Selfconsistent field

Interaction energy of two charges depends on their distance $|\vec{r}_1 - \vec{r}_2|$:

$$W(|\vec{r}_1 - \vec{r}_2|) = \frac{q_1 q_2}{|\vec{r}_1 - \vec{r}_2|}$$

The two charges are an electron and a little volume dV at $\vec{r}_2$ containing charge cloud of density ρ

$$q_1 \to (-e) \qquad q_2 \to \rho(\vec{r}_2)dV \qquad \to \quad \rho(\vec{r}_2)d^3r_2$$

and the interaction energy of these two charges is

$$dW(|\vec{r}_1 - \vec{r}_2|) = \frac{(-e)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d^3r_2$$

and summing over all the small volume elements means integrating over the whole volume of the cloud gives the potential energy due to the interaction with a cloud

$$W(\vec{r}) = \int \frac{(-e)\rho(\vec{x})}{|\vec{r} - \vec{x}|}\, d^3x$$

If the charge cloud represents one electron in state $\psi_i(\vec{x})$

$$\rho(\vec{x}) = (-e)|\psi_i(\vec{x})|^2$$

If we have N electrons, each in its state, the total density becomes

$$\rho(\vec{x}) = (-e)\sum_{i=1}^{N} |\psi_i(\vec{x})|^2$$

and again integrating over the whole volume of the cloud gives the potential energy due to the interaction with a (probability based density) cloud of electrons

$$W(\vec{r}) = \int \frac{(-e)^2 \sum_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|}\, d^3x$$

Now solving the Schrödinger equation with $W(\vec{r})$,

$$(T + V + W)\,\psi_i(\vec{x}) = E_i \psi_i(\vec{x})$$

We first need to know the $W(\vec{r})$, but that depends on all the other N solutions

$$W(\vec{r}) = \int \frac{(-e)^2 \sum_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|}\, d^3x$$

We thus start an approximation chain. First we choose some simple approximation, e.g. the hydrogen-like states, or we might know the states foranother atom. We call it

$$\psi_i^{(0)}(\vec{x})$$

From the set of all N $\psi_i^{(0)}$ we construct

$$W^{(1)}(\vec{r}) = \int \frac{e^2 \sum_{i=1}^{N} |\psi_i^{(0)}(\vec{x})|^2}{|\vec{r} - \vec{x}|}\, d^3x$$

In atomic units the whole Schrödinger equation is

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(1)}(\vec{r})\right)\psi_i^{(1)}(\vec{x}) = E_i^{(1)}\psi_i^{(1)}(\vec{x})$$

Now we show the chain in steps: first step

$$\psi_i^{(0)}(\vec{x}) \qquad \rightarrow \qquad W^{(1)}(\vec{r}) = \int \frac{\sum_{i=1}^{N} |\psi_i^{(0)}(\vec{x})|^2}{|\vec{r}-\vec{x}|}\, d^3x$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(1)}(\vec{r})\right)\psi_i^{(1)}(\vec{x}) = E_i^{(1)}\psi_i^{(1)}(\vec{x})$$

Second step

$$\psi_i^{(1)}(\vec{x}) \qquad \rightarrow \qquad W^{(2)}(\vec{r}) = \int \frac{\sum_{i=1}^{N} |\psi_i^{(1)}(\vec{x})|^2}{|\vec{r}-\vec{x}|}\, d^3x$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(2)}(\vec{r})\right)\psi_i^{(2)}(\vec{x}) = E_i^{(2)}\psi_i^{(2)}(\vec{x})$$

Third step

$$\psi_i^{(2)}(\vec{x}) \qquad \rightarrow \qquad W^{(3)}(\vec{r}) = \int \frac{\sum_{i=1}^{N} |\psi_i^{(2)}(\vec{x})|^2}{|\vec{r}-\vec{x}|}\, d^3x$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(3)}(\vec{r})\right)\psi_i^{(3)}(\vec{x}) = E_i^{(3)}\psi_i^{(3)}(\vec{x})$$

This chain can continue, until the set of $\psi_i^{(n)}$ produces a potential $W^{(n+1)}$ which is the same as $W^{(n)}$, which was the one to determine $\psi_i^{(n)}$. The potentials and functions become consistent, hence the name *Selfconsistent field*.

Criterium for self-consistency: the (n+1)-th solution does not differ from th n-th solution

$$\int \sum_{i=1}^{N} \left| \; |\psi_i^{(n+1)}(\vec{x})|^2 \; - \; |\psi_i^{(n)}(\vec{x})|^2 \; \right| d^3x \quad < \epsilon$$

where $\epsilon \;\propto\; 10^{-8}$

The total energy of N electrons and connection to Hartree-Fock theory

Please, correct and fill in the text as excercise

Is the energy of N-electrons approximately equal to the sum of energies from the above solutions?

$$\sum_{i=1}^{N} (E_i) \approx E?$$

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i}\right) + \sum_{(i,j)pairs} \frac{1}{|\vec{r}-\vec{x}|}\right]\Phi\left(r_1, r_2, ...r_N\right) = E\Phi\left(r_1, r_2, ...r_N\right)$$

$$\Phi\left(r_1, r_2, ...r_N\right) \approx \psi_1(r_1)\psi_2(r_2)......\psi_N(r_N)$$

$$\sum_{i=1}^{N}\left(E_i\right) \approx E?$$

$$\sum_{j=1}^{N}\left(E_j\right) \propto \sum_{j=1}^{N}\int \psi_j^*(\vec{y})\left(\int \frac{e^2\sum\limits_{i=1}^{N}|\psi_i(\vec{x})|^2 d^3x}{|\vec{y}-\vec{x}|}\right)\psi_j(\vec{y})d^3y$$

$$\sum_{(i,j)pairs}\int \psi_j^*(\vec{y})\left(\int \frac{e^2\sum\limits_{i=1}^{N}|\psi_i(\vec{x})|^2 d^3x}{|\vec{y}-\vec{x}|}\right)\psi_j(\vec{y})d^3y$$

$$\sum_{(i,j)pairs} f(r_j, r_i) = \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1, i\neq j}^{N} f(r_j, r_i)$$

$$E \approx \sum_{i=1}^{N}\left(E_i\right) - \sum_{(i,j)pairs}\int \psi_j^*(\vec{y})\left(\int \frac{e^2\sum\limits_{i=1}^{N}|\psi_i(\vec{x})|^2 d^3x}{|\vec{y}-\vec{x}|}\right)\psi_j(\vec{y})d^3y$$

$$\Phi^{HF}_{a,b,...N}\left(r_1, r_2, ...r_N\right) \rightarrow \left| \begin{array}{l} \psi_a(r_1)\psi_b(r_1)......\psi_N(r_1) \\ \psi_a(r_2)\psi_b(r_2)......\psi_N(r_2) \\ .... \\ \psi_a(r_N)\psi_b(r_N)......\psi_N(r_N) \end{array} \right|$$

$$\left\langle \psi_a\psi_b \left| \frac{1}{|\vec{r}-\vec{x}|} \right| \psi_a\psi_b \right\rangle \rightarrow$$
$$\left\langle \psi_a\psi_b \left| \frac{1}{|\vec{r}-\vec{x}|} \right| \psi_a\psi_b \right\rangle - \left\langle \psi_a\psi_b \left| \frac{1}{|\vec{r}-\vec{x}|} \right| \psi_b\psi_a \right\rangle$$

$$\langle a, b\,|f(r_1, r_2)|\,a, b\rangle \rightarrow \langle a, b\,|f(r_1, r_2)|\,a, b\rangle - \langle a, b\,|f(r_1, r_2)|\,b, a\rangle$$