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12.1

12.1.2 Solving Closed-shell HF Eq with Variational Method

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(2)\alpha(2) & \cdots & \psi_1(N)\alpha(N) \\ \psi_2(1)\alpha(1) & \psi_2(2)\alpha(2) & \cdots & \psi_2(N)\alpha(N) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_p(1)\alpha(1) & \psi_p(2)\alpha(2) & \cdots & \psi_p(N)\alpha(N) \\ \psi_{p+1}(1)\beta(1) & \psi_{p+1}(2)\beta(2) & \cdots & \psi_{p+1}(N)\beta(N) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_N(1)\beta(1) & \psi_N(2)\beta(2) & \cdots & \psi_N(N)\beta(N) \end{vmatrix} \tag{12.1}$$

where $N = 2p$.

$$\hat{\mathbf{H}} = \sum_{i=1}^{N} \hat{\mathbf{h}}_i + \sum_{i<j} \hat{\mathbf{g}}_{ij} \tag{12.2}$$

Thus

$$E = \sum_i f_i + \sum_{i<j} (J_{ij} - K_{ij}) \tag{12.3}$$

where

$$f_i = \langle \phi_i | \hat{\mathbf{h}}_i | \phi_i \rangle \tag{12.4}$$

$$J_{ij} = \langle \phi_i | \hat{\mathbf{J}}_j | \phi_i \rangle = \langle \phi_i \phi_j | \, \hat{\mathbf{g}}_{ij} \, | \phi_i \phi_j \rangle \tag{12.5}$$

$$K_{ij} = \delta(m_{s_i} m_{s_j}) \langle \phi_i | \hat{\mathbf{K}}_j | \phi_i \rangle = \langle \phi_i \phi_j | \, \hat{\mathbf{g}}_{ij} \, | \phi_j \phi_i \rangle \tag{12.6}$$

We need to minimize functional

$$W = E - \sum_{i<j} \delta(m_{s_i} m_{s_j}) \varepsilon_{ij} \langle \psi_i | \psi_j \rangle \tag{12.7}$$

when $\psi_i \to \psi_i + \delta\psi_i$

$$
\begin{aligned}
\delta E =& \int \delta\psi_i^*(1)\hat{\mathbf{h}}(1)\psi_i(1)\mathrm{d}\tau_1 + \int \psi_i^*(1)\hat{\mathbf{h}}(1)\delta\psi_i(1)\mathrm{d}\tau_1 \\
&+ \sum_j \Big[\int (\delta\psi_i^*(1)\psi_j^*(2)\hat{\mathbf{g}}_{ij}\psi_i(1)\psi_j(2) + \psi_i^*(1)\psi_j^*(2)\hat{\mathbf{g}}_{ij}\delta\psi_i(1)\psi_j(2))\mathrm{d}\tau_1\mathrm{d}\tau_2 \\
&- \delta(m_{s_i}m_{s_j}) \int (\delta\psi_i^*(1)\psi_j^*(2)\hat{\mathbf{g}}_{ij}\psi_j(1)\psi_i(2) + \psi_i^*(1)\psi_j^*(2)\hat{\mathbf{g}}_{ij}\delta\psi_j(1)\psi_i(2))\mathrm{d}\tau_1\mathrm{d}\tau_2\Big] \\
&= \int \delta\psi_i^*(1)\Bigg\{\hat{\mathbf{h}}(1)\psi_i(1)\mathrm{d}\tau_1 + \sum_j \Big[\int \psi_j^*(2)\hat{\mathbf{g}}_{ij}\psi_i(1)\psi_j(2) - \delta(m_{s_i}m_{s_j}) \int \psi_j^*(2)\hat{\mathbf{g}}_{ij}\psi_j(1)\psi_i(2)\Big]\mathrm{d}\tau_1\mathrm{d}\tau_2\Bigg\}
\end{aligned}
\tag{12.8}
$$

13 HF Roothaan Eq

For N nuclei and n electrons, denote spatial orbitals as $\{\phi_i\}\Big(i = 1, 2, \cdots, \dfrac{n}{2}\Big)$, thus the wavefunction is

$$\Psi_0 = \Big|\phi_1\alpha(1)\phi_1\beta(2)\cdots\phi_{\frac{1}{2}}\alpha(n-1)\phi_{\frac{1}{2}}\beta(n)\Big| \tag{13.1}$$

def:

$$\hat{\mathbf{h}}_i = -\frac{1}{2}\nabla_i^2 - \sum_{s=1}^{N}\frac{Z_s}{r_{is}} \tag{13.2}$$

$$\hat{\mathbf{g}} = \frac{1}{r_{ij}} \tag{13.3}$$

thus

$$E = 2\sum_i f_i + \sum_i^{\frac{n}{2}}\sum_j^{\frac{n}{2}}(2J_{ij} - K_{ij}) \tag{13.4}$$

where

$$f_i = \langle\phi_i|\hat{\mathbf{h}}_i|\phi_i\rangle \tag{13.5}$$

$$J_{ij} = \langle\phi_i|\hat{\mathbf{J}}_j|\phi_i\rangle = \langle\phi_i\phi_j|\,\hat{\mathbf{g}}_{ij}\,|\phi_i\phi_j\rangle \tag{13.6}$$

$$K_{ij} = \langle\phi_i|\hat{\mathbf{K}}_j|\phi_i\rangle = \langle\phi_i\phi_j|\,\hat{\mathbf{g}}_{ij}\,|\phi_j\phi_i\rangle \tag{13.7}$$

Suppose

$$\phi_i = \sum_\mu^m c_{\mu i}\chi_\mu \tag{13.8}$$

thus

$$f_i = \sum_\mu\sum_\nu c_{\mu i}^* c_{\nu i} h_{\mu\nu} \tag{13.9}$$

$$J_{ij} = \sum_\mu\sum_\lambda\sum_\nu\sum_\sigma c_{\mu i}^* c_{\lambda j} c_{\nu i} c_{\sigma j}(\mu\nu|\lambda\sigma) \tag{13.10}$$

$$K_{ij} = \sum_{\mu} \sum_{\lambda} \sum_{\nu} \sum_{\sigma} c^*_{\mu i} c_{\lambda j} c_{\nu i} c_{\sigma j} (\mu\sigma|\lambda\nu) \tag{13.11}$$

$$\langle \phi_i | \phi_j \rangle = \sum_{\mu\nu} c^*_{\mu i} c_{\nu j} S_{\mu\nu} \tag{13.12}$$

where

$$h_{\mu\nu} = \int \chi_\mu(1) \hat{\mathbf{h}}(1) \chi_\nu(1) \mathrm{d}\tau_1 \tag{13.13}$$

$$(\mu\nu|\lambda\sigma) = \iint \chi_\mu(1)\chi_\nu(1)\hat{\mathbf{g}}_{12}\chi_\lambda(2)\chi_\sigma(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{13.14}$$

$$S_{\mu\nu} = \int \chi_\mu(1)\chi_\nu(1)\mathrm{d}\tau_1 \tag{13.15}$$

$$E = 2\sum_{\mu}\sum_{\nu}\sum_{i} c^*_{\mu i} c_{\nu i} h_{\mu\nu} + \sum_{\mu}\sum_{\lambda}\sum_{\nu}\sum_{\sigma}\sum_{ij} c^*_{\mu i} c_{\lambda j} c_{\nu i} c_{\sigma j} [2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] \tag{13.16}$$