Lecture XI

Solving the electronic eigenvalue problem: In the Born-Oppenheimer approximation, the electronic eigenvalue problem takes the form.

$$[T_e + V_{ee} + V_{en}]\psi(\boldsymbol{x},\boldsymbol{R}) = \varepsilon(\boldsymbol{r})\psi(\boldsymbol{x},\boldsymbol{R})$$

$$V_{ee} = \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$V_{eN} = \sum_{i=1}^{M}\sum_{J=1}^{N} \frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{R}_I|}$$

$$\text{Let } V_{ext}(\mathbf{r}) = -\sum_{I=1}^{N} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

$$V_{eN} = \sum_{i=1}^{M} V_{ext}(\boldsymbol{r}_i)$$

where $\boldsymbol{x}$ denotes the electronic coordinates, and $\boldsymbol{R}$ denotes the nuclear coordinates.

Crudest approximation. Assume the equation is separable and that the electrons are distinguishable. Then, we would take a product form for the solution:

$$\psi(\boldsymbol{x}_1,\boldsymbol{R}) = \varphi_1(\boldsymbol{x}_1,\boldsymbol{R})\varphi_2(\boldsymbol{x}_2,\boldsymbol{R})\cdots\varphi_M(\boldsymbol{x}_M,\boldsymbol{R})$$

$$= \varphi_{\alpha_1}(\boldsymbol{x}_1,\boldsymbol{R})\varphi_{\alpha_2}(\boldsymbol{x}_2,\boldsymbol{R})\cdots\varphi_{\alpha_M}(\boldsymbol{x}_M,\boldsymbol{R})$$

$$= \prod_{k=1}^{M} \varphi_k(\boldsymbol{x}_k,\boldsymbol{R})$$

From here on out, the $\boldsymbol{R}$ dependence will be largely suppressed, although it should be remembered that this dependence is, nevertheless, there.

Note, also, that we are denoting the quantum numbers α_k simply by k for notational convenience and simplicity.

If $V_{ee} = 0$, this would be exact for distinguishable electrons.

The functions $\varphi_k\left(\mathbf{x}_k,\mathbf{R}\right)$, also referred to as orbitals, are required to be orthonormal to each other:

$$\sum_M \int d\boldsymbol{r}\varphi_k^*(\boldsymbol{x})\varphi_{k'}(\boldsymbol{x}) = \int d\boldsymbol{x}\varphi_k^*(\boldsymbol{x})\varphi_{k'}(\boldsymbol{x}) = \delta_{kk'}$$

Note, that, in this approximation, the total energy is simply a sum:

$$\varepsilon(\boldsymbol{R}) = \varepsilon_1(\boldsymbol{R}) + \varepsilon_2(\boldsymbol{R}) + \cdots + \varepsilon_M(\boldsymbol{R})$$

$$= \sum_{k=1}^{M} \varepsilon_k(\boldsymbol{R})$$

The functions would satisfy

$$\left[-\frac{1}{2}\nabla_k^2 + V_{ext}(\boldsymbol{r}_k)\right]\varphi_{\alpha_k}(\boldsymbol{x}_k) = \varepsilon_{\alpha_k}\varphi_{\alpha_k}(\boldsymbol{x}_k)$$

But since $V_{ee} \neq 0$, these solutions are not solutions of the full electronic structure problem. However, we **can** try to optimize the functions so as to give us the best approximate solution in a variational sense.

Let

$$E[\psi,\mathbf{R}] = \langle\psi(\mathbf{R})|H_e(\mathbf{R})|\psi(\mathbf{R})\rangle$$

$$\Rightarrow E[\{\varphi\},\boldsymbol{R}] = \int d\boldsymbol{x}_1\cdots d\boldsymbol{x}_M \varphi_1^*(\boldsymbol{x}_1)\cdots\varphi_M^*(\boldsymbol{x}_M)[T_e + V_{ee} + V_{eN}]\varphi_1(\boldsymbol{x}_1)\cdots\varphi_M(\boldsymbol{x}_M)$$

$$= \int d\boldsymbol{x}_1\cdots d\boldsymbol{x}_M \prod_{k=1}^{M}\varphi_k^*(\boldsymbol{x}_k)[T_e + V_{eN}]\prod_{k=1}^{M}\varphi_k(\boldsymbol{x}_k)$$

$$+\frac{1}{2}\int d\boldsymbol{x}_1\cdots d\boldsymbol{x}_M \prod_{k=1}^{M}\varphi_k^*(\boldsymbol{x}_k)\sum_{\substack{i,j\\ i\neq j}}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\prod_{k=1}^{M}\varphi_k(\boldsymbol{x}_k)$$

The first term in this expression is:

$$\int d\boldsymbol{x}\cdots d\boldsymbol{x}_M \prod_{k=1}^{M}\varphi_k^*(\boldsymbol{x}_k)[T_e + V_{eN}]\prod_{k=1}^{M}\varphi_k(\boldsymbol{x}_k)$$

$$= \int d\boldsymbol{x} \cdots d\boldsymbol{x}_M \prod_{k=1}^{M} \varphi_k^*(\boldsymbol{x}_k) \sum_{i=1}^{M} \left[-\frac{1}{2}\nabla_i^2 + V_{ext}(\boldsymbol{r}_i) \right] \prod_{k=1}^{M} \varphi_k(\boldsymbol{x}_k)$$

$$= \int d\boldsymbol{x}_1 \varphi_1^*(\boldsymbol{x}_1) \left[-\frac{1}{2}\nabla_1^2 + V_{ext}(\boldsymbol{r}_1) \right] \varphi_1(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \varphi_2^*(\boldsymbol{x}_2) \varphi_2 \boldsymbol{x}_2 \cdots \int d\boldsymbol{x}_M \varphi_M^*(\boldsymbol{x}_M) \varphi_M \boldsymbol{x}_M$$

$$+ \int d\boldsymbol{x}_1 \varphi_1^*(\boldsymbol{x}_1) \varphi_1(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \varphi_2^*(\boldsymbol{x}_2) \left[-\frac{1}{2}\nabla_2^2 + V_{ext}(\boldsymbol{r}_1) \right] \varphi_2(\boldsymbol{x}_2) \cdots \int d\boldsymbol{x}_M \varphi_M^*(\boldsymbol{x}_M) \varphi_M \boldsymbol{x}_M$$

$$+ \cdots + \int d\boldsymbol{x}_1 \varphi_1^*(\boldsymbol{x}_1) \varphi_1(\boldsymbol{x}_1) \cdots \int d\boldsymbol{x}_M \varphi_M^*(\boldsymbol{x}_M) \left[-\frac{1}{2}\nabla_M^2 + V_{ext}(\boldsymbol{r}_M) \right] \varphi_M \boldsymbol{x}_M$$

$$= \sum_{k=1}^{M} \int d\boldsymbol{x}_k \varphi_k^*(\boldsymbol{x}_k) h(\boldsymbol{r}_k) \varphi_k(\boldsymbol{x}_k)$$

$$h(\boldsymbol{r}_k) = -\frac{1}{2}\nabla_k^2 + V_{ext}(\boldsymbol{r}_k)$$

$$\Rightarrow \sum_{k=1}^{M} \langle \varphi_k | h(\boldsymbol{r}) | \varphi_k \rangle$$

Second term:

$$\frac{1}{2} \int d\boldsymbol{x}_1 \cdots d\boldsymbol{x}_M \prod_{k=1}^{M} \varphi_k^*(\boldsymbol{x}_k) \sum_{i,j}{}' \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \prod_{k=1}^{M} \varphi_k(\boldsymbol{x}_k)$$

$$= \frac{1}{2} \sum_{k,l}{}' \int d\boldsymbol{x}_k d\boldsymbol{x}_l \varphi_k^*(\boldsymbol{x}_k) \varphi_l^*(\boldsymbol{x}_l) \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l|} \varphi_k(\boldsymbol{x}_k) \varphi_l(\boldsymbol{x}_l)$$

$$= \frac{1}{2} \sum_{k,l}{}' \langle \varphi_k \varphi_l | \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l|} | \varphi_k \varphi_l \rangle$$

$$E[\{\varphi\}, \boldsymbol{R}] = \sum_{k=1}^{M} \langle \varphi_k | h(\boldsymbol{r}_k) | \varphi_k \rangle + \frac{1}{2} \sum_{k,l}{}' \langle \varphi_k \varphi_l | \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l|} | \varphi_k \varphi_l \rangle$$

Now, we variationally optimize the functions $\varphi_k(\boldsymbol{x}_k)$
In principle, we should solve

$$\frac{\partial E}{\partial \langle \varphi_k |} = 0$$

However, we need to ensure $\langle \varphi_k | \varphi_k \rangle = 1$, a condition we need to include via Lagrange multipliers:

$$\frac{\partial}{\partial \langle \varphi_k |} \left\{ E\left[\{\varphi\}, \mathbf{R}\right] - \sum_i \lambda_i \left(\langle \varphi_i | \varphi_i \rangle - 1 \right) \right\} = 0$$

$$\frac{\partial}{\partial \langle \varphi_k |} \left[\sum_i \langle \varphi_i | h(\mathbf{r}_i) | \varphi_j \rangle + \frac{1}{2} \sum_{i,j}{}' \langle \varphi_i \varphi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \varphi_i \varphi_j \rangle - \sum_i \lambda_i \langle \varphi_i | \varphi_i \rangle - 1 \right] = 0$$

$$\left[-\frac{1}{2} \nabla^2 + \sum_{\ell \neq j} \int d\boldsymbol{x}' \frac{|\varphi_\ell(\boldsymbol{x}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + V_{ext}(\boldsymbol{r}) \right] \varphi_j(\boldsymbol{r}) = \lambda_j \varphi_j(\boldsymbol{r})$$

called the *Hartree equation*.

When we treat the electrons as indistinguishable, we cannot use the product form. Rather, we take

$$\psi(\boldsymbol{x}, \boldsymbol{R}) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \varphi_1(\boldsymbol{x}_1) & \cdots & \varphi_1(\boldsymbol{x}_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(\boldsymbol{x}_1) & \cdots & \varphi_N(\boldsymbol{x}_N) \end{pmatrix}$$

Again, we need to compute $E[\{\varphi\}, \boldsymbol{R}] = \langle \psi | H_e | \psi \rangle$.

We find:

$$E[\{\varphi\}, \boldsymbol{R}] = \langle \psi | H_e | \psi \rangle \sum_{k=1}^{N} \langle \varphi_k | h | \varphi_h \rangle + \frac{1}{2} \sum_{k,\ell} \langle \varphi_k \varphi_\ell | \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_\ell|} | \varphi_k \varphi_\ell \rangle - \frac{1}{2} \sum_{k,\ell} \langle \varphi_k \varphi_\ell | \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_\ell|} | \varphi_\ell \varphi_k \rangle$$

Note the sums are **not** restricted. The first two-body integral gives

$$\sum_{k,\ell} \langle \varphi_k \varphi_\ell | \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_\ell|} | \varphi_k \varphi_\ell \rangle = \sum_{k,\ell} \int d\boldsymbol{x} d\boldsymbol{x}' \frac{\varphi_k^*(\boldsymbol{x}) \varphi_\ell^*(\boldsymbol{x}') \varphi_k(\boldsymbol{x}) \varphi_\ell(\boldsymbol{x}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

$$= \sum_{k,\ell} \int d\boldsymbol{x} d\boldsymbol{x}' \frac{|\varphi_k(\boldsymbol{x})|^2 |\varphi_\ell(\boldsymbol{x}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

$$= \sum_{k,\ell} J_{k\ell}$$

$J_{k\ell}$ is called the *Coulomb integral*. Note the change in the names of the integration variables. Since these are just integration variables, they can be called whatever we like.

$$\sum_{k,\ell}\left\langle\varphi_k\varphi_\ell\left|\frac{1}{\left|\boldsymbol{r}_k-\boldsymbol{r}_\ell\right|}\right|\varphi_k\varphi_\ell\right\rangle=\sum_{k,\ell}\int d\boldsymbol{x}d\boldsymbol{x}'\frac{\varphi_k^*(\boldsymbol{x})\varphi_\ell^*(\boldsymbol{x}')\varphi_\ell(\boldsymbol{x})\varphi_k(\boldsymbol{x}')}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}$$

$$=\sum_{k,\ell}K_{k\ell}$$

$K_{k\ell}$ is called the *exchange integral*.

Unitary invariance: Consider a transformation to a new set of orbitals

$$\left|\psi_i\right\rangle=\sum_j U_{ij}\left|\varphi_j\right\rangle$$

where U_{ij} is a unitary matrix.

$$\left|\varphi_j\right\rangle=\sum_i U_{ji}^\dagger\left|\psi_i\right\rangle=\sum_i\left|\psi_i\right\rangle U_{ij}^*$$

$$\sum_k\left\langle\varphi_k\left|h\right|\varphi_k\right\rangle=\sum_k\sum_i\sum_j U_{ki}\left\langle\psi_i\left|h\right|\psi_j\right\rangle U_{jk}^*$$

$$=\sum_{i,j}\sum_k U_{jk}^*U_{ki}\left\langle\psi_i\left|h\right|\psi_j\right\rangle$$

$$=\sum_{i,j}\delta_{ji}\left\langle\psi_i\left|h\right|\psi_j\right\rangle$$

$$=\sum_i\left\langle\psi_i\left|h\right|\psi_i\right\rangle$$

Coulomb integral:

$$\frac{e^2}{2}\sum_{k,\ell}\int d\mathbf{x}_1\,d\mathbf{x}_2\frac{\left|\varphi_k(\mathbf{x}_1)\right|^2\left|\varphi_\ell(\mathbf{x}_2)\right|^2}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}$$

Note

$$\sum_k |\varphi_k(\boldsymbol{x}_1)|^2 = \sum_k \varphi_k^*(\boldsymbol{x}_1)\varphi_k(\boldsymbol{x}_1)$$

$$= \sum_k \sum_{i,j} U_{ki}\psi_i^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_1)U_{jk}^*$$

$$= \sum_{i,j} \psi_i^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_1)\sum_k U_{jk}^* U_{ki}$$

$$= \sum_{i,j} \psi_i^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_1)\delta_{jk}$$

$$= \sum_i |\psi_i(\boldsymbol{x}_1)|^2$$

$$\Rightarrow \frac{e^2}{2}\sum_{k,\ell}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{|\varphi_k(\boldsymbol{x}_1)|^2|\varphi_\ell(\boldsymbol{x}_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{e^2}{2}\sum_{i,j}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{|\psi_i(\boldsymbol{x}_1)|^2|\psi_j(\boldsymbol{x}_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

Exchange integral:

$$\frac{e^2}{2}\sum_{k,\ell}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{\varphi_k^*(\boldsymbol{x}_1)\varphi_k(\boldsymbol{x}_2)\varphi_\ell^*(\boldsymbol{x}_2)\varphi_\ell(\boldsymbol{x}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

Note

$$\sum_k \varphi_k^*(\boldsymbol{x}_1)\varphi_k(\boldsymbol{x}_2) = \sum_k \sum_{i,j} U_{ki}\psi_i^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_2)U_{jk}^*$$

$$= \sum_{i,j} \psi_i^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_2)\sum_k U_{jk}^* U_{ki}$$

$$= \sum_i \psi_i^*(\boldsymbol{x}_1)\psi_i(\boldsymbol{x}_2)$$

Thus,

$$\frac{e^2}{2}\sum_{k,\ell}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{\varphi_k^*(\boldsymbol{x}_1)\varphi_k(\boldsymbol{x}_2)\varphi_\ell^*(\boldsymbol{x}_2)\varphi_\ell(\boldsymbol{x}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{e^2}{2}\sum_{i,j}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{\psi_i^*(\boldsymbol{x}_1)\psi_i(\boldsymbol{x}_2)\psi_j^*(\boldsymbol{x}_2)\psi_j(\boldsymbol{x}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

Thus, total energy is invariant!

Choose U so as to diagonalize λ. Let ε_j be the eigenvalues. Then, we obtain,

$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2+V_{ext}\left(\mathbf{r}\right)+e^2\sum_\ell\int d\mathbf{x}'\frac{\left|\psi_\ell\left(\mathbf{x}'\right)\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|}\right]\psi_j\left(\mathbf{x}\right)-e^2\sum_\ell\int d\mathbf{x}'\frac{\psi_\ell^*\left(\mathbf{x}'\right)\psi_j\left(\mathbf{x}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}\psi_\ell\left(\mathbf{x}\right)=\varepsilon_j\psi_j\left(\mathbf{x}\right)$$

which is known as the *Hartree-Fock* equation.

Koopman's Theorem (Meaning of ε_i)

Consider removing i^{th} electron from the system. The wave function can be constructed by starting with a Slater determinant for the *M*-electron system and crossing out the i^{th} row and column.

$$\psi'\left(\boldsymbol{x}_1\cdots\boldsymbol{x}_{i-1},\boldsymbol{x}_{i+1}\cdots\boldsymbol{x}_M\boldsymbol{R}\right)=\frac{1}{\sqrt{N!}}\det\begin{pmatrix}\varphi_1\left(\boldsymbol{x}_1\right) & \cdots & \varphi_1\left(\boldsymbol{x}_i\right) & \cdots & \varphi_1\left(\boldsymbol{x}_N\right)\\ \vdots & \ddots & & & \vdots\\ \varphi_i\left(\boldsymbol{x}_1\right) & \cdots & \varphi_i\left(\boldsymbol{x}_i\right) & \cdots & \varphi_i\left(\boldsymbol{x}_N\right)\\ \vdots & & \vdots & \ddots & \vdots\\ \varphi_N\left(\boldsymbol{x}_1\right) & \cdots & \varphi_N\left(\boldsymbol{x}_i\right) & \cdots & \varphi_N\left(\boldsymbol{x}_N\right)\end{pmatrix}$$

The change in energy between the *M*-electron system and the (*M*-*1*)-electron system is:

$$\Delta E=\left\langle\psi'\left(\boldsymbol{R}\right)\right|H_e\left(\boldsymbol{R}\right)\left|\psi'\left(\boldsymbol{R}\right)\right\rangle-\left\langle\psi\left(\boldsymbol{R}\right)\right|H_e\left(\boldsymbol{R}\right)\left|\psi\left(\boldsymbol{R}\right)\right\rangle$$

$$\Delta E=-\int d\boldsymbol{x}\varphi_i^*\left(\boldsymbol{x}\right)h\varphi_i\left(\boldsymbol{x}\right)-\sum_k\int d\boldsymbol{x}d\boldsymbol{x}'\frac{\left|\varphi_i\left(\boldsymbol{x}\right)\right|^2\left|\varphi_k\left(\boldsymbol{x}\right)\right|^2}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}$$

$$+\sum_k\int d\boldsymbol{x}d\boldsymbol{x}'\frac{\varphi_i^*\left(\boldsymbol{x}'\right)\varphi_k^*\left(\boldsymbol{x}\right)\varphi_k\left(\boldsymbol{x}'\right)\varphi_i\left(\boldsymbol{x}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}$$

$$=-\varepsilon_i$$

Hence, $-\varepsilon_i$ is the energy required to remove 1 electron from the system. Thus, this energy is simply the ionization energy. It is actually positive, since the Hartree-Fock energies tend to be all negative.

Note $\varepsilon_k-\varepsilon_i$ equals the energy needed to move an electron from orbital *i* to orbital *k*.

Define operators J_l and K_l by their action on an orbital:

$$J_\ell(\boldsymbol{x})\varphi_j(\boldsymbol{x}) = \int d\boldsymbol{x}' \frac{|\varphi_\ell(\boldsymbol{x}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_j(\boldsymbol{x})$$

$$K_\ell(\boldsymbol{x})\varphi_j(\boldsymbol{x}) = \int d\boldsymbol{x}' \frac{\varphi_\ell^*(\boldsymbol{x}')\varphi_j(\boldsymbol{x}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\varphi_\ell(\boldsymbol{x})$$

Define the Fock operator by

$$F = -\frac{1}{2}\nabla^2 + V_{ext}(\boldsymbol{r}) + \sum_\ell [J_\ell(\boldsymbol{x}) - K_\ell(\boldsymbol{x})]$$

so that the Hartree-Fock (HF) equations can be written compactly as

$$F\varphi_j(\boldsymbol{x}) = \varepsilon_j\varphi_j(\boldsymbol{x}).$$

The electron charge density

The wave function for the M-electron system is

$$\psi(1,2,\ldots,M) = \psi(\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_M, s_M)$$

The electronic charge density $n(\boldsymbol{r})$ is defined to be the number of electrons per unit volume.

The quantity

$$\sum_s \int d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_M |\psi(\boldsymbol{r}, s, 2, 3, \ldots, M)|^2$$

is the probability per unit volume that an electron will be found at $\boldsymbol{r}$.

Thus, $n(\boldsymbol{r}) = M\sum_s \int d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_M |\psi(\boldsymbol{r}, s, 2, 3, \ldots, M)|^2$ is the number of electrons per unit volume.

Clearly, $\int d\boldsymbol{r}n(\boldsymbol{r}) = M$ total number of electrons.

For a Slater determinant composed of orthogonal orbitals, consider the example of $M = 2$

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\boldsymbol{x}_1) & \psi_1(\boldsymbol{x}_2) \\ \psi_2(\boldsymbol{x}_1) & \psi_2(\boldsymbol{x}_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_2(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_2)$$

$$n(\boldsymbol{r}_1) = \sum_{s_1} \int d\boldsymbol{x}_2 \left[\psi_1^*(\boldsymbol{x}_1)\psi_2^*(\boldsymbol{x}_2) - \psi_1^*(\boldsymbol{x}_2)\psi_2^*(\boldsymbol{x}_1)\right]\left[\psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_2(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_2)\right]$$

$$= \sum_s \psi_1^*(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \psi_2^*(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_2) + \sum_s \psi_2^*(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \psi_1^*(\boldsymbol{x}_2)\psi_1(\boldsymbol{x}_2)$$

$$- \sum_s \psi_1^*(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \psi_1^*(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_2) \to 0$$

$$- \sum_s \psi_1^*(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_1) \int d\boldsymbol{x}_2 \psi_2^*(\boldsymbol{x}_2)\psi_1(\boldsymbol{x}_2) \to 0$$

} orthogonality

$$n(\boldsymbol{r}_1) = \sum_s \left[|\psi_1(\boldsymbol{x}_1)|^2 + |\psi_2(\boldsymbol{x}_1)|^2\right]$$

If we separate spatial and spin factors in the single-particle orbitals, we have:

$$\psi_1(\boldsymbol{x}_1) = \varphi_1(\boldsymbol{r}_{\varphi_1})\chi_{m_1}(s)$$

$$\psi_2(\boldsymbol{x}_1) = \varphi_2(\boldsymbol{r}_{\varphi_1})\chi_{m_2}(s_1)$$

Then, summing over spin gives

$$n(\mathbf{r}_1) = 2|\varphi_1(\mathbf{r}_1)|^2 + 2|\varphi_2(\mathbf{r}_1)|^2$$

Generally,

$$n(\mathbf{r}_1) = 2\sum_{k=1}^{M} |\varphi_k(\mathbf{r}_1)|^2 = \sum_{s_1}\sum_{k=1}^{M} |\psi_k(\mathbf{x}_1)|^2$$

Note that the Coulomb integral can be written as:

$$\frac{e^2}{2}\sum_{k,\ell}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{|\psi_k(\boldsymbol{x}_1)|^2|\psi_\ell(\boldsymbol{x}_2)|^2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} = \frac{e^2}{2}\int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{\left(\sum_k |\psi_k(\boldsymbol{x}_1)|^2\right)\left(\sum_\ell |\psi_\ell(\boldsymbol{x}_2)|^2\right)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

$$= \frac{e^2}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{\left(\sum_{s_1}\sum_k |\psi_k(\boldsymbol{x}_1)|^2\right)\left(\sum_{s_2}\sum_\ell |\psi_\ell(\boldsymbol{x}_2)|^2\right)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

$$= \frac{e^2}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

which is called the Hartree energy.

Note that the Coulomb integral in the Hartree equation

$$e^2\sum_{\ell\neq j}\int \frac{|\varphi_\ell(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' = e^2\sum_\ell \int d\boldsymbol{r}\frac{|\varphi_\ell(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} - e^2\int d\boldsymbol{r}\frac{|\varphi_j(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$= e^2\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + e\int d\boldsymbol{r}'\frac{n_j^H(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Thus, in the Hartree equation, we subtract off the so-called self-interaction term, which would be the interaction of an electron with its own spatial density.

$$n_j^H(\boldsymbol{r}) = \mp e|\varphi_j(\boldsymbol{r})|^2$$

Thus,

$$\int d\boldsymbol{r} n_j^H(\boldsymbol{r}) = \mp e$$

1 - particle density matrix :

Define the 1-particle density matrix as:

$$\rho(\mathbf{r},\mathbf{r}') = M\sum_m \int d\mathbf{x},\cdots d\mathbf{x}_M \psi^*(\mathbf{r},s,2,\ldots,M)\psi(\mathbf{r}',s,2,3,\ldots,M)$$

$$n(\mathbf{r}) = \rho(\mathbf{r},\mathbf{r})$$

In HF theory,

$$\rho(\mathbf{r},\mathbf{r}') = \sum_k \sum_m \varphi_k^*(\mathbf{r},m)\varphi_k(\mathbf{r}',m) = \sum_k \sum_{m,m'} \varphi_k^*(\mathbf{r},m)\varphi_k(\mathbf{r}',m')$$

Exchange energy:

$$K = -\frac{1}{2}\sum_{k,\ell}\int d\boldsymbol{x}d\boldsymbol{x}'\,\frac{\varphi_k^*(\boldsymbol{x})\varphi_\ell^*(\boldsymbol{x}')\varphi_\ell(\boldsymbol{x})\varphi_k(\boldsymbol{x}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$= -\frac{1}{2}\sum_{k,\ell}\sum_{m,m'}\int d\boldsymbol{r}d\boldsymbol{r}'\,\frac{\varphi_k^*(\boldsymbol{r},m)\varphi_\ell^*(\boldsymbol{r}',m')\varphi_\ell(\boldsymbol{r},m)\varphi_k(\boldsymbol{r}',m')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$= -\frac{1}{2}\int d\boldsymbol{r}d\boldsymbol{r}'\left(\sum_{k,m}\varphi_k^*(\boldsymbol{r},m)\varphi_k(\boldsymbol{r}',m)\right)\left(\sum_\ell\sum_{m'}\varphi_\ell^*(\boldsymbol{r}',m')\varphi_\ell(\boldsymbol{r},m')\right)$$

$$= -\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\,\frac{\rho(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$= -\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\,\frac{|\rho(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

MØller-Plesset Perturbation Theory:

Take $H_0 = \sum_{k=1}^{M} F_k$ = Total HF Hamiltonian.

Then, a perturbation can be defined by

$$H_e = H_0 + H'$$

where $H' = H_e - H_0$ and H_e is the exact Hamiltonian:

$$H_e = -\frac{1}{2}\sum_{k=1}^{M}\nabla_k^2 + \sum_{k=1}^{M}V_{ext}(\boldsymbol{r}_k) + \frac{1}{2}\sum_{k\neq\ell}\frac{1}{|\boldsymbol{r}_k-\boldsymbol{r}_\ell|}$$

$$H' = \frac{1}{2}\sum_{k\neq\ell}\frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_\ell|} - \sum_k\sum_\ell\left[J_\ell(\boldsymbol{x}_k) - K_\ell(\boldsymbol{x}_k)\right]$$

$$H_0 = -\frac{1}{2}\sum_{k=1}^{M}\nabla_k^2 + \sum_{k=1}^{M}V_{ext}(\boldsymbol{r}_k) + \sum_{k,\ell}\left[J_\ell(\boldsymbol{x}_k) - K_\ell(\boldsymbol{x}_k)\right]$$

In perturbation theory, recall:

First order energy correction is

$$E^{(1)} = \langle\psi_0|H'|\psi_0\rangle$$

while the zeroth order energy is $E^{(0)} = \langle\psi_0|H_0|\psi_0\rangle$.

$$E^{(0)} + E^{(1)} = \langle\psi_0|H_0 + H'|\psi_0\rangle = \langle\psi_0|H_e|\psi_0\rangle$$

But this is the original energy functional we varied to se the HF equation.

Second order:

$$E^{(2)} = \sum_{s\neq 0}\frac{\left|\langle\psi_0^{(s)}|H'|\psi_0\rangle\right|^2}{E^{(0)} - E^{(s)}}$$

$|\psi_0^{(s)}\rangle$ created from virtual orbitals used in determinants, i.e. excitations of single-particle orbitals to unoccupied states.