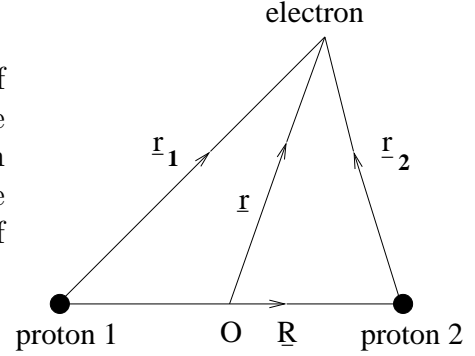


7 The H_2^+ Ion and Bonding

As the simplest example of covalent bonding, we consider the hydrogen molecular ion.

The hydrogen molecular ion H_2^+ is a system composed of two protons and a single electron. It is useful to use centre of mass (CM) coordinates by defining the relative position vector, \mathbf{R} , of proton 2 with respect to proton 1, and the position vector \mathbf{r} of the electron relative to the centre of mass of the two protons.



The Schrödinger equation is

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu_e} \nabla_{\mathbf{r}}^2 - \frac{e^2}{(4\pi\epsilon_0)r_1} - \frac{e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)R} \right] \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

where the reduced mass of the two-proton system is $\mu_{12} = M/2$, with M the proton mass, and μ_e is the reduced mass of the electron/two-proton system:

$$\mu_e = \frac{m(2M)}{m + 2M} \simeq m$$

where m is the electron mass.

7.1 Born-Oppenheimer Approximation

Because nuclei are a great deal more massive than electrons, the motion of the nuclei is much slower than that of the electrons. Thus the nuclear and electronic motions can be treated more or less independently and it is a good approximation to determine the electronic states at any value of \mathbf{R} by treating the nuclei as fixed. This is the basis of the *Born-Oppenheimer approximation*.

In this approximation, the electron is described by an eigenfunction $U_j(\mathbf{r}, \mathbf{R})$ satisfying the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_e} \nabla_{\mathbf{r}}^2 - \frac{e^2}{(4\pi\epsilon_0)r_1} - \frac{e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)R} \right] U_j(\mathbf{r}, \mathbf{R}) = E_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})$$

This is solved keeping \mathbf{R} constant. For each \mathbf{R} , a set of energy eigenvalues $E_j(\mathbf{R})$ and eigenfunctions $U_j(\mathbf{r}, \mathbf{R})$ is found. The functions $U_j(\mathbf{r}, \mathbf{R})$ are known as *molecular orbitals*.

The full wavefunction for the j^{th} energy level at given \mathbf{R} is taken to be the simple product

$$\psi(\mathbf{r}, \mathbf{R}) = F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})$$

where $F_j(\mathbf{R})$ is a wavefunction describing the nuclear motion.

Substituting this form into the full Schrödinger equation and using the electronic equation yields

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_{\mathbf{R}}^2 + E_j(\mathbf{R}) - E \right] F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R}) = 0$$

A little vector calculus gives

$$\begin{aligned} \nabla_{\mathbf{R}}^2 \{F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})\} &= \nabla_{\mathbf{R}} \cdot \left\{ \nabla_{\mathbf{R}} [F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})] \right\} \\ &= \nabla_{\mathbf{R}} \cdot \left\{ U_j(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{R}} F_j(\mathbf{R}) + F_j(\mathbf{R}) \nabla_{\mathbf{R}} U_j(\mathbf{r}, \mathbf{R}) \right\} \\ &= U_j(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{R}}^2 F_j(\mathbf{R}) + F_j(\mathbf{R}) \nabla_{\mathbf{R}}^2 U_j(\mathbf{r}, \mathbf{R}) \\ &\quad + 2 \left(\nabla_{\mathbf{R}} U_j(\mathbf{r}, \mathbf{R}) \right) \cdot \left(\nabla_{\mathbf{R}} F_j(\mathbf{R}) \right) \end{aligned}$$

Assuming that the variation of the molecular orbitals with inter-proton separation, \mathbf{R} , is weak, we can neglect the terms involving $\nabla_{\mathbf{R}} U_j(\mathbf{r}, \mathbf{R})$, and $\nabla_{\mathbf{R}}^2 U_j(\mathbf{r}, \mathbf{R})$ leaving a single-particle type Schrödinger equation for the nuclear motion

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_{\mathbf{R}}^2 + E_j(\mathbf{R}) - E \right] F_j(\mathbf{R}) = 0$$

in which $E_j(\mathbf{R})$ plays the role of a potential. We will return to this later.

7.2 The Electronic Ground State

We now try to investigate the lowest electronic levels of H_2^+ . First we look for symmetries, and note that, since $\mathbf{r}_1 = \mathbf{r} + \mathbf{R}/2$ and $\mathbf{r}_2 = \mathbf{r} - \mathbf{R}/2$, the electronic Hamiltonian is invariant under the parity operation $\mathbf{r} \rightarrow -\mathbf{r}$. If $\hat{\mathcal{P}}$ denotes the parity operator, then

$$[\hat{\mathcal{P}}, \hat{H}] = 0$$

These are commuting operators, so they can have the same eigenfunctions. These eigenfunctions are called *gerade* if the parity is even and *ungerade* if the parity is odd:

$$\hat{\mathcal{P}}U_j^g(\mathbf{r}, \mathbf{R}) = U_j^g(\mathbf{r}, \mathbf{R}), \quad \hat{\mathcal{P}}U_j^u(\mathbf{r}, \mathbf{R}) = -U_j^u(\mathbf{r}, \mathbf{R})$$

Now think about wave functions. If R is large, the system separates into a hydrogen atom and a proton (two degenerate states). The hydrogen atom has a large spacing between levels, so we use degenerate perturbation theory with $1s$ levels only. Quite generally, this procedure of taking linear combinations of atomic orbitals is known as the LCAO method. Note that this basis set is normalised, but neither complete nor orthogonal.

Since there must be solutions which are eigenfunctions of the parity operator, we take normalised linear combinations of gerade or ungerade symmetry of $1s$ orbitals:

$$\psi^g = [u_{1s}(r_1) + u_{1s}(r_2)]/\sqrt{2} \quad \text{and} \quad \psi^u = [u_{1s}(r_1) - u_{1s}(r_2)]/\sqrt{2}$$

We calculate the expectation value of the electronic Hamiltonian using these LCAO molecular wavefunctions:

$$E^{g,u}(\mathbf{R}) = \int \psi^{g,u*}(\mathbf{r}, \mathbf{R}) \hat{H} \psi^{g,u}(\mathbf{r}, \mathbf{R}) d^3r = \langle u_{1s}(r_1) | \hat{H} | u_{1s}(r_1) \rangle \pm \langle u_{1s}(r_1) | \hat{H} | u_{1s}(r_2) \rangle$$

where + and - correspond to u and g respectively, giving $E^g(\mathbf{R})$ and $E^u(\mathbf{R})$ for each value of \mathbf{R} ;

The evaluation of the integrals is complicated, but the results have the form:

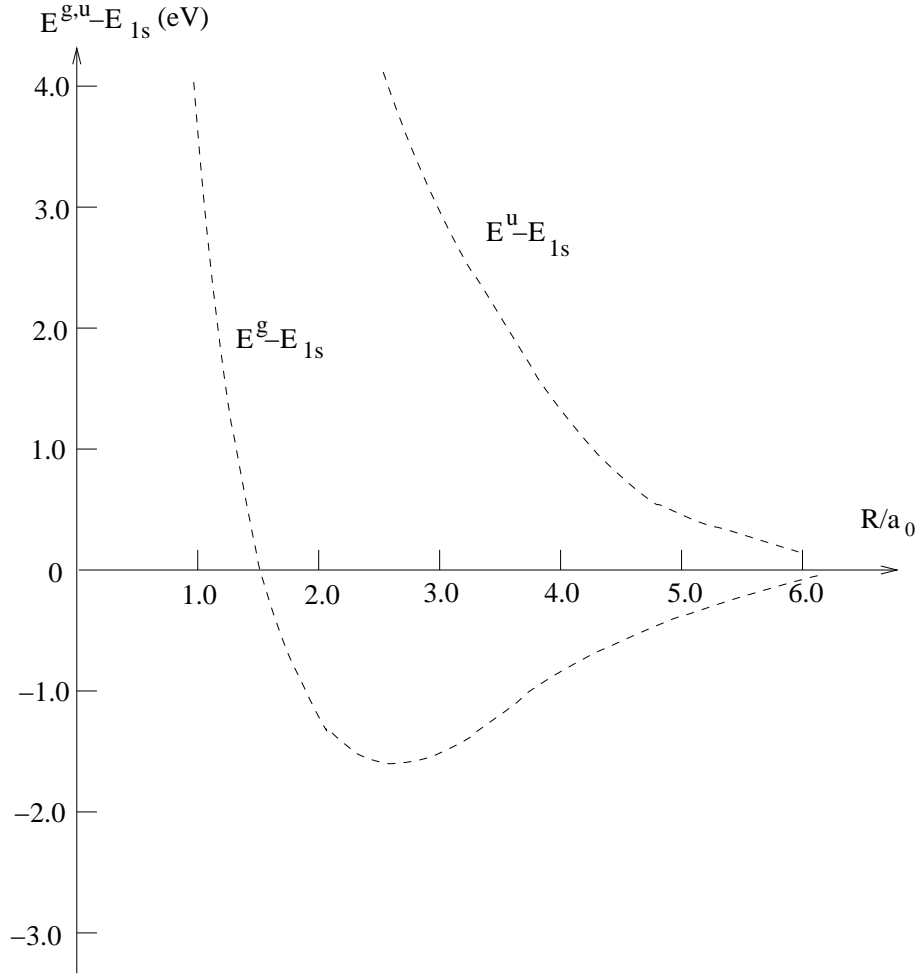
$$E^g(\mathbf{R}) = E_{1s} + \frac{e^2}{(4\pi\epsilon_0)R} \times \frac{(1 + R/a_0) \exp(-2R/a_0) + [1 - (2/3)(R/a_0)^2] \exp(-R/a_0)}{1 + [1 + (R/a_0) + (1/3)(R/a_0)^2] \exp(-R/a_0)}$$

and

$$E^u(\mathbf{R}) = E_{1s} + \frac{e^2}{(4\pi\epsilon_0)R} \times \frac{(1 + R/a_0) \exp(-2R/a_0) - [1 - (2/3)(R/a_0)^2] \exp(-R/a_0)}{1 - [1 + (R/a_0) + (1/3)(R/a_0)^2] \exp(-R/a_0)}$$

where a_0 is the Bohr radius and E_{1s} is the ground-state energy of atomic hydrogen.

The two curves $E^g - E_{1s}$ and $E^u - E_{1s}$ are plotted as a function of R . Note that the curve which corresponds to the symmetric (gerade) orbital exhibits a minimum at $R = R_0$, where $R_0/a_0 \simeq 2.5$, corresponding to $E^g - E_{1s} = -1.77$ eV. Since this is an upper bound on the ground-state energy, this implies that there is a stable bound state, a molecular ion. The curve represents an effective attraction between the two protons. By contrast, the curve corresponding to the ungerade orbital has no minimum, so that a H_2^+ ion in this state will dissociate into a proton and a hydrogen atom. If we think of the protons being attracted by the electron and repelled by each other, the symmetrical state should be the more tightly bound because the electron spends more of its time between the protons, where it attracts both of them. This is an example of *covalent* bonding.



7.3 Rotational and Vibrational Modes

We can now study the effective one-body Schrödinger equation for the nuclear motion by setting $E_j(\mathbf{R}) = E^g(R)$ for the ground state. Because $E^g(R)$ only depends on the magnitude of R it represents an effective central potential, so the solutions are of the form

$$F^g(\underline{R}) = \frac{1}{R} \mathcal{R}_{NL}(R) Y_{LM_l}(\theta, \phi)$$

where $Y_{LM_l}(\theta, \phi)$ are the spherical harmonics and the function $\mathcal{R}_{NL}(R)$ satisfies the radial equation

$$\left[-\frac{\hbar^2}{2\mu_{12}} \left(\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} \right) + E^g(R) - E \right] \mathcal{R}_{NL} = 0$$

We can approximate the centrifugal barrier term by setting it equal to its value at $R = R_0$, writing

$$E_r = \frac{\hbar^2}{2\mu_{12}R_0^2} L(L+1)$$

In this approximation we are treating the molecule as a rigid rotator. We can also approximate $E^g(R)$ by Taylor expanding about $R = R_0$. Because this point is a minimum, the first derivative is zero:

$$E^g(R) \simeq E^g(R_0) + \frac{1}{2}k(R - R_0)^2 + \dots$$

where k is the value of the second derivative of E^g at $R = R_0$.

With these two approximations, the radial equation becomes

$$\left[-\frac{\hbar^2}{2\mu_{12}} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_0)^2 - E_N \right] \mathcal{R}_{NL} = 0$$

where

$$E_N = E - E^g(R_0) - E_r$$

This is the equation for a simple harmonic oscillator with energies

$$E_N = \hbar\omega_0(N + \frac{1}{2}), \quad N = 0, 1, 2, \dots$$

where $\omega_0 = \sqrt{k/\mu_{12}}$. The vibrational energies are of the order of a few tenths of an eV, whereas the rotational energies are of the order of 10^{-3} eV. Both are much smaller than the spacing of the electronic levels. Transitions between these various levels give rise to *molecular spectra*. The pure rotational spectrum consists of closely-spaced lines in the infrared or microwave range. Transitions which also involve changes to the vibrational state give rise to *vibrational-rotational band spectra*

7.4 Electronic states of the H_2 Molecule

Electrons are fermions with spin $\frac{1}{2}$, so the gerade state can be double occupied, as can the ungerade state (four states in all, same as two $1s$ orbitals for each ion). The second electron changes the structure of the wavefunction. Staying within LCAO, and ignoring spin, we can label basis states as, e.g. $u_{1s}^1(\mathbf{r}_2)$ indicating the first electron on the second atom. The electrons are indistinguishable, so the total wavefunctions (spin times spatial) must be eigenstates of parity and the *exchange* operator \hat{P}_{12} which switches the electron labels, e.g. $\hat{P}_{12}u_{1s}^1(\mathbf{r}_2) = u_{1s}^2(\mathbf{r}_2)$. They are fermions, hence antisymmetric: $P = -1$.

Assuming both electrons are $1s$ and in the bonding g state, and ignoring their interaction, the LCAO $1s^2$ spatial wavefunction is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = [u_{100}^1(\mathbf{r}_1) + u_{100}^1(\mathbf{r}_2)][u_{100}^2(\mathbf{r}_1) + u_{100}^2(\mathbf{r}_2)]$$

This must be combined with a spin eigenfunction $\uparrow\uparrow, \downarrow\downarrow, (\uparrow\downarrow + \downarrow\uparrow)$, or $(\uparrow\downarrow - \downarrow\uparrow)$, where the first arrow represents the spin state ($m_s = \pm 1$) of the first electron. Since the spatial wavefunction is symmetric under label exchange, in fact it must be combined with the antisymmetric spin wavefunction $\uparrow\downarrow - \downarrow\uparrow$ to give the overall wavefunction in spin and space.

$$\psi(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) = [u_{100}^1(\mathbf{r}_1) + u_{100}^1(\mathbf{r}_2)][u_{100}^2(\mathbf{r}_1) + u_{100}^2(\mathbf{r}_2)][\uparrow\downarrow - \downarrow\uparrow]$$

This wavefunction describes two electrons, and is non-degenerate.

The second electron also adds an electron-electron repulsion to the Hamiltonian, which can be treated by perturbation theory.

$$\Delta E = \langle \psi(\mathbf{r}_1, \mathbf{r}_2) | e^2/4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2| | \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$$

There is a lot of subtlety here, since the electrons don't interact with themselves, only with each other, and we must avoid double-counting the interaction of 1-2 and 2-1. We'll return to this in more detail later in the context of Helium.