Structure of diatomic molecules

January 28, 2002

1 Nature of molecules; energies of molecular motions

Molecules are of course atoms that are held together by shared valence electrons. That is, most of each atom is pretty much as it would be if the atom were isolated, but one or a few electrons are located in regions (for example, between two atomic cores) where they lead to an overall attractive effect. To see roughly how this works, you might consider the case of two protons and two electrons at the corners of a square. If you calculate (classically) the total electrostatic energy of this arrangement, you will find that it is negative – the system is bound.

Molecules have several kinds of motion, with quite different energy scales. Assume that a couple of nuclei and a couple of electrons are confined to a volume with characteristic size a (a couple of Å, typically). Then the uncertainty principle requires that at a minimum, $p \sim \hbar/a$, so the typical electron energies will be of order

$$E_{\mathrm{e}} \sim p^2/2m \sim \hbar^2/ma^2,$$

while the purely nuclear motion of rotation for nuclei of mass M will have sizes like

$$E_{\mathrm{r}} \sim \hbar^2/Ma^2 \sim (m/M)E_{\mathrm{e}}.$$

The nuclear rotation energy may also be estimated using our previous solution for the rigid rotator, in which the energy of the lowest level was found to be of order $\hbar^2/I \sim \hbar^2/Ma^2$. Thus nuclear rotation will involve energies that are of order 10^{-4} times smaller than electronic energies.

The nuclei may also participate in vibrations, in which they interact directly with the electron cloud. The energies of such motions are larger than E_{r}, and may be estimated by treating the interaction between electrons and nuclei as simple harmonic motion with a spring constant k, the same (of course) for both parties. In this case the ratio of electronic (E_{e}) to nuclear vibrational energies (E_{v}) will be of order

$$\frac{E_{\mathrm{v}}}{E_{\mathrm{e}}} \sim \frac{\hbar\omega_{\mathrm{v}}}{\hbar\omega_{\mathrm{e}}} \sim \frac{\hbar(k/M)^{1/2}}{\hbar(k/m)^{1/2}} \sim \left(\frac{m}{M}\right)^{1/2}.$$

Thus we have three rather different energy scales, rotational, vibrational, and electronic, a fact which will help us to study simple molecular structure.

2 Diatomic molecules: the adiabatic approximation

Consider the Schrödinger equation for a system of two identical nuclei and two electrons, in the centre of mass system of the nuclei, neglecting spin:

$$[T_{\mathrm{N}} + T_1 + T_2 + V]\,\psi(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2)$$

where

$$T_{\mathrm{N}} + T_1 + T_2 = \left[-\frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\nabla_{r_2}^2\right],$$

$$V = -\frac{Ze^2}{(4\pi\varepsilon_0)|\mathbf{r}_1 - \mathbf{R}/2|} - \frac{Ze^2}{(4\pi\varepsilon_0)|\mathbf{r}_1 + \mathbf{R}/2|} + \frac{e^2}{(4\pi\varepsilon_0)|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{Z^2e^2}{(4\pi\varepsilon_0)R},$$

$\mathbf{R}$ is the separation of the nuclei, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the two electrons.

We will solve this system by a separation and some approximations. Because the electrons are *much* lighter than the nuclei, the nuclei will hardly move at all in the time that an electron takes to "orbit" once, so let's suppose that we can solve the simpler problem of electron motion in the presence of motionless nuclei separated by a fixed $\mathbf{R}$, for which the electronic wave equation is

$$(T_1 + T_2 + V)\Phi_q(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2) = E_q(\mathbf{R})\Phi_q(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2).$$

The energies $E_q(\mathbf{R})$ of this system depend parametrically on $\mathbf{R}$. Because these wave functions form a complete set, we may expand the exact wave function in them:

$$\psi(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2) = \sum_q F_q(\mathbf{R})\Phi_q(\mathbf{R};\mathbf{r}_1,\mathbf{r}_2).$$

The coefficients $F_q(\mathbf{R})$ are the wave functions describing the nuclear motion when the electrons are in the state q.

To find equations satisfied by the $F_q(\mathbf{R})$'s, put ψ into the exact Schrödinger equation and projects using each of the Φ_s's:

$$\sum_q \langle\Phi_s^\star|[T_{\mathrm{N}} + T_1 + T_2 + V - E]F_q(\mathbf{R})|\Phi_q\rangle = 0.$$

Using the equation satisfied by the Φ's, we get

$$\sum_q \langle\Phi_s^\star|T_N F_q(\mathbf{R})|\Phi_q\rangle + [E_s(\mathbf{R}) - E]F_s(\mathbf{R}) = 0.$$

The complicated part of this is the action of T_{N} on the product $\Phi_q F_q$, since both depend on $\mathbf{R}$:

$$T_{\mathrm{N}}F_q\Phi_q = -\frac{\hbar^2}{2\mu}[F_q\nabla_R^2\Phi_q + 2\nabla_R F_q\cdot\nabla_R\Phi_q + \Phi_q\nabla_R^2 F_q].$$

We now make the *adiabatic* or *Born-Oppenheimer* approximation by assuming that we can neglect $|\nabla_R\Phi_q|$ compared to $|\nabla_R F_q|$. In this case, we get the *nuclear wave equation*

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_s(\mathbf{R}) - E\right]F_s(\mathbf{R}) = 0.$$

3 Nuclear motions: rotation and vibration

The equation for F_s is in the form of a wave equation with the function $E_s(\mathbf{R})$ playing the role of potential energy. Let us consider the specific case of the electrons in a state of zero orbital angular momentum. In this case, $E_s(\mathbf{R}) = E_s(R)$ is a function only of the radial variable R, and the wave equation for F_s becomes one for a spherically symmetric potential. In this case, the Hamiltonian commutes with $\mathbf{J}^2$ and J_z. The simultaneous eigenfunctions of these operators are the spherical harmonics, and have eigenvalues $J(J+1)\hbar^2$ and M_J.

Since there is no privileged direction in space, the total energy of the system cannot depend on M_J, but it does depend on J. (You may wonder why the direction of $\mathbf{R}$ is not a privileged direction now. It is for the electron cloud, but in a spherically symmetric electron potential, it is just a coordinate as far as the nuclei are concerned. Thus $\mathbf{R}$ can rotate in space, and the nuclei may have non-zero angular momentum.) It will be found that there is also another quantum number in the system, v, which acts as a principal quantum number and will be found to number vibrational states. Thus we may write (dividing the radial function by R to get a simple form for the resulting equation)

$$F_s(\mathbf{R}) = (\mathcal{F}^s_{v,J}(\mathbf{R})/R)Y_{J,M_J}(\Theta, \Phi).$$

We substitute this into the wave equation for $F_s(\mathbf{R})$ and find that the functions $\mathcal{F}^s_{v,J}$ satisfy

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}R^2} - \frac{J(J+1)}{R^2}\right) + E_s(R)\right]\mathcal{F}^s_{v,J} = E_{s,v,J}\mathcal{F}^s_{v,J}.$$

Now in a bound molecular state, the energy $E_s(R)$ varies from the sum of the energies of the two atoms separately for large R, through a local minimum, to a large positive value as the two nuclei get close to one another. We may approximate the minimum region of $E_s(R)$ by a second order expansion:

$$E_s(R) \approx E_s(R_0) + \tfrac{1}{2}k(R-R_0)^2,$$

where

$$k = \left.\frac{\mathrm{d}^2\mathrm{E_s}}{\mathrm{d}R^2}\right|_{R=R_0}.$$

In the same spirit, evaluate the term with J at $R = R_0$, and call this quantity E_r:

$$E_r = \frac{\hbar^2}{2\mu R_0^2}J(J+1) = \frac{\hbar^2}{2I_0}J(J+1) = BJ(J+1),$$

where $I_0 = \mu R_0^2$ is the moment of inertia for the reduced mass μ and B is known as the *rotational constant* of the molecule. Now if we write $E_{s,v,J}$ as a sum of the minimum electronic energy, the rotational energy, and a (still unknown) quantity E_v, we see that the equation for $\mathcal{F}^s_{v,J}$ becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{k}{2}(R-R_0)^2\right]\mathcal{F}^s_{v,J} = E_v\mathcal{F}^s_{v,J},$$

the familiar simple harmonic oscillator equation, so we see immediately that the energies E_v are given by

$$E_v = \hbar\omega_0(v + \tfrac{1}{2}), \qquad v = 0, 1, 2, \ldots$$

Because of the relative sizes of E_r and E_v, each vibrational level is split into a number of closely spaced rotational levels.

4 Diatomic molecules: electronic structure

4.1 Classification of electronic states

For the electron cloud, the (slowly rotating) internuclear axis $\mathbf{R}$ picks out a direction in space which we take as the z-axis. The electronic structure of the molecule is invariant under rotation around this axis, so L_z commutes with H. However, $\mathbf{L}^2$, L_x and L_y do not commute with H. The electronic eigenstates Φ_s of H may also be made to be eigenstates of L_z, so that

$$L_z\Phi_s = \pm\Lambda\hbar\Phi_s, \qquad \Lambda = 0, 1, 2, \ldots$$

where Λ is the absolute value of the projection of the total electronic angular momentum on the internuclear axis. We label states of the electron cloud by their Λ values with a system like that used in atomic spectroscopy: $\Lambda = 0, 1, 2, \ldots$ states are called Σ, Π, Δ, etc.

Diatomic molecules are symmetric to reflections through planes including $\mathbf{R}$, such as the xz plane. Thus if operator A_y does this,

$$[A_y, H] = 0,$$

but since $L_z = -i\hbar(x\partial/\partial y - y\partial/\partial x)$,

$$A_y L_z = -L_z A_y,$$

which means that – if $\Lambda \neq 0$ – A_y converts an eigenstate with eigenvalue $\Lambda\hbar$ into one of $-\Lambda\hbar$. But because of commutation of A_y with H, both states have the same energy, and such states are degenerate: two states of different L_z eigenvalues have the same energy (spin effects may break this, an effect called Λ-doubling).

If Λ *is* 0, the state is not degenerate, and A_y can only multiply it by a constant. Since $A_y^2 = 1$, such states are either symmetric or anti-symmetric to reflection through a plane, and one distinguishes Σ^+ and Σ^- states.

If the molecule has two nuclei with identical charge (a homonuclear molecule), the centre is also a symmetry point, and states have parity. States of even (g) and uneven (u) parity are denoted by Π_g, Δ_u, etc. A homonuclear diatomic molecule has four non-degenerate sigma states, Σ_g^+, Σ_g^-, Σ_u^+, and Σ_u^-.

Finally, each electronic eigenstate has a total spin $\mathbf{S}$, with eigenvalues of $\mathbf{S}^2$ of $S(S+1)\hbar^2$. The value of $2S+1$ is given as a left superscript (the *multiplicity*) on the designation. Thus, since most molecular ground states (often labelled X) are Σ states of zero total spin, the complete label for a ground state could be $\mathrm{X}^1\Sigma^+$ or $\mathrm{X}^1\Sigma_\mathrm{g}^+$.

4.2 The hydrogen molecular ion

We may start our study of electronic wave functions with the simplest molecule of all, H_2^+, with two protons and one electron. To simplify writing, we will switch to Hartree's dimensionless *atomic units*, in which the units of mass, charge, angular momentum, and length are chosen to be m_e, e, $\hbar$, and $a_0 = 4\pi\varepsilon_0\hbar^2/m_\mathrm{e}e^2$, with the result (you may check this) that the units for time, velocity, and energy become $m_\mathrm{e}a_0^2/\hbar$, $\hbar/m_\mathrm{e}a_0 = \alpha c$, and $\hbar^2/m_\mathrm{e}a_0^2 = e^2/4\pi\varepsilon_0 a_0 = 2E_1$, where E_1 is the ground state binding energy of H. In these units, the electronic wave equation becomes

$$\left(-\frac{1}{2}\nabla_r^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R} - E_s\right)\Phi_s = 0,$$

where r_A and r_B are the distances to the electron from nuclei A and B, r is the distance to the electron from the centre of mass, and R is the internuclear separation. Note that the energy operator could be with respect to r, r_A, or r_B.

We will solve this equation using the simple approximation of a linear combination of atomic orbitals (LCAO). If the nuclei are far apart, the electron will be attached to one (say A), with wave function

$$\Phi(\mathbf{R};\mathbf{r}) = \psi_{1\mathrm{s}}(r_\mathrm{A}) = \frac{1}{\sqrt{\pi}}\exp(-r_\mathrm{A}).$$

To give the wave function the correct symmetry about the midpoint of $\mathbf{R}$, construct the functions

$$\Phi_\mathrm{g}(\mathbf{R};\mathbf{r}) = [\psi_{1\mathrm{s}}(r_\mathrm{A}) + \psi_{1\mathrm{s}}(r_\mathrm{B})]/\sqrt{2}$$

and

$$\Phi_\mathrm{u}(\mathbf{R};\mathbf{r}) = [\psi_{1\mathrm{s}}(r_\mathrm{A}) - \psi_{1\mathrm{s}}(r_\mathrm{B})]/\sqrt{2}.$$

These wave functions will only be accurate for large R, but may be used as trial wave functions in a variational solution, in which the true ground state energy should be less than

$$E_\mathrm{g,u} = \int \Phi_\mathrm{g,u}^\star H \Phi_\mathrm{g,u}\mathrm{d}\mathbf{r} \Big/ \int |\Phi_\mathrm{g,u}|^2 \mathrm{d}\mathbf{r}.$$

The denominator of this expression is

$$D = \frac{1}{2}\int [|\psi_{1\mathrm{s}}(r_\mathrm{A})|^2 + |\psi_{1\mathrm{s}}(r_\mathrm{B})|^2 \pm 2\psi_{1\mathrm{s}}(r_\mathrm{A})\psi_{1\mathrm{s}}(r_\mathrm{B})]\mathrm{d}\mathbf{r}.$$

This integral may be taken over $\mathbf{r}$, $\mathbf{r}_\mathrm{A}$, or $\mathbf{r}_\mathrm{B}$, since all the integrals extend over all space. Because of the normalization of $\psi_{1\mathrm{s}}(r)$, we find

$$D = 1 \pm I(R)$$

where

$$I(R) = \int \psi_{1\mathrm{s}}(r_\mathrm{A})\psi_{1\mathrm{s}}(r_\mathrm{B})\mathrm{d}\mathbf{r} = \left(1 + R + \frac{1}{3}R^2\right)e^{-R}$$

using the result for two-centre integrals proved by B & J (appendix 9).

The numerator is

$$N = H_{\mathrm{AA}} + H_{\mathrm{AB}} = \int \psi_{1\mathrm{s}}(r_{\mathrm{A}}) H \psi_{1\mathrm{s}}(r_{\mathrm{A}}) \mathrm{d}\mathbf{r}_{\mathrm{A}} \pm \int \psi_{1\mathrm{s}}(r_{\mathrm{A}}) H \psi_{1\mathrm{s}}(r_{\mathrm{B}}) \mathrm{d}\mathbf{r}_{\mathrm{B}}.$$

Again we use the two-centre integrals, as well as the fact that the $\psi_{1\mathrm{s}}$'s are solutions of

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r} - E_{1\mathrm{s}}\right) \psi_{1\mathrm{s}}(r) = 0,$$

where the kinetic energy operator may be with respect to r, r_{A}, or r_{B}, since all measure the position of the electron. The final result is

$$E_{\mathrm{g,u}}(R) = E_{1\mathrm{s}} + \frac{1}{R} \frac{(1+R)e^{-2R} \pm (1 - \frac{2}{3}R^2)e^{-R}}{1 \pm (1 + R + \frac{1}{3}R^2)e^{-R}}.$$

The variation of $E_{\mathrm{g}}(R)$, using the symmetric wave function, shows a minimum below $E_{1\mathrm{s}}$ of 1.77 eV at $R_0 = 1.32$ Å, and thus is a bonding molecular orbital. The minimum energy and equilibrium separation are reasonable (though not very accurate) estimates of the exact values of 2.79 eV at 1.06 Å.The curve of $E_{\mathrm{u}}(R)$ has no minimum; it is an anti-bonding state. The symmetric bonding state is held together by an excess of charge between the two protons, while in the anti-bonding state the electron spends most of its time away from the centre of the molecule.

This problem may be solved exactly (although numerically, not analytically) through the use of confocal elliptic coordinates, which are also used in the evaluation of the two-centre integrals.

4.3 Molecular hydrogen

4.3.1 Spin considerations

With two electrons, we must consider the effects of the exclusion principle, which states that eigenstates must be antisymmetric to exchange of two identical fermions. The eigenstates of the two-electron cloud are products of spatial wave functions and spin functions. How does the spin affect the situation?

The total spin operator is

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2,$$

where $\mathbf{S}_1$ operates only on electron 1, and $\mathbf{S}_2$ only on electron 2. Individual electrons have spin eigenfunctions $\alpha(1)$, $\alpha(2)$, etc, as previously discussed. We need to find spin eigenstates of both S_z and of $\mathbf{S}^2$. Try the simple combinations

$$\begin{aligned}
\chi_1(1,2) &= \alpha(1)\alpha(2) \\
\chi_2(1,2) &= \alpha(1)\beta(2) \\
\chi_3(1,2) &= \beta(1)\alpha(2) \\
\chi_4(1,2) &= \beta(1)\beta(2).
\end{aligned}$$

It is easily shown by operating on these functions that each is an eigenstate of $S_z = S_{z,1} + S_{z,2}$ with eigenvalues respectively 1, 0, 0, and -1. However, when we operate with $\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$, using the relations (proved in B & J, appendix 4, with the aid of raising and lowering operators)

$$\begin{aligned} S_x\alpha &= \tfrac{\hbar}{2}\beta, & S_x\beta &= \tfrac{\hbar}{2}\alpha \\ S_y\alpha &= \tfrac{i\hbar}{2}\beta, & S_y\beta &= -\tfrac{i\hbar}{2}\alpha \\ S_z\alpha &= \tfrac{\hbar}{2}\alpha, & S_z\beta &= \tfrac{\hbar}{2}\beta, \end{aligned}$$

we find that neither χ_2 nor χ_3 is an eigenstate of $\mathbf{S}^2$. But it is easy to make linear combinations of these two functions that *are* eigenstates, and that also have symmetry under particle exchange:

$$\chi_+(1,2) = \frac{1}{\sqrt{2}}[\chi_2(1,2) + \chi_3(1,2)]$$

and

$$\chi_-(1,2) = \frac{1}{\sqrt{2}}[\chi_2(1,2) - \chi_3(1,2)].$$

It is easily shown that χ_+ has eigenvalues of $\mathbf{S}^2$ and S_z of $S = 1$ and $M_S = 0$, while χ_- has $S = 0$ and $M_S = 0$. We now have four normalized and orthogonal spin eigenstates that we will denote by χ_{S,M_S} for clarity. $\chi_{0,0}$ is antisymmetric to particle exchange, while the other three states are symmetric. We call the one $S = 0$ state a spin singlet, while the other three states form a spin triplet.

4.3.2 Molecular orbital treatment of H_2

In solving (approximately) the problem of the electron cloud structure for the two-electron system H_2, we have the obvious choice of using as a basis set the molecular orbitals found for H_2^+, or the atomic orbitals of the individual H atoms. Either provides a useful basis for solution. We will start with the molecular orbitals.

Recall that we have two molecular orbitals Φ_g and Φ_u (which are even and odd under reflection through the midpoint of $\mathbf{R}$). The product $\Phi_\mathrm{g}(1)\Phi_\mathrm{g}(2)$ is symmetric under exchange of electrons 1 and 2, as are the combinations $\Phi_\mathrm{u}(1)\Phi_\mathrm{u}(2)$ and $[\Phi_\mathrm{g}(1)\Phi_\mathrm{u}(2) + \Phi_\mathrm{u}(1)\Phi_\mathrm{g}(2)]/\sqrt{2}$. On the other hand, the function $[\Phi_\mathrm{g}(1)\Phi_\mathrm{u}(2) - \Phi_\mathrm{u}(1)\Phi_\mathrm{g}(2)]/\sqrt{2}$ is antisymmetric under exchange of the electrons. Thus we may form (only) four orthogonal eigenfunctions that are antisymmetric under exchange:

$$\begin{aligned} \Phi_\mathrm{A}(1,2) &= \Phi_\mathrm{g}(1)\Phi_\mathrm{g}(2)\chi_{0,0}(1,2) \\ \Phi_\mathrm{B}(1,2) &= \Phi_\mathrm{u}(1)\Phi_\mathrm{u}(2)\chi_{0,0}(1,2) \\ \Phi_\mathrm{C}(1,2) &= (1/\sqrt{2})[\Phi_\mathrm{g}(1)\Phi_\mathrm{g}(2) + \Phi_\mathrm{u}(1)\Phi_\mathrm{u}(2)]\chi_{0,0}(1,2) \\ \Phi_\mathrm{D}(1,2) &= (1/\sqrt{2})[\Phi_\mathrm{g}(1)\Phi_\mathrm{g}(2) - \Phi_\mathrm{u}(1)\Phi_\mathrm{u}(2)]\chi_{1,M_S}(1,2), \end{aligned}$$

where in Φ_D M_S can take the values 0 and ±1. It is easy to see that Φ_A and Φ_B are ${}^1\Sigma_\mathrm{g}^+$ states, while Φ_C is a ${}^1\Sigma_\mathrm{u}^+$ state and the three Φ_D states are ${}^3\Sigma_\mathrm{u}^+$ states.

To get a bonding state, we need the two electrons to prefer to be between the two protons. If they both occupy the bonding orbitals of the H_2^+ system, and have opposite spins (so that the exclusion principle will not require them to occupy different spatial states), we guess that we should get maximum bonding. Thus we guess that $\Phi_{\mathrm{A}}(1,2)$ may a reasonable approximation to the ground state of H_2.

We now need to solve the equation

$$(H - E_s)\Phi_s = [(H_0(1) + H_0(2) + \left(\frac{1}{r_{12}} + \frac{1}{R}\right)]\Phi_s = 0$$

where H_0 is given by

$$H_0(i) = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_{\mathrm{A}_i}} - \frac{1}{r_{\mathrm{B}_i}}.$$

Using the fact that the individual molecular orbitals are solutions of

$$H_0(i)\Phi_{\mathrm{g,u}} = \left(E_{\mathrm{g,u}} - \frac{1}{R}\right)\Phi_{\mathrm{g,u}},$$

one finds that the Rayleigh-Ritz variational functional is given by

$$E_{\mathrm{A}} = 2E_{\mathrm{g}}(R) - \frac{1}{R} + \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \frac{|\Phi_{\mathrm{g}}(1)\Phi_{\mathrm{g}}(2)|^2}{r_{12}}.$$

If one uses the approximate LCAO molecular orbitals found above, the binding energy D_{e} is calculated to be 2.68 eV (compared to an accurate value of 4.75 eV), with a computed equilibrium R_0 of 0.8 Å, compared to an accurate value of 0.74 Å.

The trial wavefunction that we have used may be written as the sum of two terms,

$$\Phi_{\mathrm{A}} = \Phi_{\mathrm{A}}^{\mathrm{cov}} + \Phi_{\mathrm{A}}^{\mathrm{ion}}$$

where

$$\Phi_{\mathrm{A}}^{\mathrm{cov}} = \frac{1}{2}[\psi_{1\mathrm{s}}(r_{\mathrm{A}1})\psi_{1\mathrm{s}}(r_{\mathrm{B}2}) + \psi_{1\mathrm{s}}(r_{\mathrm{A}2})\psi_{1\mathrm{s}}(r_{\mathrm{B}1})]\chi_{0,0}(1,2)$$

and

$$\Phi_{\mathrm{A}}^{\mathrm{ion}} = \frac{1}{2}[\psi_{1\mathrm{s}}(r_{\mathrm{A}1})\psi_{1\mathrm{s}}(r_{\mathrm{A}2}) + \psi_{1\mathrm{s}}(r_{\mathrm{B}1})\psi_{1\mathrm{s}}(r_{\mathrm{B}2})]\chi_{0,0}(1,2).$$

$\Phi_{\mathrm{A}}^{\mathrm{cov}}$ represents the situation in which one electron is associated with *each* nucleus (a sum of terms in which either electron 1 is measured from nucleus A and electron 2 is measured from nucleus B, or vice versa), while $\Phi_{\mathrm{A}}^{\mathrm{ion}}$ represents a situation in which both electrons are associated *either* with nucleus A *or* with nucleus B. These are two basic limiting forms of the electronic wavefunctions which represent *covalent* bonding (bonding by electron sharing) and *ionic* bonding (exchange of electrons and bonding by ionic attraction). In the case of H_2, the exact wavefunction has predominantly a covalent character for all values of R, but particularly so for large R, where the probability that both electrons will be associated with one nucleus is very small, and for small R where the two nuclei are close and so the two electron clouds must largely overlap. Other molecules (e.g. NaCl) have wavefunctions that have a much more nearly ionic character.