MOLECULAR SCF PROBLEM

We return now to the Hamiltonian

$$\mathcal{H}(q,Q) = -\frac{1}{2}\sum_{i=1}^{n}\partial_i^2 + \sum_{\substack{i,j=1\\i<j}}^{n}|q_i-q_j|^{-1} - \sum_{i=1}^{n}\sum_{\alpha=1}^{N} Z_\alpha |q_i - Q_\alpha|^{-1}$$

$$+ \sum_{\substack{\alpha,\beta=1\\ \alpha<\beta}}^{N} Z_\alpha Z_\beta |Q_\alpha - Q_\beta|^{-1}$$

which describes the electronic motion in a many-electron molecule. We now restrict ourselves to closed shell systems and make the notational changes

$$q_i \longrightarrow r_i$$

$$q_i - Q_\alpha \longrightarrow r_{i\alpha}$$

$$q_i - q_j \longrightarrow r_{ij}$$

$$V_{NN} = \sum_{\substack{\alpha,\beta=1\\ \alpha<\beta}}^{N} Z_\alpha Z_\beta |Q_\alpha - Q_\beta|^{-1}$$

Then, the above Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_{el} + V_{NN}$$

where

$$\mathcal{H}_{el} = \sum_{i=1}^{n} \left(-\frac{1}{2}\partial_i^2 - \sum_{\alpha=1}^{N} \frac{Z_\alpha}{r_{i\alpha}} \right) + \sum_{\substack{i,j=1 \\ i<j}}^{n} \frac{1}{r_{ij}}$$

$$= \sum_{i=1}^{n} f_i + \sum_{\substack{i,j=1 \\ i<j}}^{n} g_{ij}$$

Thus, the Hartree-Fock energy for a closed shell slater determinant D is

$$E_{HF} = \langle D|\mathcal{H}|D\rangle$$

$$= \langle D|\mathcal{H}_{el}|D\rangle + \langle D|V_{NN}|D\rangle$$

$$= \langle D|\mathcal{H}_{el}|D\rangle + V_{NN} \cancel{\langle D|D\rangle}^{1}$$

and

$$\langle D|\mathcal{H}_{el}|D\rangle = 2\sum_{i=1}^{n/2} \mathcal{H}_i^{core} + \sum_{i,j=1}^{n/2} (2J_{ij} - K_{ij})$$

where

$$\mathcal{H}_i^{Core} = \langle \phi_i(1) | -\tfrac{1}{2}\partial_1^2 - \sum_\alpha Z_\alpha / r_{1\alpha} | \phi_i(1) \rangle$$

$$J_{ij} = \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle$$

$$K_{ij} = \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \rangle$$

and the ϕ_i's are (doubly occupied) spatial orbitals.

The ϕ_i's that solve the variational problem (i.e., minimize E_{HF}) are given by

$$F(1)\,\phi_i(1) = \epsilon_i\,\phi_i(1)$$

where the Fock operator is

$$F(1) = \mathcal{H}^{core} + \sum_{j=1}^{n/2} \left[2J_j(1) - K_j(1) \right]$$

with

$$\mathcal{H}^{core} = -\tfrac{1}{2}\partial_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}}$$

$$J_j(1) f(1) = f(1) \int |\phi_j(2)|^2 \frac{1}{r_{12}}\, d\tau_2$$

$$K_j(1) f(1) = \phi_j(1) \int \phi_j^*(2) f(2) \frac{1}{r_{12}}\, d\tau_2$$

The orbital energies are given by

$$\epsilon_i = \langle \phi_i(1) | F(1) | \phi_i(1) \rangle$$

$$= \langle \phi_i(1) | \mathcal{H}^{core} | \phi_i(1) \rangle$$

$$+ \sum_j \left[2 \langle \phi_i(1) | J_j(1) | \phi_i(1) \rangle - \langle \phi_i(1) | K_j(1) | \phi_i(1) \rangle \right]$$

$$= \mathcal{H}_i^{core} + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

Therefore,

$$\sum_{i=1}^{n/2} \epsilon_i = \sum_{i=1}^{n/2} \mathcal{H}_i^{core} + \sum_{i,j=1}^{n/2} (2J_{ij} - K_{ij})$$

or,

$$E_{HF} = 2\sum_{i=1}^{n/2} \epsilon_i - \sum_{i,j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN}$$

Roothaan expanded the ϕ_i MOs in a basis of one-electron functions (usually termed AOs) χ_s

$$\phi_i = \sum_s c_{si} \chi_s$$

Substitution of this expansion into the Hartree-Fock equations gives

$$\sum_s c_{si} F \chi_s = \epsilon_i \sum_s c_{si} \chi_s$$

Multiplication by χ_r^* and integration yields

$$\sum_s c_{si} (F_{rs} - \epsilon_i) S_{rs} = 0$$

HF - ROOTHAAN EQUATIONS

where

$$F_{rs} = \langle \chi_r | F | \chi_s \rangle$$

$$S_{rs} = \langle \chi_r | \chi_s \rangle$$

In practice, the AO basis is truncated to a finite set $s = 1, \ldots, b$. And, in this case the condition for a nontrivial solution is

$$\det [F_{rs} - \epsilon_i S_{rs}] = 0 .$$

MATRIX ELEMENTS

$$F_{rs} = \langle \chi_r(1) | F(1) | \chi_s(1) \rangle$$

or (closed shell)

$$F_{rs} = \langle \chi_r(1) | \mathcal{H}^{core} | \chi_s(r) \rangle + \sum_{j=1}^{n/2} \left[2\langle \chi_r(1) | J_j(1) | \chi_s(1) \rangle - \langle \chi_r(1) | K_j(1) | \chi_s(1) \rangle \right]$$

Now,

$$J_j(1)\chi_s(1) = \chi_s(1) \int \frac{\phi_j^*(2)\,\phi_j(2)}{r_{12}}\, d\tau_2$$

$$= \chi_s(1) \sum_{t,u} c_{tj}^* c_{uj} \int \frac{\chi_t^*(2)\chi_u(2)}{r_{12}}\, d\tau_2$$

Thus,

$$\langle \chi_r(1) | J_j(1) | \chi_s(1) \rangle = \sum_{t,u} c_{tj}^* c_{uj} \int \frac{\chi_r^*(1)\chi_s(1)\chi_t^*(2)\chi_u(2)}{r_{12}}\, d\tau_1 d\tau_2$$

$$= \sum_{t,u} c_{tj}^* c_{uj}\, (rs|tu)$$

where

$$(rs|tu) := \int \frac{\chi_r^*(1)\chi_s(1)\chi_t^*(2)\chi_u(2)}{r_{12}}\, d\tau_1 d\tau_2$$

is the <u>two-electron</u> <u>repulsion</u> <u>integral</u>.

Likewise,

$$K_j(1)\,\chi_s(1) = \phi_j(1)\int \frac{\phi_j^*(2)\,\chi_s(2)}{r_{12}}\,d\tau_2$$

$$= \sum_{t,u} c_{tj}^*\, c_{uj}\, \chi_u(1)\int \frac{\chi_t^*(2)\,\chi_s(2)}{r_{12}}\,d\tau_2$$

and

$$\langle \chi_r \,|\, K_j(1) \,|\, \chi_s(1)\rangle = \sum_{t,u} c_{tj}^*\, c_{uj} \int \frac{\chi_r^*(1)\,\chi_u(1)\,\chi_t^*(2)\,\chi_s(2)}{r_{12}}\,d\tau_1 d\tau_2$$

$$= \sum_{t,u} c_{tj}^*\, c_{uj}\, (ru|ts)$$

Hence,

$$F_{rs} = \mathcal{H}_{rs}^{core} + \sum_{j=1}^{n/2}\sum_{t,u} c_{tj}^*\, c_{uj}\left[2(rs|tu) - (ru|ts)\right]$$

Defining

$$P_{tu} = \sum_{j=1}^{n/2} 2\, c_{tj}^*\, c_{uj}$$

<u>electron</u> <u>density</u> <u>matrix</u>, or charge-density, bond-order matrix

we have

$$F_{rs} = \mathcal{H}_{rs}^{core} + \sum_{t,u} P_{tu}\left[(rs|tu) - \frac{1}{2}(ru|ts)\right]$$

Moreover, the electron probability density is

$$\rho = 2\sum_{j=1}^{n/2} \phi_j^* \phi_j$$

$$= \sum_{r,s} P_{rs}\, \chi_r^* \chi_s$$

and the Hartree-Fock energy is

$$E_{HF} = \sum_{i=1}^{n/2} \epsilon_i + \sum_{i=1}^{n/2} \mathcal{H}_i^{core} + V_{NN}$$

$$= \sum_{i=1}^{n/2} \epsilon_i + \frac{1}{2}\sum_{r,s} P_{rs}\, \mathcal{H}_{rs}^{core} + V_{NN}$$

where

$$\sum_{i=1}^{n/2} \epsilon_i = \sum_{i=1}^{n/2} \mathcal{H}_i^{core} + \sum_{i,j=1}^{n/2} (2J_{ij} - K_{ij})$$

which was introduced previously.

The Roothaan equations now become

$$\sum_s F_{rs} c_{si} = \sum_s S_{rs} c_{si} \epsilon_i \quad , \forall r$$

or

$$FC = SC\epsilon$$

MATRIX FORM

If we now introduce a basis

$$\chi'_s = \sum_t b_{ts} \chi_t$$

such that

$$S'_{rs} = \langle \chi'_r | \chi'_s \rangle = \delta_{rs} \, ,$$

the Roothaan equations become

$$F'c' = c'\epsilon$$

or, since F' is Hermitian and c' is unitary,

$$c'^{\dagger} F' c' = \epsilon$$

DIAGONAL FORM OF THE FOCK MATRIX