Lecture Thursday 20. September 2007

Topics: Final Derivation of Hartree-Fock Equations

Comments

Preliminary version

4 particle total energy 4 orbitals - 6 pairs

$$T_1 + V_1 + T_2 + V_2 + T_3 + V_3 + T_4 + V_4 + V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34}$$

$$\binom{4}{2} = \frac{4 \cdot 3 \cdot 2 \cdots}{2!\ 2!} = 6 \quad \text{6 pairs} \qquad \varphi_a\ \varphi_b\ \varphi_c\ \varphi_d$$

$$\langle \varphi_a | (T+V) | \varphi_a \rangle + \langle \varphi_b | T+V | \varphi_b \rangle + \langle \varphi_c | T+V | \varphi_c \rangle$$

$$+ \langle \varphi_d | T+V | \varphi_d \rangle + \langle \varphi_a \varphi_b | V_{12} | \varphi_a \varphi_b \rangle - \langle ba | V_{12} | ab \rangle$$

$$+ \langle ac | V_{12} | ac \rangle - \langle ca | V_{12} | ac \rangle$$

$$+ \langle ad | V_{12} | ad \rangle - \langle da | V_{12} | ad \rangle$$

$$+ \langle bc | V_{12} | bc \rangle - \langle cb | V_{12} | bc \rangle$$

$$+ \langle bd | V_{12} | bd \rangle - \langle db | V_{12} | bd \rangle$$

$$+ \langle cd | V_{12} | cd \rangle - \langle dc | V_{12} | cd \rangle$$

Show how the direct term and exchange actually differ

$$\langle \varphi_c \varphi_d | V_{12} | \varphi_c \varphi_d \rangle \qquad \langle \varphi_d \varphi_c | \cancel{\ } | \varphi_d \varphi_c \rangle$$

$$= \int d^3\vec{x}_1 \int d^3\vec{x}_2 \; \varphi_c^*(\vec{x}_1)\varphi_d^*(\vec{x}_2) \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \varphi_c(\vec{x}_1)\varphi_d(\vec{x}_2)$$

$$\langle \varphi_d \varphi_c | V_{12} | \varphi_c \varphi_d \rangle$$

$$= \int d^3\vec{x}_1 \int d^3\vec{x}_2 \; \varphi_d^*(\vec{x}_1)\varphi_c^*(\vec{x}_2) \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \varphi_c(\vec{x}_1)\varphi_d(\vec{x}_2)$$

$$\int \int d^3 1 \, d^3 2 \; |\varphi_c(1)|^2 |\varphi_d(2)|^2 \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}$$

$$\int d^3 1 \int d^3 2 \quad \varphi_d^*(1)\varphi_c(1) \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \varphi_c^*(2)\varphi_d(2)$$

Comment ...Showing that < d c | V | c d > is the same as < c d | V | d c >

$$\langle \varphi_d \varphi_c | V_{12} | \varphi_c \varphi_d \rangle$$

$$= \int d^3\vec{x}_1 \int d^3\vec{x}_2 \; \varphi_d^*(\vec{x}_1) \varphi_c^*(\vec{x}_2) \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \varphi_c(\vec{x}_1) \varphi_d(\vec{x}_2)$$

$$\int d^3 1 \int d^3 2 \; \varphi_d^*(1) \varphi_c(1) \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \varphi_c^*(2) \varphi_d(2)$$

$1 \to x$
$2 \to y$

$$\langle \varphi_c \varphi_d | V_{12} | \varphi_d \varphi_c \rangle$$

$$\int d^3 1 \, d^3 2 \; \varphi_c^*(1) \varphi_d(1) \frac{e^2}{|x_1 - x_2|^2} \varphi_d^*(2) \varphi_c(2)$$

$1 \to y$
$2 \to x$

$$\int d^3x \int d^3y \; \varphi_d^*(x) \varphi_c(x) \frac{e^2}{|x-y|} \varphi_c^*(y) \varphi_d(y)$$

$$\int d^3y \int d^3x \; \varphi_c^*(y) \varphi_d(y) \frac{e^2}{|y-x|} \varphi_d^*(x) \varphi_c(x)$$

The green and black are the same!

About Dirac Notation (Remember the matlab paper)

$$\int d\tau\, \psi_a^*(\tau)\, O_p(\tau)\, \psi_b(\tau) \equiv \langle \psi_a | O_p | \psi_b \rangle$$

"vectors" in Hilbert space

$|\alpha\rangle$ $\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \vdots \end{pmatrix}$ $\langle\alpha|$

$(\alpha_1^* \; \alpha_2^* \; \alpha_3^* \; \cdots \; \alpha_n^* \cdots)$

Operator

$O_p \Rightarrow \begin{pmatrix} O_{11} & O_{12} & O_{13} & \cdots \\ O_{21} & O_{22} & O_{23} & \cdots \\ O_{31} & O_{32} & \cdots & \end{pmatrix}$

$\langle\alpha | O_p | \beta\rangle$

$(\beta_1 \; \beta_2 \; \cdots) \begin{pmatrix} O & & \\ & \ddots & \\ & & O \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha \end{pmatrix}$

$\cancel{\langle\alpha\|\beta\rangle}$ $\langle\alpha|\beta\rangle$ Matrix Mechanics

Anschaulichkeit x Abscheulichkeit

C Direct term – remains function; Exchange Term.. ... NONLOCAL POTENTIAL

$$(T+V)|\alpha\rangle + \left[\sum_{\beta\neq\alpha} (\beta|V_{12}|\beta)\right]|\alpha\rangle$$

$$-\sum_{\beta\neq\alpha} (\beta|V_{12}|\alpha)|\beta\rangle = \lambda_\alpha|\alpha\rangle$$

$$\left\{\sum_{\beta\neq\alpha} \underbrace{\int d^3x\, \varphi_\beta^*(\vec{x}) \frac{e^2}{|\vec{r}-\vec{x}|} \varphi_\beta(\vec{x})}_{\text{remains function of } r}\right\} \varphi_\alpha(\vec{r}) \quad (\text{Hartree})$$

multiply $\varphi_\alpha(\vec{r})$ by $W(\vec{r})$

$$\left\{\sum_{\beta\neq\alpha} \int d^3x\, \varphi_\beta^*(\vec{x}) \frac{e^2}{|\vec{r}-\vec{x}|} \varphi_\alpha(\vec{x})\right\} \varphi_\beta(\vec{r})$$

. Take $W(\vec{r},\vec{x})$

$$\int W(\vec{r},\vec{x})\,\varphi_\alpha(\vec{x})\,d^3\vec{x} \to W \to$$

$(W + W)|\varphi_\alpha\rangle$

$\to W|\varphi_\alpha\rangle \cdot W(r)\varphi(r)$

Non-local potential ; $|x\rangle$ .... particle in point $\underline{\underline{x}}$

$|\psi\rangle$ .... $\langle x|\psi\rangle$ is $\psi(x)$

$\sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \to \mathbb{1}$; $\int d^3x\, |x\rangle\langle x| \to \mathbb{1}$

$V|\psi\rangle$ in dirac ; in Schrödinger $V(x)\psi(x)$

$\langle x|V|\psi\rangle$ But $\langle x|V|\left\{\int dy\, |y\rangle\langle y|\right\}|\psi\rangle$

$\to \int dy \langle x|V|y\rangle\langle y|\psi\rangle \to V(x)\psi(x)$

$V(x)\,\delta(x-y)$ .... local Bu But for

nonlocal, $V(x,y) = \langle x|V|y\rangle$

$$\left\{\sum_{\beta\neq\alpha}\int d^3x\, \varphi^*_\beta(\vec{x})\, \frac{e^2}{|\vec{r}-\vec{x}|}\, \varphi_\alpha(\vec{x})\right\} \varphi_\beta(\vec{r})$$

Take $\mathcal{W}(\vec{r},\vec{x})$

$$\int \mathcal{W}(\vec{r},\vec{x})\, \varphi_\alpha(\vec{x})\, d^3\vec{x} \to \mathcal{W} \to$$

nonlocal potential

$(W + \mathcal{W})|\varphi_\alpha\rangle$

$\to W|\varphi_\alpha\rangle \cdot W(r)\varphi(r)$

Differential equations X Integro-differential Eqs.

Comment ... the $e^{i\alpha}$ is an eigenvalue ... αβγδ

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