

of “many-body problems,” and have been dealt with, in recent years, through “field theoretic” or “Green’s function” methods.

### EXCHANGE: THE HARTREE-FOCK APPROXIMATION

The Hartree equations (17.7) have a fundamental inadequacy that is not at all evident from the derivation we gave. The defect emerges if we return to the exact  $N$ -electron Schrödinger equation and cast it into the equivalent variational form,<sup>7</sup> which asserts that a solution to  $H\Psi = E\Psi$  is given by any state  $\Psi$  that makes stationary the quantity:

$$\langle H \rangle_{\Psi} = \frac{(\Psi, H\Psi)}{(\Psi, \Psi)}, \quad (17.8)$$

where

$$(\Psi, \Phi) = \sum_{s_1} \cdots \sum_{s_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^*(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N) \Phi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N). \quad (17.9)$$

In particular, the ground-state wave function is that  $\Psi$  that minimizes (17.8). This property of the ground state is frequently exploited to construct approximate ground states by minimizing (17.8) not over all  $\Psi$ , but over a limited class of wave functions chosen to have a more tractable form.

It can be shown<sup>8</sup> that the Hartree equations (17.7) follow from minimizing (17.8) over all  $\Psi$  of the form:

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) = \psi_1(\mathbf{r}_1 s_1) \psi_2(\mathbf{r}_2 s_2) \cdots \psi_N(\mathbf{r}_N s_N), \quad (17.10)$$

where the  $\psi_i$  are a set of  $N$  orthonormal one-electron wave functions. Thus the Hartree equations give the best approximation to the full  $N$ -electron wave function that can be represented as a simple product of one-electron levels.

The wave function (17.10), however, is incompatible with the Pauli principle, which requires the sign of  $\Psi$  to change when any two of its arguments are interchanged:<sup>9</sup>

$$\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_i s_i, \dots, \mathbf{r}_j s_j, \dots, \mathbf{r}_N s_N) = -\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_j s_j, \dots, \mathbf{r}_i s_i, \dots, \mathbf{r}_N s_N). \quad (17.11)$$

Equation (17.11) cannot be satisfied for the product form (17.10) unless  $\Psi$  vanishes identically.

The simplest generalization of the Hartree approximation that incorporates the antisymmetry requirement (17.11) is to replace the trial wave function (17.10) by a

<sup>7</sup> See Appendix G. The discussion there is for the one-electron Schrödinger equation, but the general case is, if anything, simpler.

<sup>8</sup> We leave this as a straightforward exercise (Problem 1) for the reader.

<sup>9</sup> The antisymmetry of the  $N$ -electron wave function is the fundamental manifestation of the Pauli principle. The alternative statement of the principle, that no one-electron level can be multiply occupied, can only be formulated in an independent electron approximation. There it follows directly from the fact that (17.13) must vanish if any  $\psi_i = \psi_j$ . The Hartree state (17.10) is consistent (though not, like (17.13), automatically so) with the prohibition on multiple occupation, provided that no two  $\psi_i$  are the same. However, it fails the more fundamental test of antisymmetry.

*Slater determinant* of one-electron wave functions. This is a linear combination of the product (17.10) and all other products obtainable from it by permutation of the  $\mathbf{r}_j s_j$  among themselves, added together with weights  $+1$  or  $-1$  so as to guarantee condition (17.11):

$$\Psi = \psi_1(\mathbf{r}_1 s_1) \psi_2(\mathbf{r}_2 s_2) \dots \psi_N(\mathbf{r}_N s_N) - \psi_1(\mathbf{r}_2 s_2) \psi_2(\mathbf{r}_1 s_1) \dots \psi_N(\mathbf{r}_N s_N) + \dots \quad (17.12)$$

This antisymmetrized product can be written compactly as the determinant of an  $N \times N$  matrix:<sup>10</sup>

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) = \begin{vmatrix} \psi_1(\mathbf{r}_1 s_1) \psi_1(\mathbf{r}_2 s_2) \dots \psi_1(\mathbf{r}_N s_N) \\ \psi_2(\mathbf{r}_1 s_1) \psi_2(\mathbf{r}_2 s_2) \dots \psi_2(\mathbf{r}_N s_N) \\ \vdots \\ \psi_N(\mathbf{r}_1 s_1) \psi_N(\mathbf{r}_2 s_2) \dots \psi_N(\mathbf{r}_N s_N) \end{vmatrix}. \quad (17.13)$$

With a little bookkeeping (Problem 2) it can be shown that if the energy (17.8) is evaluated in a state of the form (17.13), with orthonormal single electron wave functions  $\psi_1 \dots \psi_N$ , then the result is:

$$\begin{aligned} \langle H \rangle_\Psi &= \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 + U^{\text{ion}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) \\ &\quad + \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2 \\ &\quad - \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \delta_{s_i s_j} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}). \end{aligned} \quad (17.14)$$

Notice that the last term in (17.14) is negative and involves the product  $\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}')$  in place of the usual one-electron combination  $|\psi_i(\mathbf{r})|^2$ . Minimizing (17.14) with respect to the  $\psi_i^*$  (Problem 2) leads to a generalization of the Hartree equations known as the Hartree-Fock equations:

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) + U^{\text{ion}}(\mathbf{r}) \psi_i(\mathbf{r}) + U^{\text{el}}(\mathbf{r}) \psi_i(\mathbf{r}) \\ - \sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \psi_j(\mathbf{r}) \delta_{s_i s_j} = \varepsilon_i \psi_i(\mathbf{r}), \end{aligned} \quad (17.15)$$

where  $U^{\text{el}}$  is defined in (17.4) and (17.6).

These equations differ from the Hartree equations (17.7) by an additional term on the left side, known as the *exchange term*. The complexity introduced by the exchange term is considerable. Like the self-consistent field  $U^{\text{el}}$  (often referred to as the *direct term*) it is nonlinear in  $\psi$ , but unlike the direct term it is not of the form  $V(\mathbf{r})\psi(\mathbf{r})$ . Instead, it has the structure  $\int V(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}'$ —i.e., it is an integral operator. As a result, the Hartree-Fock equations are in general quite intractable. The one exception is the free electron gas. When the periodic potential is zero (or constant)

<sup>10</sup> Since a determinant changes sign when any two columns are interchanged, this insures that the condition (17.11) holds.

the Hartree-Fock equations can be solved exactly by choosing the  $\psi_i$  to be a set of orthonormal plane waves.<sup>11</sup> Although the case of free electrons has dubious bearing on the problem of electrons in a real metal, the free electron solution suggests a further approximation that makes the Hartree-Fock equations in a periodic potential more manageable. We therefore comment briefly on the free electron case.

## HARTREE-FOCK THEORY OF FREE ELECTRONS

The familiar set of free electron plane waves,

$$\psi_i(\mathbf{r}) = \left( \frac{e^{i\mathbf{k}_i \cdot \mathbf{r}}}{\sqrt{V}} \right) \times \text{spin function}, \quad (17.16)$$

in which each wave vector less than  $k_F$  occurs twice (once for each spin orientation) in the Slater determinant, gives a solution to the Hartree-Fock equation for free electrons. For if plane waves are indeed solutions, then the electronic charge density that determines  $U^{\text{el}}$  will be uniform. However, in the free electron gas the ions are represented by a uniform distribution of positive charge with the same density as the electronic charge. Hence the potential of the ions is precisely canceled by the direct term:  $U^{\text{ion}} + U^{\text{el}} = 0$ . Only the exchange term survives, which is easily evaluated by writing the Coulomb interaction in terms of its Fourier transform<sup>12</sup>:

$$\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} = 4\pi e^2 \frac{1}{V} \sum_{\mathbf{q}} \frac{1}{q^2} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \rightarrow 4\pi e^2 \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')}. \quad (17.17)$$

If (17.17) is substituted into the exchange term in (17.15) and the  $\psi_i$  are all taken to be plane waves of the form (17.16), then the left side of (17.15) assumes the form

$$\varepsilon(\mathbf{k}_i)\psi_i, \quad (17.18)$$

where

$$\begin{aligned} \varepsilon(\mathbf{k}) &= \frac{\hbar^2 k^2}{2m} - \frac{1}{V} \sum_{\mathbf{k}' < k_F} \frac{4\pi e^2}{|\mathbf{k} - \mathbf{k}'|^2} = \frac{\hbar^2 k^2}{2m} - \int_{\mathbf{k}' < k_F} \frac{d\mathbf{k}'}{(2\pi)^3} \frac{4\pi e^2}{|\mathbf{k} - \mathbf{k}'|^2} \\ &= \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right), \end{aligned} \quad (17.19)$$

and

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|. \quad (17.20)$$

This shows that plane waves do indeed solve (17.15), and that the energy of the one-electron level with wave vector  $\mathbf{k}$  is given by (17.19). The function  $F(x)$  is plotted in Figure 17.1a, and the energy  $\varepsilon(\mathbf{k})$  in Figure 17.1b.

Several features of the energy (17.19) deserve comment:

1. Although the Hartree-Fock one-electron levels continue to be plane waves, the energy of an electron in the level  $e^{i\mathbf{k} \cdot \mathbf{r}}$  is now given by  $\hbar^2 k^2/2m$  plus a term describing

<sup>11</sup> More complicated solutions, known as spin density waves, are also possible (Chapter 32).

<sup>12</sup> See Problem 3.