Lattice Waves and Electron States

Hartree - Fock equation:

Let us consider a system of electrons described by the field operator

$$\psi(x) = \sum_j c_j \phi_j(x) \qquad (1)$$

where c_j is a fermion operator and $\phi_j(x)$ is a one-particle eigenfunction. Our object is to find approximate solutions of the equation of motion $i\dot{\psi} = -[H, \psi]$. The prescription for the hamiltonian in this representation is to write the mean energy in terms of individual particle wavefunctions and then replace the wavefunctions by the field operator $\psi(x')$. Thus

$$H = \int d^3x' \, \psi^+(x') \left[\frac{1}{2m} p^2 + V(x') \right] \psi(x')$$

$$+ \frac{1}{2} \int d^3x' \, d^3y \, \psi^+(x') \psi^+(y) V(x'-y) \psi(y) \psi(x') , \qquad (2)$$

where $V(x'-y)$ is the interaction energy of two particles at x' and y. The factor $\frac{1}{2}$ arises because of the self-energy. The order of terms is significant because $\psi(x')\psi(y) = -\psi(y)\psi(x')$.

For convenience we suppose $V(x') = 0$ and write

$$H = \int d^3x' \, \psi^+(x') \frac{1}{2m} p^2 \psi(x') + \frac{1}{2} \int d^3x' \, d^3y \, \psi^+(x') \psi^+(y) V(x'-y) \psi(y) \psi(x') , \qquad (3)$$

where

$$\int d^3x' \, \psi^+(x') \psi(x') = \int d^3x' \sum_{j,l} c_j^+ c_l \phi_j^*(x') \phi_l(x') = \sum_j c_j^+ c_j = \hat{N} \qquad (4)$$

is the operator for the total number of particles. The first term in the commutator $[H, \psi(x)]$ is, with p operating on $\psi(x')$,

$$\frac{1}{2m} \int d^3x' \left[\psi^+(x') p^2 \psi(x'), \psi(x) \right] = -\frac{1}{2m} \int d^3x' \left\{ \psi^+(x'), \psi(x) \right\} p^2 \psi(x') , \qquad (5)$$

because the anticommutator

$$\left\{ \psi(x'), \psi(x) \right\} = 0 \qquad (6)$$

It is noted the mixture of Commutators and anticommutators in eqn. (5).

Now $$-\frac{1}{2m}\int d^3x' \{\psi^\dagger(x'), \psi(x)\} p^2 \psi(x') = -\frac{1}{2m}\int d^3x' \, \delta(x'-x) p^2 \psi(x')$$

$$= -\frac{1}{2m} p^2 \psi(x). \qquad (7)$$

The second term in the commutator $[H, \psi(x)]$ is

$$\frac{1}{2}\int d^3x' \, d^2y \left[\psi^\dagger(x')\psi^\dagger(y) V(x'-y)\psi(y)\psi(x'), \psi(x)\right]$$

$$= -\int d^3y \, V(y-x)\psi^\dagger(y)\psi(y)\psi(x). \qquad (8)$$

Here $$-\int d^3y \, V(y-x)\psi^\dagger(y)\psi(y)\psi(x) = -\sum_{klm} c_k^\dagger c_l c_m \int d^3y \, V(y-x)\phi_k^*(y)\phi_l(y)\phi_m(x). \qquad (9)$$

This expression involves products of three operators.

In the lowest or Hartree-Fock approximation we consider only terms in a single operator times the number operator $c_k^\dagger c_k$. We thus keep the terms $c_k^\dagger c_k c_m$ and $c_k^\dagger c_l c_k = -c_l c_k^\dagger c_k$, whence

$$-\int d^3y \, V(y-x)\psi^\dagger(y)\psi(y)\psi(x) \cong -\int d^3y \, V(y-x)\langle\psi^\dagger(y)\psi(y)\rangle\psi(x) + \int d^3y \, \psi(y) V(y-x)\langle\psi^\dagger(y)\psi(x)\rangle, \qquad (10)$$

where we have resumed the series for $\psi(x)$ and $\psi(y)$; the angular brackets indicate the expectation value in the ground state, that is, only terms of the form $c_k^\dagger c_k$ are retained within the angular brackets, where $c_k^\dagger c_k$ is evaluated for the ground state. The first term on the r.h.s. of eqn (10) is the direct Coulomb term, and the second term is the exchange term.

Collecting (7) and (10),

$$[H, \psi(x)] \cong -\sum_j c_j \left[\left(\frac{1}{2m}p^2 + \int d^3y \, V(y-x)\langle\psi^\dagger(y)\psi(y)\rangle\right)\phi_j(x) - \int d^3y \, \phi_j(y) V(y-x)\langle\psi^\dagger(y)\psi(x)\rangle\right] \qquad (11)$$

Let us suppose now that the $\phi_j(x)$ are eigenfunctions of the operator in the square brackets on the right-hand side of (11), with the eigenvalues ε_j; then the equation of motion is

$$[H, \psi(x)] \cong -i\sum_j c_j \phi_j(x) = -\sum_j \varepsilon_j c_j \phi_j(x), \qquad (12)$$

where

$$\varepsilon_j \phi_j(x) = \left(\frac{p^2}{2m} + \int d^3y \, V(y-x)\langle\psi^\dagger(y)\psi(y)\rangle\right)\phi_j(x) - \int d^3y \, \phi_j(y) V(y-x)\langle\psi^\dagger(y)\psi(x)\rangle \qquad (13)$$

This is the Hartree-Fock equation.

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