

used to generate a better field. Iterating in this way, one eventually achieves self-consistency between the field and the electron density.

9.2 Hartree-Fock (HF) Theory

The physically appealing self-consistent field method becomes more rigorous in HF theory. Its major advance over Hartree theory is the inclusion of exchange.

There are many equivalent ways of expressing HF theory. Each has its merit and emphasizes a particular aspect of the theory. Which method is adopted is largely a matter of taste. However, in extending HF theory in any one of the several possible directions indicated in the Introduction to Part Two, a particular statement of the basic theory seems to be especially appropriate. For this reason we shall discuss HF theory from a number of viewpoints, although avoiding undue repetition.

(i) Variational method

The fundamental assumption of HF theory is that the nuclear wave function is an antisymmetrized product of independent particle wave functions

$$\phi(12 \dots A) = \mathcal{A}\psi_1(1)\psi_2(2)\dots\psi_A(A). \quad (9.5)$$

Here \mathcal{A} represents an antisymmetrization operation that generates the normalized Slater determinant

$$\mathcal{A}\psi_1(1)\psi_2(2)\dots\psi_A(A) \equiv \frac{1}{(A)!^{1/2}} \begin{vmatrix} \psi_1(1)\psi_2(1)\dots\psi_A(1) \\ \psi_1(2)\psi_2(2)\dots\psi_A(2) \\ \vdots \\ \psi_1(A)\psi_2(A)\dots\psi_A(A) \end{vmatrix} \quad (9.6)$$

The best possible wave function of this form is determined by application of a variational principle. The variational principle states that for small variations of an eigenstate, the energy expectation is stationary, for the ground state in particular it is a minimum. Thus

$$\delta \langle \phi | H | \phi \rangle = \langle \delta \phi | H | \phi \rangle = 0 \quad (9.7)$$

for small variations $\delta \phi$ which preserve the normalization of the single-particle wave functions

$$\int |\psi_i(r)|^2 d\mathbf{r} = 1. \quad (9.8)$$

Consider the Hamiltonian

$$H = \sum_i T_i + \frac{1}{2} \sum_{ij} v(r_i r_j). \quad (9.9)$$

Its energy expectation is given by

$$\begin{aligned} \langle \phi | H | \phi \rangle &= -\frac{\hbar^2}{2M} \sum_i \int \psi_i^*(r) \nabla^2 \psi_i(r) dr \\ &+ \frac{1}{2} \sum_{ij} \iint \psi_i^*(r) \psi_j^*(r') v(r, r') \psi_i(r) \psi_j(r') dr dr' \\ &- \frac{1}{2} \sum_{ij} \iint \psi_i^*(r) \psi_j^*(r') v(r, r') \psi_i(r') \psi_j(r) dr dr' \end{aligned} \quad (9.10)$$

Applying the variation on $\psi_i^*(r)$, we obtain the single-particle wave equation

$$-\frac{\hbar^2}{2M} \nabla^2 \psi_i(r) + \sum_j \int d\mathbf{r}' \psi_j^*(r') v(r, r') \psi_j(r') \psi_i(r) - \sum_j \int d\mathbf{r}' \psi_j^*(r') v(r, r') \psi_j(r) \psi_i(r') = \epsilon_i \psi_i(r) \quad (9.11)$$

where ϵ_i is the Lagrange multiplier that enforces the constraint (9.8). It has the significance of a single-particle energy. This is more apparent when (9.11) is written in the form

$$-\frac{\hbar^2}{2M} \nabla^2 \psi_i(r) + \int d\mathbf{r}' u(r, r') \psi_i(r') = \epsilon_i \psi_i(r) \quad (9.12)$$

where $u(r, r')$ is the self-consistent field

$$u(r, r') = \delta(r - r') \sum_i \int d\mathbf{r}'' v(r, r'') \psi_i(r'') \psi_i^*(r'') - \sum_j v(r, r') \psi_j(r) \psi_j^*(r'). \quad (9.13)$$

The first term is the direct term, corresponding to the Hartree field (cf. eqn. 9.3). The second is the exchange contribution and is non-local. It is seen that the range of non-locality of the HF field is closely related to the range of the two-body interaction $v(r, r')$.

In general, the two-body interaction is not a simple function of particle coordinates as we have supposed, but also depends on their relative momentum. Thus a general two-body interaction is an

To solve the HF equations one can again proceed iteratively in the cycle

$$u^{(0)} \rightarrow \psi_i \rightarrow \rho \rightarrow u^{(1)} = Tr(V\rho).$$

Starting from an initial guess $u^{(0)}$ for the field, a set of single-particle wave functions is calculated. These are then used to calculate a better approximation $u^{(1)}$ for the field, and so on, until self-consistency is achieved between the field and the density.

As one would expect, the field is a function (eqn. 9.14) only of occupied single-particle wave functions. Nevertheless the wave equation (9.12) generates a complete set of single-particle wave functions. In constructing the HF determinant one naturally selects



Figure 9.1. Labelling of particle and hole states with respect to the HF Fermi sea (the particle-hole vacuum).

the A lowest energy wave functions. Thus the HF state corresponds to a Fermi sea of particles with a sharp Fermi surface.

For many purposes it will be convenient to regard the HF state as the *particle-hole vacuum* and write it $|\rangle$. *Particle states* are then defined as the unoccupied single-particle states above the Fermi surface (see figure 9.1) and will be distinguished by subscripts m, n, p , or q . *Hole states* are defined as the occupied single-particle states below the Fermi surface and will be distinguished by subscripts i, j, k , or l . Greek subscripts will be used when no distinction is to be made.

(ii) Use of Wick's theorem

A disadvantage of the variational method is that it is not obvious how good is the answer. In particular one does not know what part

operator or non-local function. For a general two-body interaction, the expression for the field becomes

$$u(r_1, r'_1) = \sum_j \int dt_2 dt_2' v(r_1 t_2, r'_1 t_2') \psi_i(r_2) \psi_j^*(r_2) - \sum_j \int dt_2 dt_2' v(r_1 t_2, r'_1 t_2') \psi_j(r_2) \psi_i^*(r_2) \quad (9.14)$$

$$\text{or } u(r_1, r'_1) = \int \int dt_2 dt_2' V(r_1 t_2, r'_1 t_2') \rho(r_2, r_2) \equiv Tr_2 (v_{12} \rho_{22}) \quad (9.15)$$

where V is the antisymmetrized interaction

$$V(r_1 t_2, r'_1 t_2') = v(r_1 t_2, r'_1 t_2') - v(r_1 t_2, r_2' t_2') \quad (9.16)$$

and $\rho(r', r)$ is the single-particle density.

The diagonal element $\rho(r, r)$ of the single-particle density is just the classical density $\rho(r)$; the probability of finding a particle at position r . The general density $\rho(r', r)$ is the probability amplitude that a particle can be removed from the nucleus at r' and replaced at r without exciting the nucleus. In the language of second quantization (see Appendix C)

$$\rho(r', r) \equiv \langle \phi | a_r^\dagger a_{r'} | \phi \rangle.$$

We shall also have cause to use the density in configuration representation. Its matrix elements are then defined

$$\rho_{r' r} \equiv \langle \phi | a_{r'}^\dagger a_r | \phi \rangle.$$

From the relationship

$$a_r^\dagger = \int dt \psi_r(r) a_t^\dagger$$

(Appendix C) it follows that

$$\rho_{r' r} = \int dt dt' \psi_{r'}^*(r') \rho(r', r) \psi_r(r) = \langle \psi' | \rho | \psi \rangle.$$

The density for a product wave function, of form (9.5), is simply

$$\rho(r', r) = \sum_j \psi_j(r') \psi_j^*(r) \quad (9.17)$$

and has special properties. In particular

$$\int dt'' \rho(r', r'') \rho(r'', r) = \rho(r', r). \quad (9.18)$$

This result, which can be expressed abstractly in any representation,

$$\rho^2 = \rho, \quad (9.19)$$

is the hallmark of an independent-particle or product wave function.