

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):

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

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

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

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  $\psi_1 \cdots \psi_N$ , then the result is:

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

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:

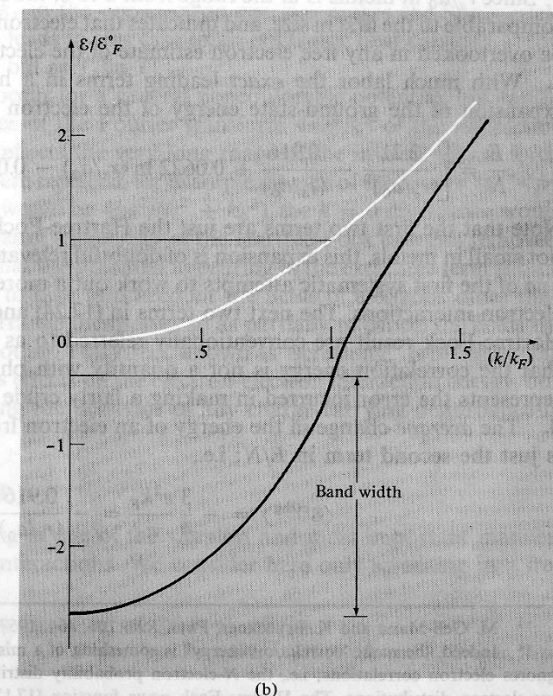
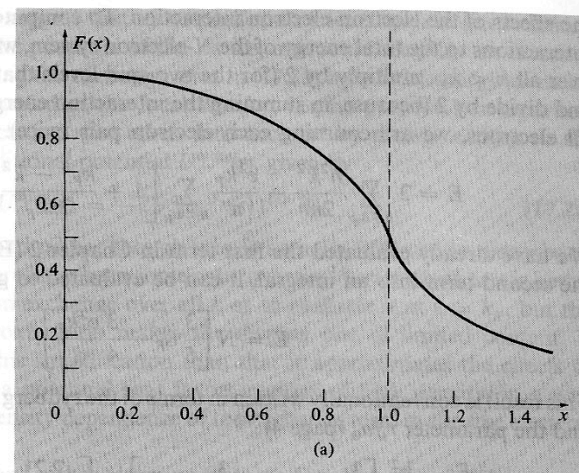
1. Although the Hartree-Fock one-electron levels continue to be plane waves, the energy of an electron in the level  $e^{i\mathbf{k} \cdot \mathbf{r}}$  is now given by  $\hbar^2 k^2/2m$  plus a term describing

Figure 17.1

(a) A plot of the function  $F(x)$ , defined by Eq. (17.20). Although the slope of this function diverges at  $x = 1$ , the divergence is logarithmic, and cannot be revealed by changing the scale of the plot. At large values of  $x$  the behavior is  $F(x) \rightarrow 1/3x^2$ . (b) The Hartree-Fock energy (17.19) may be written

$$\frac{\varepsilon_k}{\varepsilon_F^0} = \left[ x^2 - 0.663 \left( \frac{r_s}{a_0} \right) F(x) \right],$$

where  $x = k/k_F$ . This function is plotted here for  $r_s/a_0 = 4$ , and may be compared with the free electron energy (white line). Note that in addition to depressing the free electron energy substantially, the exchange term has led to a considerable increase in the bandwidth (in these units from 1 to 2.33), an effect not corroborated by experiments such as soft X-ray emission or photoelectron emission from metals, which purport to measure such bandwidths.



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

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

the effects of the electron-electron interaction. To compute the contribution of these interactions to the total energy of the  $N$ -electron system, we must sum this correction over all  $k < k_F$ , multiply by 2 (for the two spin levels that are occupied for each  $k$ ), and divide by 2 (because, in summing the interaction energy of a given electron over all electrons, we are counting each electron pair twice). In this way we find that

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{\pi} \sum_{k < k_F} \left[ 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]. \quad (17.21)$$

We have already evaluated the first term in Chapter 2 (Eq. (2.31)). If we transform the second term into an integral, it can be evaluated to give:

$$E = N \left[ \frac{3}{5} \varepsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right]. \quad (17.22)$$

This result is conventionally written in terms of the rydberg ( $e^2/2a_0 = 1 \text{ Ry} = 13.6 \text{ eV}$ ) and the parameter  $r_s/a_0$  (page 4):

$$\frac{E}{N} = \frac{e^2}{2a_0} \left[ \frac{3}{5} (k_F a_0)^2 - \frac{3}{2\pi} (k_F a_0) \right] = \left[ \frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \right] \text{ Ry}. \quad (17.23)$$

Since  $r_s/a_0$  in metals is in the range from 2 to 6, the second term in (17.23) is quite comparable to the first in size, and indicates that electron-electron interactions cannot be overlooked in any free electron estimate of the electronic energy of a metal.

2. With much labor the *exact* leading terms in a high-density (i.e., small  $r_s/a_0$ ) expansion of the ground-state energy of the electron gas have been calculated:<sup>13</sup>

$$\frac{E}{N} = \left[ \frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} + 0.0622 \ln(r_s/a_0) - 0.096 + O(r_s/a_0) \right] \text{ Ry}. \quad (17.24)$$

Note that the first two terms are just the Hartree-Fock result (17.23). Since  $r_s/a_0$  is not small in metals, this expansion is of doubtful relevance, but its derivation marked one of the first systematic attempts to work out a more accurate theory of electron-electron interactions. The next two terms in (17.24) and all other corrections to the Hartree-Fock result are conventionally referred to as the *correlation energy*. Note that the correlation energy is not a quantity with physical significance; it merely represents the error incurred in making a fairly crude first-order approximation.<sup>14</sup>

3. The *average* change in the energy of an electron from  $\hbar^2 k^2/2m$  due to exchange is just the second term in  $E/N$ ; i.e.,

$$\langle \varepsilon^{\text{exch}} \rangle = -\frac{3}{4} \frac{e^2 k_F}{\pi} = -\frac{0.916}{(r_s/a_0)} \text{ Ry}. \quad (17.25)$$

<sup>13</sup> M. Gell-Mann and K. Brueckner, *Phys. Rev.* **106**, 364 (1957).

<sup>14</sup> Indeed, the name 'correlation energy' is something of a misnomer. The Hartree approximation ignores electron correlations; i.e., the  $N$ -electron probability distribution factors into a product of  $N$  one-electron distributions. The Hartree-Fock wave function (17.13) does not so factor; i.e., electron correlations are introduced at this next level of approximation. Nevertheless the "correlation energy" is defined to exclude the exchange contribution, containing only further corrections beyond that provided by Hartree-Fock theory.

This form led Slater<sup>15</sup> to suggest that in nonuniform systems and, in particular, in the presence of the periodic potential of the lattice, one could simplify the Hartree-Fock equations by replacing the exchange term in (17.15) by a local energy given by twice (17.25) with  $k_F$  evaluated at the local density; i.e., he proposed an equation in which the effect of exchange was taken into account by merely adding to the Hartree term  $U^{\text{el}}(\mathbf{r})$  an additional potential  $U^{\text{exch}}(\mathbf{r})$ , given by

$$U^{\text{exch}}(\mathbf{r}) = -2.95(a_0^3 n(\mathbf{r}))^{1/3} \text{ Ry}. \quad (17.26)$$

This procedure, gross and *ad hoc* though it is, is actually followed in many band structure calculations. There have been some controversies<sup>16</sup> over whether it is better to average the free electron exchange over all  $k$  or to evaluate it at  $k = k_F$ , but the crude nature of the approximation makes the dispute one of limited content. It is hard to say more for this simplification than that it approximates the effects of exchange by introducing a potential that favors regions of high density, in a way that roughly mimics the density dependence of the exchange term in the free electron energy density.

4. Equation (17.19) has one rather alarming feature: The derivative  $\partial \varepsilon / \partial k$  becomes logarithmically infinite<sup>17</sup> at  $k = k_F$ . Since  $(1/\hbar) \partial \varepsilon / \partial k|_{k=k_F}$  is precisely the velocity of those electrons most important for metallic properties, this is an unsettling result. A singularity at  $k = k_F$  in the one-electron energies makes the Sommerfeld expansion (2.70) invalid, and leads in this case to an electronic heat capacity at low temperatures going not as  $T$ , but as  $T/|\ln T|$ .

The singularity does not occur for a general noncoulombic potential, but can be traced back to the divergence of the Fourier transform  $4\pi e^2/k^2$  of the interaction  $e^2/r$ , at  $k = 0$ . This in turn reflects the very long range of the inverse square force. If the Coulomb interaction were replaced, for example, by one of the form  $e^2(e^{-k_0 r}/r)$ , then its Fourier transform<sup>18</sup> would be  $4\pi e^2/(k^2 + k_0^2)$ , the  $k = 0$  divergence would be eliminated, and the unphysical singularity of the Hartree-Fock energies removed. It can be argued (see below) that the potential appearing in the exchange term should be modified in just this way to take into account the fields of electrons other than the two at  $\mathbf{r}$  and  $\mathbf{r}'$ , which rearrange themselves so as partially to cancel the fields the two electrons exert on one another. This effect, known as "screening," is of fundamental importance not only for its effects on the electron-electron interaction energy, but, more generally, in determining the behavior of any charge-carrying disturbance in a metal.<sup>19</sup>

## SCREENING (GENERAL)

The phenomenon of screening is one of the simplest and most important manifestations of electron-electron interactions. We consider here only screening in a free

<sup>15</sup> J. C. Slater, *Phys. Rev.* **81**, 385 (1951); **82**, 538 (1951); **91**, 528 (1953).

<sup>16</sup> See, for example, W. Kohn and L. J. Sham, *Phys. Rev.*, **140**, A1193 (1965), and R. Gaspar, *Acta. Phys. Acad. Sci. Hung.* **3**, 263 (1954).

<sup>17</sup> See Figure 17.1.

<sup>18</sup> Problem 3.

<sup>19</sup> The ions in a metal are an important case and will be referred to in the context of dynamic screening in Chapter 26.