3 Electron-Electron Interaction

3.1 Hartree Approximation

$$\phi^e = \phi^{Hartree}(\{\vec{r}_i\}) =$$
$$= \varphi_{0_1}(\vec{r}_1)\,\varphi_{0_2}(\vec{r}_2)\cdots\varphi_{0_N}(\vec{r}_N)$$

What are the best function $\varphi_{0_i}(\vec{r})$

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

$$\langle \phi^{Hartree} | H^e | \phi^{Hartree} \rangle = \int \varphi^*_{0_1}(\vec{r}_1)\cdots\varphi^*_{0_N}(\vec{r}_N)$$
$$\left[\sum_{k=1}^{N} \frac{-\hbar^2}{2m}\nabla^2_{r_k} + v(\vec{r}_k)\right]\varphi_{0_1}(\vec{r}_1)\cdots\varphi_{0_N}(r_N)\,d^3r_1\cdots d^3r_N$$
$$+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\int \varphi^*_{0_1}(\vec{r}_1)\cdots\varphi^*_{0_N}(\vec{r}_N)\sum_{\substack{k,k'\\k\neq k'}}^{N,N}\frac{1}{|\vec{r}_k-\vec{r}_{k'}|}\varphi_{0_1}(r)\cdots$$

$$\cdots\varphi_{0_N}(\vec{r}_N)\,d^3\vec{r}_1\,d^3\vec{r}_N$$
$$=\sum_{k=1}^{N}\int \varphi^*_{0_k}(\vec{r}_k)\left[\frac{-\hbar^2}{2m}\nabla^2_{r_k}+v(\vec{r}_k)\right]$$
$$\times\,\varphi_{0_k}(\vec{r}_k)\,d^3r_k$$
$$+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{k,k'\\k\neq k'}}\iint \varphi^*_{0_k}(\vec{r}_k)\,\varphi^*_{0_{k'}}(\vec{r}_{k'})$$

$$\times \left[\frac{1}{\vec{r}_k - \vec{r}_{k'}}\right] \varphi_{0k}(\vec{r}_k)\varphi_{0k'}(\vec{r}_{k'})\, d^3\vec{r}_k\, d^3 r_{k'}$$

$\equiv$ energy functional

$$\doteq \tilde{E}^{\text{Hartree}}\left[\varphi_{0_1}, \varphi_{0_2} \cdots \varphi_{0_N}; \varphi^*_{0_1} \varphi^*_{0_2} \cdots \varphi^*_{0_N}\right]$$

= side remark

function: number(s) $\longrightarrow$ number
$\quad\quad\quad\quad\quad\quad\quad\quad$ $\parallel$
$\quad\quad\quad\quad\quad\quad\quad\quad$ $f(\vec{r})$
$\quad\quad\quad\quad\quad$ e.g. $\sin(x)$

functional: function(s) $\longrightarrow$ number
$\quad\quad\quad\quad\quad\quad\quad\quad$ $\parallel$
$\quad\quad\quad\quad\quad\quad\quad\quad$ $\tilde{E}^{\text{Hartree}}$

find the function $\varphi_{0_i}(\vec{r})$ that minimize $\tilde{E}^{\text{Hartree}}$

$$\langle \varphi_{0_i} | \varphi_{0_i} \rangle = 1$$

$\Longrightarrow$ new functional

$$Q[\varphi_{0_1} \cdots \varphi_{0_N} \cdots \varphi^*_{0_N}] = \tilde{E}^{Hartree}$$

$$- \sum_{k=1}^{N} \epsilon_{0_k} \underbrace{\left(1 - \langle \varphi_{0_k} | \varphi_{0_k} \rangle\right)}_{\text{should zero}}$$

$\equiv$ minimum

ϵ_{0_k}: Lagrange parameter

Min. $\equiv$ change any φ_{0_k} by $\delta\varphi_{0_k}$ $\equiv$ arbitrary function

$\longrightarrow \delta Q \equiv$ zero

$$\delta Q = Q[\varphi^*_{0_1} \cdots \varphi^*_{0_k} + \delta\varphi_k, \cdots \varphi^*_{0_N}, \varphi_{0_1} \cdots \varphi_{0_N}]$$

$$- Q[\varphi^*_{0_1} \cdots \varphi^*_{0_k} \cdots \varphi^*_{0_N}, \varphi_{0_1} \cdots \varphi_{0_N}]$$

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

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

$$\times \varphi_{0_i} \varphi_{0_k} \rangle = \epsilon_{0_i} \langle \delta\varphi_{0_i} | \varphi_{0_k} \rangle$$

This must hold for <u>any</u> $\delta\varphi_{0_i}$ & $\delta\varphi^*_{0_i}$ for all $i = 1 \cdots N$.

$$\Longrightarrow \left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) + \sum_{\substack{k=1 \\ k \neq i}}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \varphi_{0_k} \left| \frac{1}{|\vec{r}_k - \vec{r}_i|} \right| \varphi_{0_i} \rangle \right]$$

$$\times \varphi_{0_i}(\vec{r}) = \epsilon_{0_i}\, \varphi_{0_i}(\vec{r})$$ Hartree equ.

$$= \boxed{\left[\frac{-\hbar^2}{2m}\nabla^2 + v^{eff}(\vec{r})\right]\varphi_{0_i}(\vec{r}) = \epsilon_{0_i}(\vec{r})\varphi_{0_i}(\vec{r})}$$

$$v^{eff}(\vec{r}) = v(\vec{r}) + v^{Hartree}(\vec{r}) + v^{SIC}_{0_i}(\vec{r})$$

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

$$v^{SIC}_{0_i} = -\frac{e^2}{4\pi\epsilon}\int \frac{|\varphi_{0_i}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\, d^3\vec{r}\,'$$

SIC self interaction correction

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

$$\underset{\uparrow \phi^{Hartree}}{\equiv} \quad = \sum_{k=1}^{N} |\varphi_{0_k}(r)|^2$$

<u>looks</u> like single particle equ.

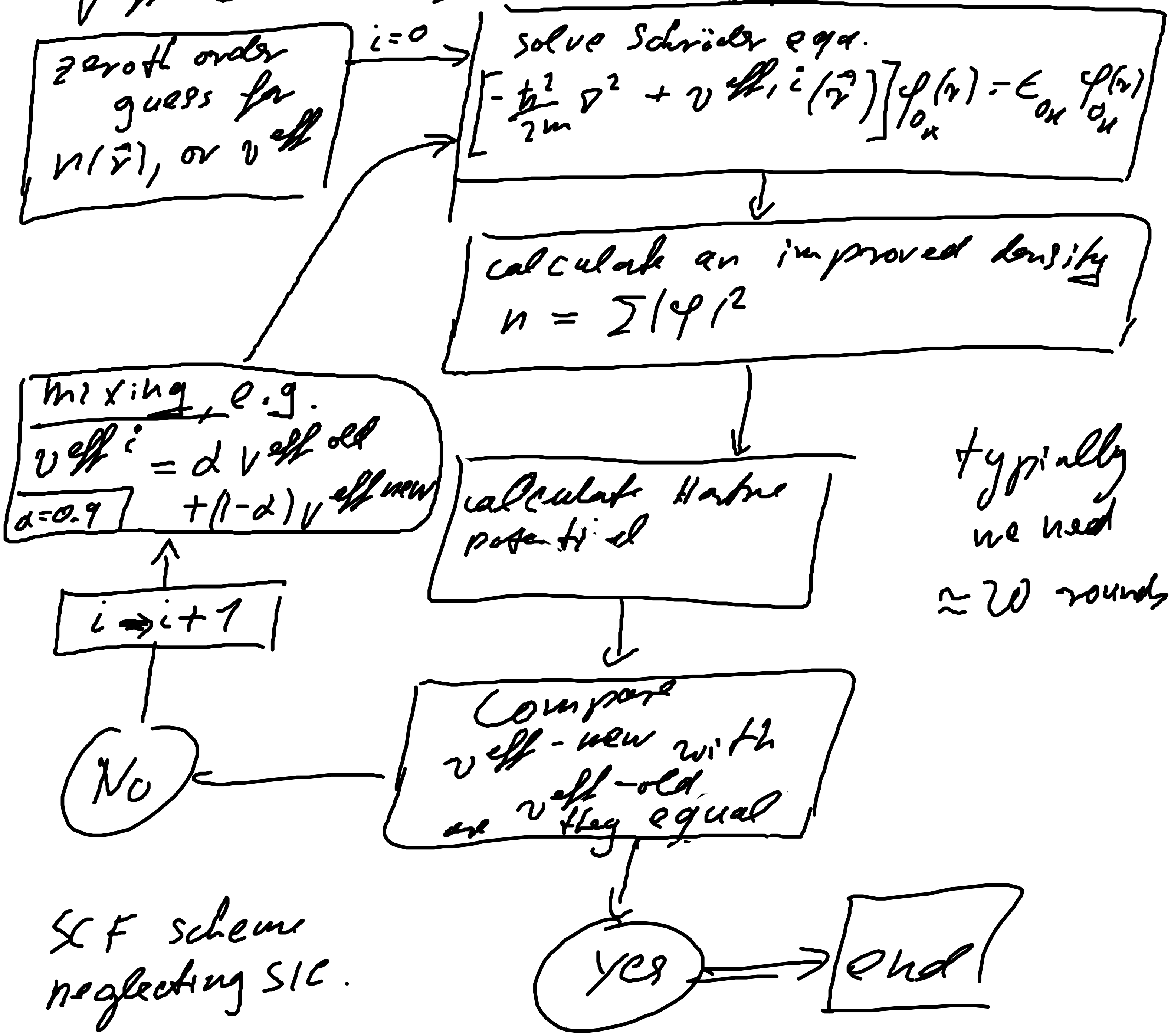
v^{eff} needs the final solutions

<u>total</u> energy is <u>not</u> $\sum_{k=1}^{N} \epsilon_{0_k} \equiv \langle \phi^{Hartree} | H | \phi^{Hartree} \rangle$

How to find φ_{0i}, how to find v^{eff} ? $\Longrightarrow$ self consistent field approach

start with a guess of v^{eff}
calculate the solutions, then build a new v^{eff} etc.

guess : $n(\vec{r}) = \sum_{I=1}^{M} n_I^{atom}(\vec{r})$



typically we need ≈ 20 rounds

SCF scheme neglecting SIC.

Hartree did this for many atoms
$\approx$ 1930

D. R. Hartree $\rightarrow$ asked his father.
$\Uparrow$
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

$$\Phi^{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{o_1 s_1}(\vec{r}_1, \sigma_1) & \cdots & \varphi_{o_N s_N}(\vec{r}_1, \sigma_1) \\ \vdots & & \vdots \\ \varphi_{o_1 s_1}(r_N, \sigma_N) & \cdots & \varphi_{o_N s_N}(r_N, \sigma_N) \end{vmatrix}$$

example: 2 electron system, H^-, He

$$\phi^{HF} = \frac{1}{\sqrt{1\cdot 2}} \Big[\varphi_1(\vec{r}_1 \sigma_1)\, \varphi_2(\vec{r}_2 \sigma_2) - \varphi_2(r_1 \sigma_1)\, \varphi_1(\vec{r}_2 \sigma_2) \Big]$$

Now analogous to Hartree approach

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

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

x = exchange

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

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

$i = j \equiv SIC$

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

... see exercise $\Longrightarrow$

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r}) + v^{Hartree}(\vec{r}) + v_k^x(\vec{r})\right)\varphi_{o_k s_k}(\vec{r}) = \epsilon_{o_k s_k}\varphi_{o_k s_k}(\vec{r})}$$

exchange potential

$$v_k^x(\vec{r})\varphi_{o_k s_k}(r) = \frac{-e^2}{4\pi\epsilon_0}\sum_{i,j}\delta_{s_i s_j}\int\frac{\varphi_{o_i s_i}(\vec{r}')\varphi_{o_k s_k}(r')\varphi_{o_i s_i}(r)}{|\vec{r}-\vec{r}'|}d^3r'$$

integral operator

Slater (1951) multiply $v_x^k(\vec{r}) \times \frac{\varphi_{o_k s_k}(\vec{r})}{\varphi_{o_k s_k}(\vec{r})} = 1$

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

$$n^{HF}(\vec{r},\vec{r}') = \sum_{i=1}^{N}\delta_{s_i s_k}\frac{\varphi^*_{o_i s_i}(\vec{r}')\varphi_{o_k s_k}(r')\varphi_{o_i s_i}(r)}{\varphi_{o_k s_k}(\vec{r})}$$

Interpretation of

v^x, n^{HF} next week