Heuristic Derivation of Hartree Fock Equations

Split Hamiltonian into a single-particle term and electron-electron Coulomb potential.

**Single-particle term** of Hamiltonian is $\Sigma_{ab} t_{ab} c_a^+ c_b$ involving electron kinetic energy $T$ and the electron-ion interaction $V_{el-nuc}$: $t_{ab} = \int d^3 x \phi_a^*(\vec{x}) (T + V_{el-nuc}) \phi_b(\vec{x})$.

**Coulomb Potential in real space.** The potential energy can be rewritten, using for 3rd line: (i) $\psi(\vec{x})\psi^+(\vec{x}') = -\psi^+(\vec{x}')\psi(\vec{x}) + \delta(\vec{x} - \vec{x}')$ with the 2nd term excluded from integral and (ii) $\psi(\vec{x})\psi(\vec{x}') = -\psi(\vec{x}')\psi(\vec{x})$.

$$V = \frac{1}{2} \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \rho(\vec{x}) \rho(\vec{x}')$$
$$= \frac{1}{2} \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \psi^+(\vec{x}) \psi(\vec{x}')$$
$$= \frac{1}{2} \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \psi^+(\vec{x}') \psi(\vec{x})$$

**Coulomb Potential in orbital space.** Writing $\psi(\vec{x}) = \sum_i \phi_i(\vec{x}) c_i$ in terms of orbitals, and defining $\langle ab|V|cd \rangle \equiv V_{ab,cd} = \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \phi_a^*(\vec{x}) \phi_c(\vec{x}') \phi_b^*(\vec{x}') \phi_d^*(\vec{x}')$; the potential energy term is

$$V = \frac{1}{2} \sum_{abdc} V_{ab,cd} c_a^+ c_b^+ c_d c_c$$
$$= \frac{1}{2} \sum_{abcd,ss'} V_{ab,cd} c_a^c c_{bs} c_{ds'} c_{cs}$$

where the second term includes spin for the first time.

**Notes:** (i) $V_{ab,cd} = V_{ba,dc}$ as result of interchange $x$ and $x'$ and (ii) the important terms Hartree (or direct) and Exchange (or Fock):

- Hartree
  $$V_{ab,ab} = \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \rho(\vec{x}) \rho(\vec{x}')$$
- Exchange
  $$V_{ab,ba} = \int d^3 x d^3 x' V(\vec{x} - \vec{x}') \phi_a^*(\vec{x}) \phi_b(\vec{x}') \phi_b^*(\vec{x}') \phi_a(\vec{x})$$

**Setting up variational derivation of HF equation.** The many-body fermion wavefunction is a sum of Slater determinants, each ensuring the Pauli principle. Of all HF versions, the simplest is a single Slater determinant of filled orbitals: in terms of creation operators: $|\Phi\rangle = \Pi_i^N c_i^+ |0\rangle$; in real space: $|\bar{x}_1 \bar{x}_2 \ldots \bar{x}_N \rangle$.

**Variational derivation.** Imagine moving one fermion from a filled orbital ($f$, say) to an empty orbital ($e$, say). The resulting variation in the wave function $|\delta \Phi\rangle = c_{f\sigma} c_{e\sigma} |\Phi\rangle$. The optimized choice of retained terms is given by $\langle \delta \Phi | H \Phi \rangle = \langle \delta \Phi | E \Phi \rangle$. The two term of left-hand side are evaluated separately. First, the single-particle term (omitting spin $\sigma$)

$$\langle \phi | c_f^+ c_e \sum_{ab} t_{ab} c_a^+ c_b | \phi \rangle = t_{ef}$$

where $e$ ($f$) refer to empty (full) state.

*Includes spins* 22 April 2005
Coulomb terms: The computation yield four terms:

Writing only non-zero terms, \( \frac{1}{2} \sum_{abcd,ss'} V_{ab,cd} \langle \Phi | c_f^+ a_{\sigma} c_{as}^+ b_{s'} c_{ds'} c_{es} | \Phi \rangle = \)

for \( f = d, e = a, \sigma = s' = s \) (implies \( b = c \) and sum over \( c \)) \(- \frac{1}{2} \sum_c V_{ee,cf} \)

for \( f = d, e = b, \sigma = s' \) (implies \( a = c \) and sum over \( c, s \)) \(+ \frac{1}{2} \sum_c V_{ce,cf} \)

for \( f = c, e = a, \sigma = s \) (implies \( d = b \) and sum over \( d, s' \)) \(+ \frac{1}{2} \sum_{d,s'} V_{ed,fd} \)

for \( f = c, e = b, \sigma = s = s' \) (implies \( d = a \) and sum over \( d \)) \(- \frac{1}{2} \sum_d V_{de,fd} \)

Grouping terms of the same sign, observing that in 3rd and dummy index \( s \) can be replaced by \( s' \) and that Note (i) says 3rd term \( V_{ec,fc} = V_{ce,cf} \), so

\[ \langle \delta \Phi H \Phi \rangle = t_{ef} + \sum_c (\sum_{s'} V_{ec,fc} - V_{ce,cf}). \]

This suggests defining HF Hamiltonian as:

\[ H_{HF} = \sum_{ef,s} \left[ t_{ef} + \sum_{c} (\sum_{s'} V_{ec,fc} - V_{ce,cf}) \right] \]

that can be diagonalized immediately to

\[ H_{HF} = \sum_{f,s} \epsilon_f \]

where \( \epsilon_f = t_{ff} + \sum_c (\sum_{s'} V_{fc,fc} - V_{fc,cf}) \).

Now we rename some indices for convenience.

\[ H_{HF} = \sum_{i=1,s}^N [t_{ii} + \frac{1}{2} \sum_{j=1}^N (\sum_{s'} V_{ij,ij} - V_{ij,ji})] \] or

\[ H_{HF} = \sum_{i=1,s}^N [t_{ii} + \sum_{j<i} (\sum_{s'} V_{ij,ij} - V_{ij,ji})] \]

\[ \epsilon_i = t_{ii} + \sum_{j=1}^N (\sum_{s'} V_{ij,ij} - V_{ij,ji}) \]

Note that Exchange term substracts from Hartree term.

Includes spins