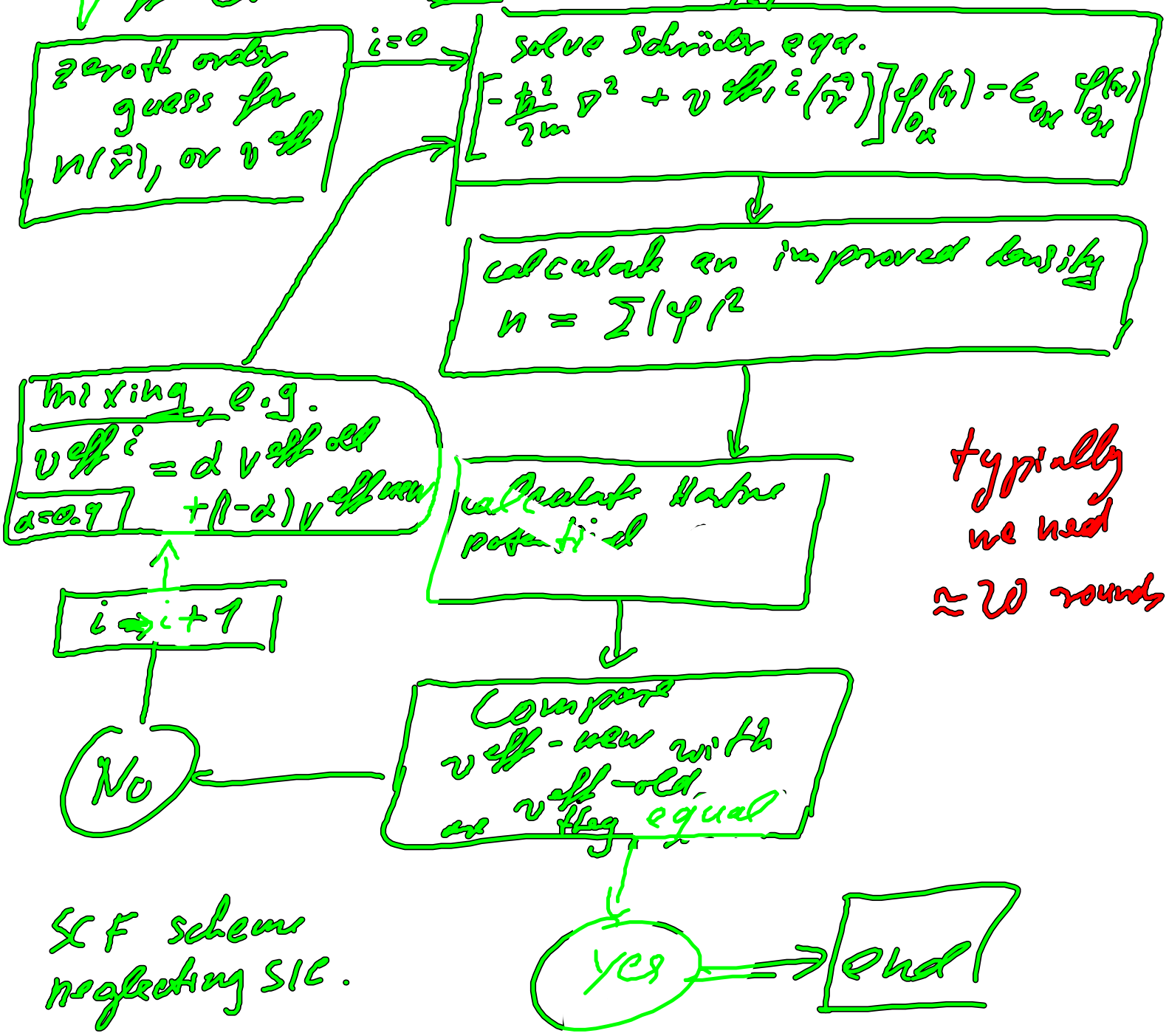
v^{eff} needs all final solutions

total energy is not $\sum_{k=1}^{N}\epsilon_{o_k} = \langle\phi^{Hartree}|\hat{H}|\phi^{Hartree}\rangle$

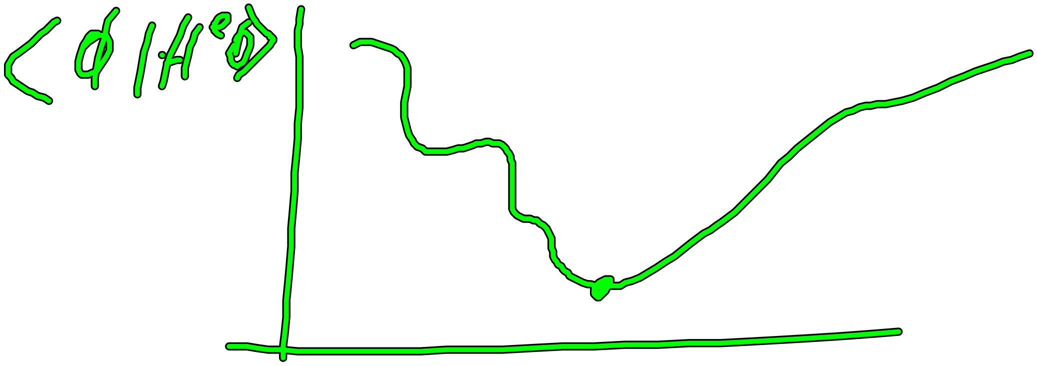
How to find φ_{0i}, how to find v_{eff} ? $\Rightarrow$ self consistent field approach

start with a guess of v_{eff} calculate the solutions, then build an new guess: $n(\vec{r}) = \sum_{I=1}^{M} n_I^{atom}(\vec{r})$

v_{eff} etc.



SCF scheme neglecting SIC.



Hartree did this for many atoms $\approx$ 1930

D. R. Hartree → asked his father.
⇑
W. R. Hartree

3.2. Hartree - Fock approximation

many - electron wavefunction must be antisymm. upon interchanging the coordinates of 2 electrons. = Pauli principle.

$\phi^{Hartree}$ = is symmetric.

Fock

$$\phi^{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{o_1 s_1}(\vec{r}_1, \vec{s}_1) & \cdots & \varphi_{o_N s_N}(\vec{r}_1, \vec{s}_1) \\ \vdots & & \vdots \\ \varphi_{o_1 s_1}(r_N, s_N) & \cdots & \varphi_{o_N s_N}(r_N, s_N) \end{vmatrix}$$

example: 2 electron system, H^-, He

$$\phi^{HF} = \frac{1}{\sqrt{1\cdot 2}} \left[\varphi_1(\vec{r}_1, z_1)\varphi_2(\vec{r}_2, z_2) - \varphi_2(\vec{r}_1, z_1)\varphi_1(\vec{r}_2, z_2) \right]$$

Now analogous to Hartree approach

$$\langle \phi^{HF} | H^e | \phi^{HF} \rangle = E^{HF}\left[\{\varphi_{0_i s_i}(\vec{r})\}, \{\varphi^*_{0_i s_i}(\vec{r})\} \right]$$

$$= T_s[\dots] + E^{e\text{-ion}}[\dots] + E^{Hartree}[\dots] + E^{x}[\dots]$$

x = exchange

$$E^{Hartree} = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0} \iint \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r\, d^3r'$$

$$E^{x} = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0} \sum_{i,j}^{N,N} \delta_{s_i s_j} \iint \frac{\varphi^*_{0_i s_i}(\vec{r})\, \varphi^*_{0_j s_j}(\vec{r}')\, \varphi_{0_i s_i}(\vec{r}')\, \varphi_{0_j s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d^3r\, d^3r'$$

$i - j \equiv$ SIC

E^x = negative $\equiv$ bottle total energy.

.... see exercise $\Longrightarrow$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r}) + v^{Hartree}(\vec{r}) + v_\kappa^x(\vec{r})\right)\varphi_{o_\kappa s_\kappa}(\vec{r}) = \epsilon_{o_\kappa s_\kappa}\varphi_{o_\kappa s_\kappa}(\vec{r})$$

↑ exchange potential

$$v_\kappa^x(\vec{r})\,\varphi_{o_\kappa s_\kappa}(\vec{r}) = \frac{-e^2}{4\pi\varepsilon_0}\sum_{i,j}\delta_{s_i s_j}\int \frac{\varphi_{o_i s_i}(\vec{r}')\,\varphi_{o_\kappa s_\kappa}(\vec{r}')\,\varphi_{o_i s_i}(\vec{r})}{|\vec{r}-\vec{r}'|}\,d^3r'$$

integral operator

Slater (1951) multiply $v_\kappa^x(\vec{r}) \times \dfrac{\varphi_{o_\kappa s_\kappa}(\vec{r})}{\varphi_{o_\kappa s_\kappa}(\vec{r})} = 1$

$$v_\kappa^x(\vec{r}) = \frac{-e^2}{4\pi\varepsilon_0}\int \frac{v^{HF}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\,d^3r'$$

$$v^{HF}(\vec{r},\vec{r}') = \sum_{i=1}^{N}\delta_{s_i s_\kappa}\frac{\varphi^*_{o_i s_i}(\vec{r}')\,\varphi_{o_\kappa s_\kappa}(\vec{r}')\,\varphi_{o_i s_i}(\vec{r})}{\varphi_{o_\kappa s_\kappa}(\vec{r})}$$

Interpretation of v^x, v^{HF} next week