

The Hartree Approximation

The energy eigenvalue problem for an atom with Z electrons has the form

$$\left[\sum_{i=1}^Z \left(\frac{\mathbf{p}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i>j} \sum_j \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right] \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) \quad (14A-1)$$

and is a partial differential equation in $3Z$ dimensions. For light atoms it is possible to solve such an equation on a computer, but such solutions are only meaningful to the expert. We shall base our discussion of atomic structure on a different approach. As in the example of helium ($Z = 2$), it is both practical and enlightening to treat the problem as one involving Z independent electrons in a single potential, and to consider the electron–electron interaction later. Perturbation theory turned out to be adequate for $Z = 2$, but as the number of electrons increases, the shielding effects, not taken into account by first-order perturbation theory, become more and more important. The variational principle discussed at the end of Chapter 14 had the virtue of maintaining the single-particle picture, while at the same time yielding single-particle functions that incorporate the screening corrections.

To apply the variational principle, let us assume that the trial wave function is of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_Z(\mathbf{r}_Z) \quad (14A-2)$$

Each of the functions is normalized to unity. If we calculate the expectation value of H in this state, we obtain

$$\langle H \rangle = \sum_{i=1}^Z \int d^3r_i \phi_i^*(\mathbf{r}_i) \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) \phi_i(\mathbf{r}_i) + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \sum_j \frac{|\phi_i(\mathbf{r}_i)|^2 |\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (14A-3)$$

The procedure of the variational principle is to pick the $\phi_i(\mathbf{r}_i)$ such that $\langle H \rangle$ is a minimum. If we were to choose the $\phi_i(\mathbf{r}_i)$ to be hydrogenlike wave functions, with a different Z_i for each electron (and with each electron in a different quantum state to satisfy the Pauli exclusion principle), we would get a set of equations analogous to (14-47) and (14-48). A more general approach is that due to Hartree. If the $\phi_i(\mathbf{r}_i)$ were the single-particle wave functions that minimized $\langle H \rangle$, then an alteration in these functions by an infinitesimal amount

$$\phi_i(\mathbf{r}_i) \rightarrow \phi_i(\mathbf{r}_i) + \lambda f_i(\mathbf{r}_i) \quad (14A-4)$$

should only change $\langle H \rangle$ by a term of order λ^2 . The alterations must be such that

$$\int d^3r_i |\phi_i(\mathbf{r}_i) + \lambda f_i(\mathbf{r}_i)|^2 = 1$$

that is, to first order in λ ,

$$\int d^3\mathbf{r}_i [\phi_i^*(\mathbf{r}_i) f_i(\mathbf{r}_i) + \phi_i(\mathbf{r}_i) f_i^*(\mathbf{r}_i)] = 0 \quad (14A-5)$$

Let us compute the terms linear in λ that arise when (14A-4) is substituted into (14A-3). Term by term, we have

$$\begin{aligned} & \sum_i \int d^3\mathbf{r}_i \left[\phi_i^*(\mathbf{r}_i) \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) \lambda f_i(\mathbf{r}_i) + \lambda f_i^*(\mathbf{r}_i) \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) \phi_i(\mathbf{r}_i) \right] \\ & = \lambda \sum_i \int d^3\mathbf{r}_i \left\{ f_i(\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \nabla_i^2 \phi_i^*(\mathbf{r}_i) \right] + f_i^*(\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \nabla_i^2 \phi_i(\mathbf{r}_i) \right] \right\} \end{aligned} \quad (14A-6)$$

To obtain this we have integrated by parts two times, and used the fact that $f_i(\mathbf{r}_i)$ must vanish at infinity in order to be an acceptable variation of a square integrable function. Next we have

$$-\lambda \sum_i \int d^3\mathbf{r}_i \left[f_i^*(\mathbf{r}_i) \frac{Ze^2}{4\pi\epsilon_0 r_i} \phi_i(\mathbf{r}_i) + \phi_i^*(\mathbf{r}_i) \frac{Ze^2}{4\pi\epsilon_0 r_i} f_i(\mathbf{r}_i) \right] \quad (14A-7)$$

and finally

$$\frac{\lambda e^2}{4\pi\epsilon_0} \sum_{i>j} \sum_j \int d^3\mathbf{r}_i \int d^3\mathbf{r}_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \{ [f_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_i) + f_i(\mathbf{r}_i) \phi_i^*(\mathbf{r}_i)] |\phi_j(\mathbf{r}_j)|^2 + (i \leftrightarrow j) \} \quad (14A-8)$$

We cannot just set the sum of these three terms equal to zero because the $f_i(\mathbf{r}_i)$ are constrained by (14A-5). The proper way to account for the constraint is by the use of Lagrange multipliers; that is, we multiply each of the constraining relations (14A-5) by a constant (the ‘‘multiplier’’) and add the sum to our three terms. The total can then be set equal to zero, since the constraints on the $f_i(\mathbf{r}_i)$ are now taken care of. With a certain amount of notational foresight we label the multipliers $-\epsilon_i$, and thus get

$$\begin{aligned} & \sum_i \int d^3\mathbf{r}_i \left\{ f_i^*(\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \nabla_i^2 \phi_i(\mathbf{r}_i) - \frac{Ze^2}{4\pi\epsilon_0 r_i} \phi_i(\mathbf{r}_i) \right] \right\} \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \sum_j \iint d^3\mathbf{r}_i d^3\mathbf{r}_j f_i^*(\mathbf{r}_i) \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \phi_i(\mathbf{r}_i) \\ & - \epsilon_i \int d^3\mathbf{r}_i f_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_i) + \text{complex conjugate terms} = 0 \end{aligned} \quad (14A-9)$$

In deriving the second line, first we converted the double sum $\sum_{i>j} \sum_j$ into $(1/2) \sum_{i \neq j} \sum_j$, which is unrestricted except for the requirement that $i \neq j$, and then used the fact that the integrand in (14A-8) is symmetric in i and j . Now $f_i(\mathbf{r}_i)$ is completely unrestricted, so that we may treat $f_i(\mathbf{r}_i)$ and $f_i^*(\mathbf{r}_i)$ as completely independent (each one has a real and an imaginary part). Furthermore, other than being square integrable, they are completely arbitrary, so that for (14A-5) to hold, the coefficients of $f_i(\mathbf{r}_i)$ and $f_i^*(\mathbf{r}_i)$ must separately vanish at each point \mathbf{r}_i , since we are allowed to make local variations in the functions $f_i(\mathbf{r}_i)$ and $f_i^*(\mathbf{r}_i)$. We are thus led to the condition that

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3\mathbf{r}_j \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \phi_i(\mathbf{r}_i) = \epsilon_i \phi_i(\mathbf{r}_i) \quad (14A-10)$$

and the complex conjugate relation.

This equation has a straightforward interpretation: It is an energy eigenvalue equation for electron “ i ” located at \mathbf{r}_i , moving in a potential

$$V_i(\mathbf{r}_i) = -\frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r_j \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (14A-11)$$

that consists of an attractive Coulomb potential due to a nucleus of charge Z , and a repulsive contribution due to the charge density of all the other electrons. We do not, of course, know the charge densities

$$\rho_j(\mathbf{r}_j) = -e|\phi_j(\mathbf{r}_j)|^2$$

of all the other electrons, so that we must search for a *self-consistent* set of $\phi_i(\mathbf{r}_i)$, in the sense that their insertion in the potential leads to eigenfunctions that reproduce themselves. The equation (14A-10) is a rather complicated integral equation, but it is at least an equation in three dimensions (we can replace the variable \mathbf{r}_i by \mathbf{r}), and that makes numerical work much easier. An even greater simplification occurs when $V_i(\mathbf{r})$ is replaced by its angular average

$$V_i(r) = \int \frac{d\Omega}{4\pi} V_i(\mathbf{r}) \quad (14A-12)$$

for then the self-consistent potential becomes central, and the self-consistent solutions can be decomposed into angular and radial functions; that is, they will be functions that can be labeled by n_i, l_i, m_i, σ_i , with the last label referring to the spin state ($s_{iz} = \pm 1/2$).

The trial wave function (14A-2) does not take into account the exclusion principle. The latter plays an important role, since if all the electrons could be in the same quantum state, the energy would be minimum with all the electrons in the $n = 1, l = 0$ “orbital.” Atoms do not have such a simple structure. To take the exclusion principle into account, we add to the *Ansatz* represented by (14A-2) the rule: *Every electron must be in a different state*, if the spin states are included in the labeling. A more sophisticated way of doing this automatically is to replace (14A-2) by a trial wave function that is a *Slater determinant* [cf. Eq. (13-39)]. The resulting equations differ from (14A-10) by the addition of an exchange term. The new Hartree-Fock equations have eigenvalues that turn out to differ by 10–20 percent from those obtained using Hartree equations supplemented by the condition arising from the exclusion principle. It is a little easier to talk about the physics of atomic structure in terms of the Hartree picture, so we will not discuss the Hartree-Fock equations.

The potential (14A-12) no longer has the $1/r$ form, and thus the degeneracy of all states with a given n and $l \leq n - 1$ is no longer present. We may expect, however, that for low Z at least, the splitting for different l values for a given n will be smaller than the splitting between different n -values, so that electrons placed in the orbitals $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, \dots$ will be successively less strongly bound. Screening effects will accentuate this: Whereas s orbitals do overlap the small r region significantly, and thus feel the full nuclear attraction, the p -, d -, f -... orbitals are forced out by the centrifugal barrier, and feel less than the full attraction. This effect is so strong that the energy of the $3d$ electrons is very close to that of the $4s$ electrons, so that the anticipated ordering is sometimes disturbed. The same is true for the $4d$ and $5s$ electrons, the $4f$ and $6s$ electrons, and so on. The dominance of the l -dependence over the n -dependence becomes more important as we go to larger Z -values, as we shall see in our discussion of the *periodic table*.

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The number of electrons that can be placed in orbitals with a given (n, l) is $2(2l + 1)$, since there are two spin states for given m -value. When all these $2(2l + 1)$ states are filled, we speak of the *closing of a shell*. The charge density for a closed shell has the form

$$-e \sum_{m=-l}^l |R_{nl}(r)|^2 |Y_{lm}(\theta, \phi)|^2 \quad (14A-13)$$

and this is spherically symmetric because of the property of spherical harmonics that

$$\sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 = \frac{2l + 1}{4\pi} \quad (14A-14)$$

The Building-Up Principle

In this section we discuss the building up of atoms by the addition of more and more electrons to the appropriate nucleus, whose only role, to good approximation, is to provide the positive charge Ze .

Hydrogen ($Z = 1$) There is only one electron, and the ground-state configuration is $(1s)$. The ionization energy is 13.6 eV, and the amount of energy needed to excite the first state above the ground state is 10.2 eV. The radius of the atom is 0.5 Å, and its spectroscopic description is ${}^2S_{1/2}$.

Helium ($Z = 2$) The lowest two-electron state, as we saw in Chapter 14, is one in which both electrons are in the $(1s)$ orbital. We denote this configuration by $(1s)^2$. In spectroscopic notation, the ground state is an $l = 0$ spin singlet state, 1S_0 because the exchange effect favors it. The total binding energy is 79 eV. After one electron is removed, the remaining electron is in a $(1s)$ orbit about a $Z = 2$ nucleus. Thus its binding energy is $13.6Z^2$ eV = 54.4 eV, and the energy required to remove the first electron, the *ionization energy*, is $79.0 - 54.4 = 24.6$ eV. A rough estimate of the energy of the first excited state, with configuration $(1s)(2s)$, is $-13.6Z^2 - 13.6(Z - 1)^2/n^2 \approx -58$ eV for $Z = 2$ and $n = 2$. This expression takes into account shielding in the second term. Thus the excitation energy is 79 eV $- 58$ eV ≈ 21 eV.¹ In any reaction with another substance, about 20 eV is required for a rearrangement of the electrons, and thus helium is chemically very inactive. This property is shared by all atoms whose electrons form closed shells, but the energy required is particularly large for helium.

Lithium ($Z = 3$) The exclusion principle forbids a $(1s)^3$ configuration, and the lowest energy electron configuration is $(1s)^2(2s)$. We are thus adding an electron to a closed shell, and since the shell is in a 1S_0 state, the spectroscopic description of the ground state is ${}^2S_{1/2}$, just as for hydrogen. If the screening were perfect, we should expect a binding energy of -3.4 eV (since $n = 2$). The screening is not perfect, especially since the outer *valence electron* being in an s -state, its wave function has a reasonable overlap with nucleus at $r = 0$. We can estimate the effective Z from the measured ionization energy of 5.4 eV, and it is $Z^* = 1.3$. It takes very little energy to excite the lithium atom. The six $(2p)$ electronic states lie just a little above the $(2s)$ state, and these $(2p)$ states, when occupied, make the atom chemically active (see our more extended discussion of carbon). Lithium, like other elements that have one electron outside a closed shell, is a very active element.

¹This is a crude estimate that ignores the electron–electron repulsion and exchange effects. The difference between the 21 eV and the 24.6 eV is the 4–5 eV that will be released when the excited atom decays to its ground state. (See Fig. 14-2*b*.)

Beryllium ($Z = 4$) The natural place for the fourth electron to go is into the second space in the ($2s$) orbital, so that the configuration is $(1s)^2(2s)^2$. We again have a closed shell and the spectroscopic description is 1S_0 . As far as the energy is concerned, the situation is very much like that of helium. If the screening were perfect, we might expect a binding energy like that of helium, since the inner electrons reduce the effective Z to something like $Z = 2$. Since $n = 2$, we would expect an ionization energy of $24.6/n^2 = 6.2$ eV. The shielding situation is somewhat like that for lithium, and if we make a guess that, as in lithium, the binding energy is increased by about 50 percent, we get approximately 9 eV. The experimental value is 9.3 eV. Although the shell is closed, the excitation of one of the electrons to a ($2p$) orbital does not cost much energy. Thus, in the presence of another element a rearrangement of electrons may yield enough energy to break up the closed shell. We therefore expect beryllium not to be as inert as helium. It is generally true that atoms in which the outer electrons have their spins “paired up” into singlet states are less reactive.

Boron ($Z = 5$) After the closing of the shell, the fifth electron can either go into a ($3s$) orbital or into a ($2p$) orbital. The latter is lower in energy, and it is the ($2p$) shell that begins to fill up, starting with boron. The configuration is $(1s)^2(2s)^2(2p)$, and the spectroscopic description of the state is $^2P_{1/2}$. This deserves comment: If we add spin $1/2$ to an $l = 1$ orbital state, we may have $J = 3/2$ or $1/2$. These states are split by a spin-orbit interaction

$$\frac{1}{2m_e^2c^2} \mathbf{L} \cdot \mathbf{S} \frac{1}{r} \frac{dV(r)}{dr} = \frac{\hbar^2}{4m_e^2c^2} [J(J+1) - L(L+1) - 3/4] \frac{1}{r} \frac{dV(r)}{dr} \quad (14B-1)$$

and the form of this leads to the higher J value having a higher energy, because the expectation value of $(1/r)(dV/dr)$ is still positive, even though it is no longer equal to the value given in (12-16). This conclusion depends on the degree to which the shell is filled, as specifically given by *Hund's rules*. These will be discussed below. The ionization energy is 8.3 eV. This meets the expectation that the value should be somewhat lower than that for beryllium, since the $2p$ state energy is somewhat higher than that of the $2s$ orbital.

Carbon ($Z = 6$) The configuration for carbon is $(1s)^2(2s)^2(2p)^2$. The second electron could be in the same p -state as the first electron, with the two of them making an up-down spin pair. It is, however, advantageous for the second to stay out of the way of the first electron, thus lowering the repulsion between the electrons. It can do so because the possible $l = 1$ states Y_{11} , Y_{10} , Y_{1-1} allow for the linear combinations $\sin \theta \cos \phi$, $\sin \theta \sin \phi$, and $\cos \theta$, which are aligned along the x -, y -, and z -axes, respectively (Fig. 14B-1). When two electrons go into orthogonally aligned arms, the overlap is minimized and the repulsion is reduced. The electrons are in different spatial states, so that their spins do not have to be antiparallel. One might expect carbon to be divalent. This is not so, because of the subtleties that arise from close-lying energy levels. It costs very little energy to promote one of the ($2s$) electrons into the third unoccupied $l = 1$ state. The configuration $(1s)^2(2s)(2p)^3$ has four “unpaired” electrons, and the gain in energy from the formation of four bonds with other atoms more than makes up for the energy needed to promote the ($2s$) electron. The reduction in the repulsion leads to a somewhat larger ionization energy than that for boron, 11.3 eV. The spectroscopic description of the ground state is 3P_0 . We can have a total spin of 0 or 1 for the two $2p$ electrons, and, since we are adding two $l = 1$ states, the total orbital angular momentum can be 0, 1, or 2. Of the various states, 1S_0 , $^3P_{2,1,0}$, and 1D_2 , the state of higher spin has the lower energy (cf. our discussion of helium) and by another of *Hund's rules*, the 3P_0 state has the lowest energy.

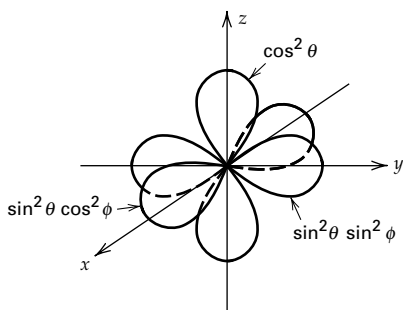


Figure 14B-1 Orthogonal distributions of electronic clouds in the $l = 1$ state.

Nitrogen ($Z = 7$) Here the configuration is $(1s)^2(2s)^2(2p)^3$, sometimes described as $(2p)^3$ for brevity (the closed shells and subshells are omitted). The three electrons can all be in nonoverlapping p -states, and thus we expect the increase in ionization energy to be the same as the increase from boron to carbon. This is in agreement with the measured value of 14.5 eV.

Oxygen ($Z = 8$) The configuration may be abbreviated to $(2p)^4$, and the shell is more than half full. Since there are four electrons, it appears as if the determination of the ground-state spectroscopic state would be very difficult. We can, however, look at the shell in another way. We know that when two more electrons are added to make a $(2p)^6$ configuration, then the shell is filled, and the total state has $L = S = 0$. We can thus think of oxygen as having a closed $2p$ shell with two *holes* in it. These holes are just like anti-electrons, and we can look at two-hole configurations. These will be the same as two-electron configurations, since the holes also have spin $1/2$. Thus, as with carbon, the possible states consistent with the antisymmetry of the two-fermion (two-hole) wave function are 1S , 3P , 1D , and the four electrons must be in the same states, since they, together with the two-hole system, give $S = 0$, $L = 0$. The highest spin is $S = 1$, and thus we must have a 3P state. Hund's rule, which will be discussed in the next section, yields the 3P_2 state. When the fourth electron is added to the nitrogen configuration, it must go into an orbital with an m -value already occupied. Thus two of the electron wave functions overlap, and this raises the energy because of the repulsion. It is therefore not surprising that the ionization energy drops to the value of 13.6 eV.

Fluorine ($Z = 9$) Here the configuration is $(2p)^5$. The monotonic increase in the ionization energy resumes, with the experimental value of 17.4 eV. Fluorine is chemically very active, because it can "accept" an electron to form a closed shell $(2p)^6$, which is very stable. Since the addition of a single electron with $s = 1/2$ and $l = 1$ yields a 1S_0 state, the shell with the hole in it must have $s = 1/2$ and $l = 1$. It is therefore a 2P state, and by Hund's rule, as we shall see, the state is $^2P_{3/2}$.

Neon ($Z = 10$) With $Z = 10$ the $(2p)$ shell is closed, and all electrons are paired off. The ionization energy is 21.6 eV, continuing the monotonic trend. Here, as in helium, the first available state that an electron can be excited into has a higher n value, and thus it takes quite a lot of energy to perturb the atom. Neon, like helium, is an inert gas.

At this point, the addition of another electron requires putting it in an orbit with a higher n value ($n = 3$), and thus neon marks the end of a *period* in the periodic table, as did helium. In neon, as in helium, the first available state into which an electron can be excited has a higher n -value, so that it takes quite a lot of energy to perturb the atom. Neon shares with helium the property of being an *inert gas*.

The next period again has eight elements in it. First the ($3s$) shell is filled, with sodium ($Z = 11$) and magnesium ($Z = 12$), and then the $3p$ shell, which includes, in order, aluminum ($Z = 13$), silicon ($Z = 14$), phosphorus ($Z = 15$), sulphur ($Z = 16$), chlorine ($Z = 17$) and, closing the shell, argon ($Z = 18$). These elements are chemically very much like the series: lithium, . . . , neon, and the spectroscopic descriptions of the ground states are the same. The only difference is that, since $n = 3$, the ionization energies are somewhat smaller, as can be seen from the periodic table at the end of this supplement.

It might appear a little strange that the period ends with argon, since the ($3d$) shell, accommodating ten elements, remains to be filled. The fact is that the self-consistent potential is not of the $1/r$ form, and the intrashell splitting here is sufficiently large that the ($4s$) state lies lower than the ($3d$) state, though not by much. Hence a competition develops, and in the next period we have ($4s$), ($4s$)², ($4s$)²($3d$), ($4s$)²($3d$)², ($4s$)²($3d$)³, ($4s$)($3d$)⁵, ($4s$)²($3d$)⁵, ($4s$)²($3d$)⁶, ($4s$)²($3d$)⁷, ($4s$)²($3d$)⁸, ($4s$)($3d$)¹⁰, ($4s$)²($3d$)¹⁰ and then the $4p$ shell gets filled until the period ends with krypton ($Z = 36$). The chemical properties of elements at the beginning and end of this period are similar to those of elements at the beginning and end of other periods. Thus potassium, with the single ($4s$) electron, is an alkali metal, like sodium with its single ($3s$) electron outside a closed shell. Bromine, with the configuration ($4s$)²($3d$)¹⁰($4p$)⁵, has a single hole in a p -shell and thus is chemically like chlorine and fluorine. The series of elements in which the ($3d$) states are being filled all have rather similar chemical properties. The reason for this again has to do with the details of the self-consistent potential. It turns out that the radii of these orbits² are somewhat smaller than those of the ($4s$) electrons, so that when the ($4s$)² shell is filled, these electrons tend to shield the ($3d$) electrons, no matter how many there are, from outside influences. The same effect occurs when the ($4f$) shell is being filled, just after the ($6s$) shell has been filled. The elements here are called the *rare earths*.

Spectroscopic Description of Ground States

In our discussion of the light atoms, we often gave the spectroscopic description of the ground states—for example, ³ P_2 for oxygen, ² $P_{3/2}$ for fluorine, and so on. The knowledge of S , L , and J for the ground states is important, because selection rules allow us to determine these quantities for the excited states of atoms. We referred to *Hund's rules* in the determination of these, and these rules are the subject of this section.

What determines the ground-state quantum numbers is an interplay of spin-orbit coupling and the exchange effect discussed in connection with helium in Chapter 14. For the lighter atoms ($Z < 40$), for which the motion of the electrons is nonrelativistic, the electron–electron repulsion effects are more important than the spin-orbit coupling. This means that it is a fairly good approximation to view L and S as separately good quantum numbers: We add up all the spins to form an S and all the orbital angular momenta of the electrons to form an L , and these are then coupled to obtain a total J . For heavier atoms it is a better approximation to first couple the spin and orbital angular momentum to form a total angular momentum for that electron, and then to couple all of the J 's together. The former case is described as Russell-Saunders coupling, the latter as j - j coupling. For Russell-Saunders coupling, F. Hund summarized the results of

²It is understood that this is just a way of talking about the peaking tendencies of the charge distribution.

various calculations by a set of rules that give the overall quantum numbers of the lowest states. The rules are:

1. The state with largest S lies lowest.
2. For a given value of S , the state with maximum L lies lowest.
3. For a given L and S , if the incomplete shell is not more than half-filled, the lowest state has the minimum value of $J = |L - S|$; if the shell is more than half-filled, the state of lowest energy has $J = L + S$.

In applying these rules we must be careful not to violate the Pauli principle.

The first of these rules is easy to understand: The largest S state is symmetric in all the spins (since it contains the state $S_z = S_{\max}$ for which all the spins are parallel), and thus the spatial wave function is antisymmetric, which minimizes the electron overlap, and thus the expectation value of the repulsive potentials.

The second rule emerges qualitatively from the fact that the higher the L -value, the more lobes the wave function has, as shown in Fig. 8-4. This allows the electrons to stay away from one another, and reduce the effect of the Coulomb repulsion.

The third rule follows from the form of the spin-orbit coupling. Since the expectation value of $[(1/r)(dV/dr)]$ is positive, the perturbation due to the spin-orbit coupling splits the degenerate J states (for a given L and S) and it is clear from (14B-1) that the lowest value of J will give the lowest lying state. Once we get to the point of having a shell that is more than half filled, it is clearer to look at the atom as consisting of a filled shell with a number of holes, as we discussed in our description of oxygen. These holes act as if they had positive charge, and for the spin-orbit interaction of the holes, the sign of $[(1/r)(dV/dr)]$ is reversed. Thus the multiplet is *inverted* and it is the largest value of J that gives the lowest lying state.

Let us illustrate the application of the Hund rules to some atoms, and the need to keep track of the Pauli principle. We shall consider the quantum numbers of carbon $(2p)^2$, oxygen $(2p)^4$, and manganese $(3d)^5$. In the first two cases we have p -states, so that we can draw a set of "shelves" corresponding to $L_z = 1, 0, -1$. The electrons are placed, as far as is possible, on different shelves, to minimize the repulsion. For carbon we place them in $L_z = 1$ and $L_z = 0$ states. By Hund's first rule, the spins will be parallel (strictly speaking they will be in a triplet state) (Fig. 14B-2). Thus we have $S_z = 1$ for the largest possible value, and we get a triplet state. The largest possible value of L_z gives the L value, which is 1. The third rule thus gives $J = |L - S| = 0$, and we have a 3P_0 state. For the $(2p)^4$ case, we fill all three shelves with one electron each, and then put the last electron in the $L_z = 1$ state, for example. The Pauli principle demands that the two electrons in the $L_z = 1$ state form a singlet. Thus only the other two electrons are relevant, and since $S_z = 1$, $S = 1$. The maximum value of $L_z = [2 + 0 + (-1)] = 1$, so that $L = 1$. Now, however, we have more than a half-filled shell, so that $J = L + S = 2$, and oxygen has a 3P_2 ground state.

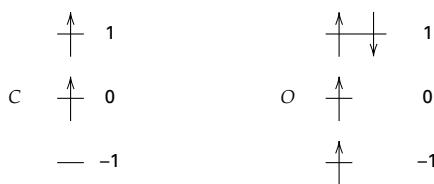


Figure 14B-2 Application of Hund's rules to six electron system.

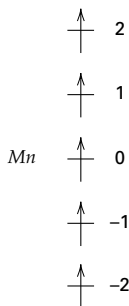


Figure 14B-3 Application of Hund's rules to atom with five valence electrons in d -state.

For manganese the shelves have $L_z = 2, 1, 0, -1, -2$, as shown in Fig. 14B-3. There are five electrons, and thus each of the spaces is filled by one. With the spins parallel we get $S_z = 5/2$, which implies that $S = 5/2$. The total value of $L_z = 0$, and thus we have an S -state. This means that the ground state is an ${}^6S_{5/2}$ state.

Limitations of space prevent us from a more detailed discussion of the periodic table. A few additional comments are, however, in order.

- (a) There is nothing in atomic structure that limits the number of elements. The reason that atoms with $Z \geq 100$ do not occur naturally is that heavy *nuclei* undergo spontaneous fission. If new, superheavy (metastable) nuclei are ever discovered, there will presumably exist corresponding atoms, and it is expected that their structure will conform to the prediction of the building-up approach outlined in this supplement.
- (b) The ionization energies all lie in the vicinity of 5–15 eV. The reason is that in spite of the increasing number of electrons, the outermost electrons “see” a charge that lies in the range $Z = 1-2$. In addition, because of the departures from a point charge distribution, the dependence of the energy is no longer of the $1/n^2$ form. Consequently, the wave functions of the outermost electrons do not extend much further than that of the electron in the hydrogen atom. Atoms are more or less the same size!
- (c) We went to a great deal of trouble to specify the S , L , and J quantum numbers of the ground states of the various elements. The reason for doing this is that in spectroscopy, the quantum numbers are of particular interest because of the selection rules

$$\begin{aligned}\Delta S &= 0 \\ \Delta L &= \pm 1 \\ \Delta J &= 0, \pm 1 \quad (\text{no } 0 - 0)\end{aligned}\tag{14B-2}$$

that will be derived later, and that may then be used to determine the quantum numbers of the excited states. The spectroscopy of atoms, once we get beyond hydrogen and helium, is very complicated. Consider, as a relatively simple example, the first few states of carbon, which are formed from different configurations of the two electrons that lie outside the closed shell in the $(2p)^2$ orbitals. As already pointed out, the possible states are 1S_0 , ${}^3P_{2,1,0}$, and 1D_2 . The 3P_0 state lies lowest, but the other states are still there. The first excited states may be described by the orbitals $(2p)(3s)$. Here $S = 0$ or 1 , but $L = 1$ only. Since the n -values are different, the exclusion principle does not restrict the states in any way, and all of the states 1P_1 , ${}^3P_{2,1,0}$ are possible, while the excited states that

arise from the orbitals $(2p)(3p)$ can have $S = 0, 1$ and $L = 2, 1, 0$, leading to all the states $^1D_2, ^1P_1, ^1S_0, ^3D_{3,2,1}, ^3P_{2,1,0}$, and 3S_1 . Even with the restrictions provided by the selection rules, there are numerous transitions. Needless to say, the ordering of these levels represents a delicate balance between various competing effects, and the prediction of the more complex spectra is very difficult. That task is not really of interest to us, since the main point that we want to make is that quantum mechanics provides a qualitative, and quantitative, detailed explanation of the chemical properties of atoms and of their spectra, without assuming an interaction other than the electromagnetic interaction between charged particles. We shall have occasion to return to the topic of spectra.

Periodic Table

Z	Element	Configuration	Term ¹	Ionization Potential eV	Radius ² in Å
1	H	(1s)	$^2S_{1/2}$	13.6	0.53
2	He	(1s) ²	1S_0	24.6	0.29
3	Li	(He)(2s)	$^2S_{1/2}$	5.4	1.59
4	Be	(He)(2s) ²	1S_0	9.3	1.04
5	B	(He)(2s) ² (2p)	$^2P_{1/2}$	8.3	0.78
6	C	(He)(2s) ² (2p) ²	3P_0	11.3	0.62
7	N	(He)(2s) ² (2p) ³	$^4S_{3/2}$	14.5	0.52
8	O	(He)(2s) ² (2p) ⁴	3P_2	13.6	0.45
9	F	(He)(2s) ² (2p) ⁵	$^2P_{3/2}$	17.4	0.40
10	Ne	(He)(2s) ² (2p) ⁶	1S_0	21.6	0.35
11	Na	(Ne)(3s)	$^2S_{1/2}$	5.1	1.71
12	Mg	(Ne)(3s) ²	1S_0	7.6	1.28
13	Al	(Ne)(3s) ² (3p)	$^2P_{1/2}$	6.0	1.31
14	Si	(Ne)(3s) ² (3p) ²	3P_0	8.1	1.07
15	P	(Ne)(3s) ² (3p) ³	$^4S_{3/2}$	11.0	0.92
16	S	(Ne)(3s) ² (3p) ⁴	3P_2	10.4	0.81
17	Cl	(Ne)(3s) ² (3p) ⁵	$^2P_{3/2}$	13.0	0.73
18	Ar	(Ne)(3s) ² (3p) ⁶	1S_0	15.8	0.66
19	K	(Ar)(4s)	$^2S_{1/2}$	4.3	2.16
20	Ca	(Ar)(4s) ²	1S_0	6.1	1.69
21	Sc	(Ar)(4s) ² (3d)	$^2D_{3/2}$	6.5	1.57
22	Ti	(Ar)(4s) ² (3d) ²	3F_2	6.8	1.48
23	V	(Ar)(4s) ² (3d) ³	$^4F_{3/2}$	6.7	1.40
24	Cr	(Ar)(4s)(3d) ⁵	7S_3	6.7	1.45
25	Mn	(Ar)(4s) ² (3d) ⁵	$^6S_{5/2}$	7.4	1.28
26	Fe	(Ar)(4s) ² (3d) ⁶	5D_4	7.9	1.23
27	Co	(Ar)(4s) ² (3d) ⁷	$^4F_{9/2}$	7.8	1.18
28	Ni	(Ar)(4s) ² (3d) ⁸	3F_4	7.6	1.14
29	Cu	(Ar)(4s)(3d) ¹⁰	$^2S_{1/2}$	7.7	1.19
30	Zn	(Ar)(4s) ² (3d) ¹⁰	1S_0	9.4	1.07
31	Ga	(Ar)(4s) ² (3d) ¹⁰ (4p)	$^2P_{1/2}$	6.0	1.25

(Continued)

Periodic Table (Continued)

Z	Element	Configuration	Term ¹	Ionization Potential eV	Radius ² in Å
32	Ge	(Ar)(4s) ² (3d) ¹⁰ (4p) ²	³ P ₀	8.1	1.09
33	As	(Ar)(4s) ² (3d) ¹⁰ (4p) ³	⁴ S _{3/2}	10.0	1.00
34	Se	(Ar)(4s) ² (3d) ¹⁰ (4p) ⁴	³ P ₂	9.8	0.92
35	Br	(Ar)(4s) ² (3d) ¹⁰ (4p) ⁵	² P _{3/2}	11.8	0.85
36	Kr	(Ar)(4s) ² (3d) ¹⁰ (4p) ⁶	¹ S ₀	14.0	0.80
37	Rb	(Kr)(5s)	² S _{1/2}	4.2	2.29
38	Sr	(Kr)(5s) ²	¹ S ₀	5.7	1.84
39	Y	(Kr)(5s) ² (4d)	² D _{3/2}	6.6	1.69
40	Zr	(Kr)(5s) ² (4d) ²	³ F ₂	7.0	1.59
41	Nb	(Kr)(5s)(4d) ⁴	⁶ D _{1/2}	6.8	1.59
42	Mo	(Kr)(5s)(4d) ⁵	⁷ S ₃	7.2	1.52
43	Tc	(Kr)(5s) ² (4d) ⁵	⁶ S _{5/2}	Not known	1.39
44	Ru	(Kr)(5s)(4d) ⁷	⁵ F ₅	7.5	1.41
45	Rh	(Kr)(5s)(4d) ⁸	⁴ F _{9/2}	7.7	1.36
46	Pd	(Kr)(4d) ¹⁰	¹ S ₀	8.3	0.57
47	Ag	(Kr)(5s)(4d) ¹⁰	² S _{1/2}	7.6	1.29
48	Cd	(Kr)(5s) ² (4d) ¹⁰	¹ S ₀	9.0	1.18
49	In	(Kr)(5s) ² (4d) ¹⁰ (5p)	² P _{1/2}	5.8	1.38
50	Sn	(Kr)(5s) ² (4d) ¹⁰ (5p) ²	³ P ₀	7.3	1.24
51	Sb	(Kr)(5s) ² (4d) ¹⁰ (5p) ³	⁴ S _{3/2}	8.6	1.19
52	Te	(Kr)(5s) ² (4d) ¹⁰ (5p) ⁴	³ P ₂	9.0	1.11
53	I	(Kr)(5s) ² (4d) ¹⁰ (5p) ⁵	² P _{3/2}	10.4	1.04
54	Xe	(Kr)(5s) ² (4d) ¹⁰ (5p) ⁶	¹ S ₀	12.1	0.99
55	Cs	(Xe)(6s)	² S _{1/2}	3.9	2.52
56	Ba	(Xe)(6s) ²	¹ S ₀	5.2	2.06
57	La	(Xe)(6s) ² (5d)	² D _{3/2}	5.6	1.92
58	Ce	(Xe)(6s) ² (4f)(5d)	³ H ₅	6.9	1.98
59	Pr	(Xe)(6s) ² (4f) ³	⁴ I _{9/2}	5.8	1.94
60	Nd	(Xe)(6s) ² (4f) ⁴	⁵ I ₄	6.3	1.92
61	Pm	(Xe)(6s) ² (4f) ⁵	⁶ H _{5/2}	Not known	1.88
62	Sm	(Xe)(6s) ² (4f) ⁶	⁷ F ₀	5.6	1.84
63	Eu	(Xe)(6s) ² (4f) ⁷	⁸ S _{7/2}	5.7	1.83
64	Gd	(Xe)(6s) ² (4f) ⁷ (5d)	⁹ D ₂	6.2	1.71
65	Tb	(Xe)(6s) ² (4f) ⁹	⁶ H _{15/2}	6.7	1.78
66	Dy	(Xe)(6s) ² (4f) ¹⁰	⁵ I ₈	6.8	1.75
67	Ho	(Xe)(6s) ² (4f) ¹¹	⁴ I _{15/2}	Not known	1.73
68	Er	(Xe)(6s) ² (4f) ¹²	³ H ₆	Not known	1.70
69	Tm	(Xe)(6s) ² (4f) ¹³	² F _{7/2}	Not known	1.68
70	Yb	(Xe)(6s) ² (4f) ¹⁴	¹ S ₀	6.2	1.66
71	Lu	(Xe)(6s) ² (4f) ¹⁴ (5d)	² D _{3/2}	5.0	1.55
72	Hf	(Xe)(6s) ² (4f) ¹⁴ (5d) ²	³ F ₂	5.5	1.48
73	Ta	(Xe)(6s) ² (4f) ¹⁴ (5d) ³	⁴ F _{3/2}	7.9	1.41
74	W	(Xe)(6s) ² (4f) ¹⁴ (5d) ⁴	⁵ D ₀	8.0	1.36
75	Re	(Xe)(6s) ² (4f) ¹⁴ (5d) ⁵	⁶ S _{5/2}	7.9	1.31
76	Os	(Xe)(6s) ² (4f) ¹⁴ (5d) ⁶	⁵ D ₄	8.7	1.27

Lanthanides (Rare Earths)

Periodic Table

Z	Element	Configuration	Term ¹	Ionization Potential eV	Radius ² in Å	
77	Ir	(Xe)(6s) ² (4f) ¹⁴ (5d) ⁷	⁴ F _{9/2}	9.2	1.23	
78	Pt	(Xe)(6s)(4f) ¹⁴ (5d) ⁹	³ D ₃	9.0	1.22	
79	Au	(Xe)(6s)(4f) ¹⁴ (5d) ¹⁰	² S _{1/2}	9.2	1.19	
80	Hg	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰	¹ S ₀	10.4	1.13	
81	Tl	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p)	² P _{1/2}	6.1	1.32	
82	Pb	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p) ²	³ P ₀	7.4	1.22	
83	Bi	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p) ³	⁴ S _{3/2}	7.3	1.30	
84	Po	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p) ⁴	³ P ₂	8.4	1.21	
85	At	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p) ⁵	² P _{3/2}	Not known	1.15	
86	Rn	(Xe)(6s) ² (4f) ¹⁴ (5d) ¹⁰ (6p) ⁶	¹ S ₀	10.7	1.09	
87	Fr	(Rn)(7s)		Not known	2.48	
88	Ra	(Rn)(7s) ²	¹ S ₀	5.3	2.04	
89	Actinides	Ac	(Rn)(7s) ² (6d)	² D _{3/2}	6.9	1.90
90		Th	(Rn)(7s) ² (6d) ²	³ F ₂		
91		Pa	(Rn)(7s) ² (5f) ² (6d)	⁴ K _{11/2}		
92		U	(Rn)(7s) ² (5f) ³ (6d)	⁵ L ₆		
93		Np	(Rn)(7s) ² (5f) ⁴ (6d)	⁶ L _{11/2}		
94		Pu	(Rn)(7s) ² (5f) ⁶	⁷ F ₀		
95		Am	(Rn)(7s) ² (5f) ⁷	⁸ S _{7/2}		
96		Cm	(Rn)(7s) ² (5f) ⁷ (6d)	⁹ D ₂		
97		Bk	(Rn)(7s) ² (5f) ⁹	⁶ H _{15/2}		
98		Cf	(Rn)(7s) ² (5f) ¹⁰	⁵ I ₈		
99		Es	(Rn)(7s) ² (5f) ¹¹	⁴ I _{15/2}		
100		Fm	(Rn)(7s) ² (5f) ¹²	³ H ₆		
101		Md	(Rn)(7s) ² (5f) ¹³	² F _{7/2}		
102		No	(Rn)(7s) ² (5f) ¹⁴	¹ S ₀		

¹Term designation is equivalent to spectroscopic description.

²Radius is defined by the peak of the calculated charge density of the outermost orbital.

A Brief Discussion of Molecules

The purpose of this supplement is to outline the basic approach to the study of simple molecules. We discuss the H_2 molecule in some detail, so as to provide an understanding of terms like *molecular orbitals* and *valence bonds*. Quantum chemistry has become a field well served by massive computers. Our discussion does not really provide an entry into this field. It is extremely simple-minded, and its only justification is that it provides an insight into the basic mechanisms that lead to molecular binding. Anything more depends on an understanding of electron–electron correlations, and these are way beyond the scope of this book. Our approach will follow the one followed in the discussion of the H_2^+ molecule. It is based on the fact that the nuclei are much more massive than the electrons, and that therefore a good first approximation treats the nuclei as *frozen*, with their location determined by the electronic distribution. We discuss the H_2 molecule as a prototype of other simple diatomic molecules.

The H_2 Molecule

The H_2 molecule is a more complicated system, because there are two electrons present, and the exclusion principle therefore plays a role. As in the case of the H_2^+ molecule, we treat the nuclei as fixed.

The nuclei (protons here) will be labeled A and B , and the two electrons 1 and 2, respectively (Fig. 14C-1). The Hamiltonian has the form

$$H = H_1 + H_2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \quad (14C-1)$$

where

$$H_i = \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_{Ai}} - \frac{e^2}{4\pi\epsilon_0 r_{Bi}} \quad (i = 1, 2) \quad (14C-2)$$

depends only on the coordinates of the electron i relative to the nuclei. We will again compute an upper bound to $E(R_{AB})$ by constructing the expectation value of H with a trial wave function. Since

$$\tilde{H}_i = H_i + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \quad (14C-3)$$

are just Hamiltonians for the H_2^+ molecule (14-50) it seems reasonable to take as our trial wave function a product of two functions of the type shown in the first line of (14-51):

$$\psi_g(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2[1 + S(R_{AB})]} [\psi_A(\mathbf{r}_1) + \psi_B(\mathbf{r}_1)][\psi_A(\mathbf{r}_2) + \psi_B(\mathbf{r}_2)] X_{\text{singlet}} \quad (14C-4)$$

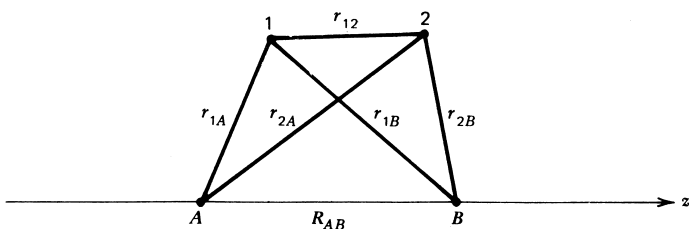


Figure 14C-1 Coordinate labels in the discussion of the H_2 molecule.

The electron spin state is a singlet, since the spatial part of the wave function is taken to be symmetric. In this trial wave function, *each electron is associated with both protons*; that is, the trial wave function is said to be a product of *molecular orbitals*. The description in terms of molecular orbitals is sometimes called the *MO* method.

The calculation of $\langle \psi_g | H | \psi_g \rangle$ yields

$$\begin{aligned} & \left\langle \psi_g \left| \left(\tilde{H}_1 - \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right) + \left(\tilde{H}_2 - \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right| \psi_g \right\rangle \\ &= E(R_{AB}) + E(R_{AB}) + \left\langle \psi_g \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \psi_g \right\rangle - \frac{e^2}{4\pi\epsilon_0 R_{AB}} \quad (14C-5) \\ &= 2E(R_{AB}) - \frac{e^2}{4\pi\epsilon_0 R_{AB}} + \left\langle \psi_g \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \psi_g \right\rangle \end{aligned}$$

where $E(R_{AB})$ is the energy of the H_2^+ molecule calculated in (14.56). The first-order electron–electron repulsion contribution can also be calculated, and when the total energy so computed is minimized with respect to the separation R_{AB} , it is found that the binding energy and internuclear separation are given by

$$\begin{aligned} E_b &= -2.68 \text{ eV} \\ R &= 0.85 \text{ \AA} \end{aligned}$$

The experimental values are

$$\begin{aligned} E_b &= -4.75 \text{ eV} \\ R &= 0.74 \text{ \AA} \end{aligned}$$

Evidently the approximation is not a very good one. We noted in our discussion of the H_2^+ molecule that the trial wave functions (the *MO*'s) are inaccurate for small proton–proton separations, and the fact that the *MO*'s are too spread out in space shows up in the numbers above. The trial wave function also has some undesirable features for large R_{AB} . The product in (14C-4) may be rewritten in the form

$$\begin{aligned} & [\psi_A(\mathbf{r}_1) + \psi_B(\mathbf{r}_1)][\psi_A(\mathbf{r}_2) + \psi_B(\mathbf{r}_2)] \\ &= [\psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2) + \psi_B(\mathbf{r}_1)\psi_B(\mathbf{r}_2)] + [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)] \quad (14C-6) \end{aligned}$$

The first term is called an “ionic” term, since it describes both electrons bound to one proton or the other. The second term, the “covalent” term, is a description in terms of linear combinations of atomic orbitals (LCAO). Our trial wave function thus implies, since the two terms enter with equal weight, that for large R_{AB} the molecule is as likely to dissociate into the ions H^+ and H^- as it is into two hydrogen atoms, and this is patently false.

The Valence Bond Method

The last difficulty can be avoided with the use of the *valence bond* (also called Heitler-London) method, in which linear combinations of atomic orbitals are used. The singlet wave function used as a trial wave function in the variational principle is taken to be

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \left\{ \frac{1}{2[1 + S^2(R_{AB})]} \right\}^{1/2} [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)] X_{\text{singlet}} \quad (14C-7)$$

where, as before, the $\psi_A(\mathbf{r}_i)$ are hydrogenic wave functions for the i th electron about proton A . We could, in principle, add a triplet term to our variational trial wave function. However, a triplet wave function must be spatially antisymmetric and yields low probability for the electrons being located in the region between the protons. We saw in our discussion of the H_2^+ molecule that just this configuration led to the lowest energy. Although it is not immediately obvious that the attraction is still largest in this configuration when there are *two* electrons that repel each other in the system, it is in fact so. The results of a variational calculation with the *VB* trial wave function are

$$E_b = -3.14 \text{ eV} \\ R = 0.87 \text{ \AA}$$

This is not a significant improvement over the *MO* results, for the simple reason that the inadequacy of the trial wave functions for small R_{AB} carries more weight. There should be no question about the quantitative successes of quantum mechanics in molecular physics. More sophisticated trial wave functions have to be used; for example, a 50-term trial wave function yields complete agreement with observations for the H_2 molecule, but it does not, as the *MO* and *VB* functions do, give us something of a qualitative feeling of what goes on between the atoms. In what follows, we will explore the relevance of these approaches to a qualitative understanding of some aspects of chemistry.

The expectation value of H for the H_2 molecule in the *VB* approach has the following schematic form:

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \frac{1}{2(1 + S^2)} \langle \psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1} | H | \psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1} \rangle \\ &= \frac{1}{1 + S^2} \left\langle \psi_{A1}\psi_{B2} \left| T_1 + T_2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}} \right. \right. \\ &\quad \left. \left. + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right| \psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1} \right\rangle \end{aligned}$$

where T_i is the kinetic energy of the i th electron, and since

$$\left(T_1 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} \right) \psi_{A1} = E_1 \psi_{A1}$$

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \frac{1}{2(1 + S^2)} \langle \psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1} | H | \psi_{A1}\psi_{B2} + \psi_{A2}\psi_{B1} \rangle \\ &= \frac{1}{1 + S^2} \left\langle \psi_{A1}\psi_{B2} \left| 2E_1 - \frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right. \right. \\ &\quad \left. \left. + \left\langle \psi_{A1}\psi_{B2} \left| 2E_1 - \frac{e^2}{4\pi\epsilon_0 r_{B2}} - \frac{e^2}{4\pi\epsilon_0 r_{A1}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \right| \psi_{A2}\psi_{B1} \right\rangle \right. \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{1+S^2} \left\{ \left(2E_1 + \frac{e^2}{4\pi\epsilon_0 r R_{AB}} \right) (1+S^2) - 2 \frac{e^2}{4\pi\epsilon_0} \left\langle \psi_{A1} \left| \frac{1}{r_{B1}} \right| \psi_{A1} \right\rangle \right. \\
&\quad - 2 \frac{e^2}{4\pi\epsilon_0} S \left\langle \psi_{A1} \left| \frac{1}{r_{A1}} \right| \psi_{B1} \right\rangle + \frac{e^2}{4\pi\epsilon_0} \int \int \frac{|\psi_{A1}|^2 |\psi_{B2}|^2}{r_{12}} \\
&\quad \left. + \int \int \frac{\psi_{A1}^* \psi_{B1} \psi_{B2}^* \psi_{A2}}{r_{12}} \right\} \quad (14C-8)
\end{aligned}$$

In obtaining this, liberal use has been made of symmetry. The terms that can make this expression more negative are

$$\left\langle \psi_{A1} \left| \frac{1}{r_{B1}} \right| \psi_{A1} \right\rangle \quad \text{and} \quad \frac{S}{1+S^2} \left\langle \psi_{A1} \left| \frac{1}{r_{A1}} \right| \psi_{B1} \right\rangle$$

The former is just the attraction of the electron cloud about one proton to the other proton; the second is the overlap of the two electrons (weighted with $1/r_{A1}$). If this can be large, there will be binding. The two electrons can only overlap significantly, however, if their spins are antiparallel; this is a consequence of the exclusion principle. The region of overlap is between the two nuclei, and there the attraction to the nuclei generally overcomes the electrostatic repulsion between the electrons.

In the *MO* picture, too, it is an overlap term—the result in (14-60)—that is crucial to bonding, and again, bonding occurs because the electron charge distribution is large between the nuclei. Thus, although here the orbitals belong to the whole molecule rather than to individual atoms, the physical reason for bonding is the same.

We note that in general there may be several bound states of the nuclei, corresponding to different electronic configurations. For example, if in (14C-7) we take the $\psi(\mathbf{r}_2)$ wave function to be a u_{200} eigenfunction, while the $\psi(\mathbf{r}_1)$ remains a u_{100} eigenfunction, the overlap may be such as to provide a second, more weakly bound state of the protons. We are not going to pursue this, except to point out the important fact that the $E(R)$ is *different for each electronic state*.

The Importance of Unpaired Valence Electrons

An important simplification in the study of electronic charge distributions in molecules occurs because we really do not need to take all electrons into account. In the construction of orbitals, be it valence or molecular, only the outermost electrons, not in closed shells—that is, the so-called *valence electrons*—have a chance to contribute to the bonding. The inner electrons, being closer to the nucleus, are less affected by the presence of another atom in the vicinity.¹ Furthermore, not all valence electrons contribute equally: if two electrons are in a spin 0 state—we call them *paired electrons*—they will *not give rise to bonding*. To see why this is so, consider what happens when an atom with a single valence electron is brought near an atom with two paired electrons. There are two cases to be considered (Fig. 14C-2).

- (a) If the two electrons that are parallel exchange [i.e., are put into a form such as (14C-7) with a minus sign between the terms], then they must be in a triplet

¹It may happen in atoms that even the valence electrons are rather close to the nucleus. This is the case for the rare earths. A consequence of the fact that the outer electrons in *5d* and *4f* shells lie close in is that the rare earths are chemically less active than the transition metals ($Z \approx 20-30$).

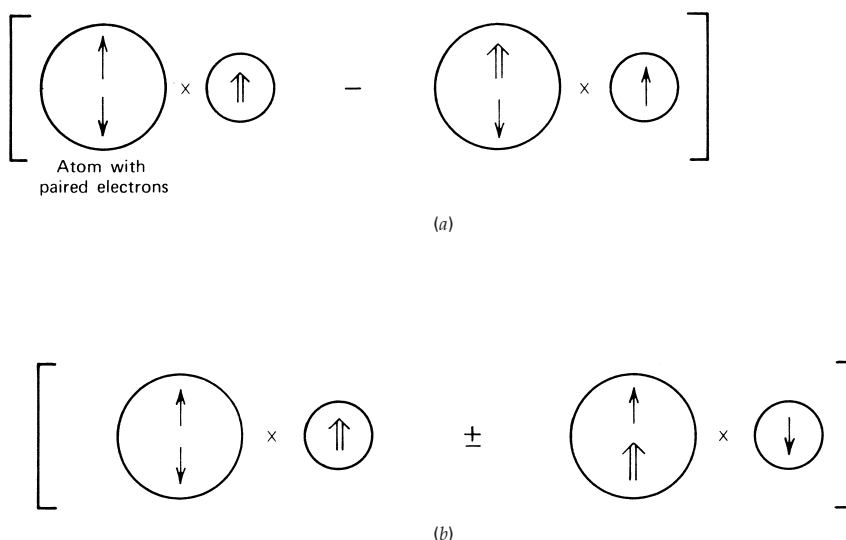


Figure 14C-2 Illustration of why paired electrons do not give rise to bonding. (a) If parallel electrons exchange, the wave function is spatially antisymmetric. (b) If antiparallel electrons exchange, one term in the wave function has electrons in the same spin state, which may require promotion to a higher energy orbit.

state, and hence the spatial wave function of this pair must be antisymmetric. This reduces the overlap, and it turns out that the exchange integral gives a repulsive contribution to the energy.

- (b) When the two electrons that are antiparallel exchange, then one atom finds itself some of the time with two electrons in the same spin state. The original atomic state will frequently no longer be a possible one, and one of the electrons will have to be promoted into another atomic orbital. Sometimes this may cost very little energy, but usually this is not the case, and again bonding is not achieved. *Chemical activity depends on the presence of unpaired outer electrons.* An example of this is the nonexistence of the H-He molecule. In He we have two electrons in the $1s$ state; promotion of one of them into a $2s$ state costs a lot of energy. It is for this reason that the atoms for which the outer shells are closed are *inert*. Not all unpaired electrons are of equal significance. As noted before, the unpaired d - and f -electrons in the transition elements tend to be close to the nucleus, and hence inactive. Thus, mainly s - and p -electrons in the outer shells contribute to chemical activity. The pairing effect is also responsible for what is called the “saturation of chemical binding forces.” Once two unpaired electrons from different atoms form a singlet state (and cause bonding), they become paired; an electron from a third atom must find an unpaired electron elsewhere—that is, participate in a different bond. Another consequence is that molecules have spin 0 in most cases.