

## 6 Diatomic molecules

*These notes refer specifically to the case of diatomic molecules, i.e., molecules formed by two atoms, and of diatomic molecular ions. However, many of the concepts mentioned also apply to more complex systems. There is much more to say about this topic. For further information, interested readers are directed, in a first instance, to Bransden and Joachain (“Quantum Mechanics”, Section 10.6). A much more detailed account can be found in “Physics of Atomic and Molecules”, by the same authors.*

### 6.1 The energy levels of molecules

*In this section: Relative motion of the nuclei; vibrational energy levels; rotational energy levels; electronic energy levels.*

As in Classical Mechanics, the motion of the two nuclei of a diatomic molecule can be decomposed into the motion of the centre of mass of the molecule, a rotation of the molecule as a whole about the centre of mass, and the motion of the two nuclei along the internuclear axis, relative to each other. The velocity of the centre of mass is constant if no external forces act on the molecule. As noted below, the motion of the nuclei relative to each other is a harmonic oscillation (or more exactly, an oscillation which is almost harmonic as long as the molecules is not too highly excited).

Owing to its speed and its small amplitude, this motion is better described as a vibration. It is quantized. The corresponding vibrational energy levels are separated typically by 0.1 eV. Radiative transitions between these energy levels therefore correspond typically to wavelengths in the infrared.

The rotation of the nuclei about the centre of mass is also quantized. In first approximation, a diatomic molecule in a low state of excitation is a rigid rotator whose energy levels are separated typically by about one or a few meV. Radiative transitions between these rotational energy levels correspond typically to wavelengths in the far infrared or in the microwave part of the electromagnetic spectrum. Radiative transitions between vibrational energy levels are normally accompanied by a change in the rotational energy level, leading to spectrum of emitted light exhibiting bands of closely spaced spectral lines (see Young and Freedman for an example of such spectra).

The motion of the centre of mass, being free, is not quantized — i.e., the kinetic energy of the centre of mass can take any value. (This might not be the case for a molecule confined to a very small region of space by some interaction; we will ignore this possibility here.)

Molecules also have electronic energy levels, like atoms, and as in atoms

the spacing of these energy levels is typically of one or a few eV (for the low lying states). The corresponding transitions are in the UV part of the spectrum.

## 6.2 The Born-Oppenheimer approximation

*In this section: The electrons' dynamics is faster than the nuclei's dynamics; decoupling of the two; the Born-Oppenheimer approximation; molecular orbitals; electronic potential energy curves.*

As indicated by the difference in the spacing between the corresponding energy levels, the time scale of the electrons' dynamics is much faster than the time scale of the nuclei's dynamics. Indeed, the electrostatic forces acting on the electrons are of the same overall magnitude as the forces acting on the nuclei, but since the nuclei are much more massive they are much less accelerated by these forces. One can say that the electrons' quantum state adapts quasi-instantaneously to a change in the relative position of the nuclei.

This difference in time scale makes it possible to “decouple” the electronic motion from the nuclear motion. That is, in good approximation one can treat the nuclei as if they were moving in a continuous charge distribution created by the electrons, and the electrons as if they were moving around fixed nuclei. Since the probability distribution of the position of the nuclei does not depend on the precise location of the electrons, one can then write the wave function of the nuclei + electrons system as a product of a nuclear wave function and an electronic wave function, the latter being obtained by treating the nuclei as if there were fixed in space. The vibrational motion of the nuclei is then determined by the charge distribution formed by the electrons. This approximation is called the Born-Oppenheimer approximation. It immensely simplifies the calculation of the wave functions and energy levels of molecules, and more generally of quantum systems with disparate time scales.

For instance, consider the molecular ion  $\text{H}_2^+$ , namely the molecule formed by two protons and a single electron. (Although it may seem unlikely that a single electron suffices to bind two protons into a molecule, this molecule really exists.) We call the two protons  $A$  and  $B$  and the position vectors of the electron with respect to these two nuclei  $\mathbf{r}_A$  and  $\mathbf{r}_B$  respectively.<sup>1</sup> Thus, if  $\mathbf{R}$  is the position vector of proton  $B$  with respect to proton  $A$  and  $\mathbf{r}$  is the position vector of the electron with respect to the centre of mass of the two protons (which is exactly half way between  $A$  and  $B$ ), then  $\mathbf{r}_A = \mathbf{r} + \mathbf{R}/2$  and  $\mathbf{r}_B = \mathbf{r} - \mathbf{R}/2$ .

Neglecting spin-orbit coupling, the Hamiltonian describing the relative motion of the three particles about the centre of mass is

$$H = -\frac{\hbar^2}{2\mu_{AB}}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B}\right), \quad (6.1)$$

where  $\mu_{AB}$  is the reduced mass of the two protons ( $\mu_{AB}$  is half the mass of a proton) and  $\mu$  is the reduced mass of the electron with respect to the two protons ( $\mu$  is almost exactly equal to the mass of the electron, and for simplicity we will not make a difference between the centre of mass of the two protons and the centre of the mass of the whole molecule). In the above,  $R = |\mathbf{R}|$ ,  $r_A = |\mathbf{r}_A|$ ,  $r_B = |\mathbf{r}_B|$ , and  $\nabla_{\mathbf{R}}$  and  $\nabla_{\mathbf{r}}$  denote the gradient operators for the  $\mathbf{R}$  coordinates and for the  $\mathbf{r}$  coordinates respectively. The potential energy term in  $1/R$  arises from the repulsive Coulomb interaction between the two protons, and those in  $1/r_A$  and  $1/r_B$  from the attractive Coulomb interaction between the electron and each of the protons.

The time-independent Schrödinger equation for the motion about the centre of mass is  $H\psi(\mathbf{R}, \mathbf{r}) = E\psi(\mathbf{R}, \mathbf{r})$ . As is clear from Eq. (6.1), this equation is, in principle, a partial differential equation in the independent variables  $\mathbf{R}$  and  $\mathbf{r}$  (six coordinates in total), in which  $\mathbf{R}$  and  $\mathbf{r}$  are coupled to each other in a complicated way by the terms in  $1/r_A$  and  $1/r_B$ . However, making the Born Oppenheimer approximation, we write  $\psi(\mathbf{R}, \mathbf{r})$  as the product of a wave function  $F(\mathbf{R})$  describing the nuclear motion only and a wave function  $\chi(\mathbf{r}; \mathbf{R})$  describing the electronic motion for a *fixed* value of  $\mathbf{R}$ :

$$\psi(\mathbf{R}, \mathbf{r}) = F(\mathbf{R})\chi(\mathbf{r}; \mathbf{R}). \quad (6.2)$$

The function  $\chi(\mathbf{r}; \mathbf{R})$  is called a molecular orbital.

Neglecting various contributions unimportant here, one finds the following equations for  $\chi(\mathbf{r}; \mathbf{R})$  and  $F(\mathbf{R})$ :

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B} \right) \right] \chi(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(R) \chi(\mathbf{r}; \mathbf{R}) \quad (6.3)$$

and

$$\left[ -\frac{\hbar^2}{2\mu_{AB}} \nabla_{\mathbf{R}}^2 + E_{\text{el}}(R) \right] F(\mathbf{R}) = EF(\mathbf{R}). \quad (6.4)$$

Note that in Eq. (6.4) the independent variables are the three components of the vector  $\mathbf{R}$ , while in Eq. (6.3) they are the three components of the vector  $\mathbf{r}$ . However, the resulting molecular orbital  $\chi(\mathbf{r}; \mathbf{R})$  and electronic energy  $E_{\text{el}}(R)$  also vary with  $\mathbf{R}$  since the shape and the depth of the potential well the electron is in depends on the distance between the two nuclei. [The energy  $E_{\text{el}}(R)$  depends only on the norm of  $\mathbf{R}$ , but the wave function  $\chi(\mathbf{r}; \mathbf{R})$  may also depend on the orientation of this vector.] As seen from Eq. (6.4),  $E_{\text{el}}(R)$  plays the role of a potential energy as far as the nuclear motion is concerned. The calculation can therefore be organised in two steps: One first solves Eq. (6.3) for a number of different values of  $R$ , which gives electronic potential energy curves  $E_{\text{el}}(R)$ . One then solves Eq. (6.4) for each of these potential energy curves to get the corresponding values of  $E$ , the total energy of the molecule.

### 6.3 Bonding orbitals and antibonding orbitals

*In this section: Atomic orbitals; gerade and ungerade states; the LCAO method; bonding and antibonding molecular orbitals.*

By contrast to molecular orbitals, atomic orbitals are wave functions centered on one nucleus only. For instance, for the  $\text{H}_2^+$  molecular ion,  $\psi_{1s}(r_A)$  is an atomic orbital describing an electron forming a hydrogen atom in the 1s state with proton  $A$  and  $\psi_{1s}(r_B)$  an atomic orbital describing an electron forming a hydrogen atom in the 1s state with proton  $B$ .

If the two protons of  $\text{H}_2^+$  are sufficiently close to each other, one would expect that the electron is delocalized between these two centres of force rather than attached exclusively to one of them. In a first approximation, its ground state wave function can therefore be taken to be a linear combination of the two atomic orbitals  $\psi_{1s}(r_A)$  and  $\psi_{1s}(r_B)$ . As proton  $A$  and proton  $B$  must play the same role, since they are identical, there are only two possibilities for such linear combinations: the “gerade molecular orbital”,

$$\chi_g(\mathbf{r}; \mathbf{R}) = \psi_{1s}(r_A) + \psi_{1s}(r_B), \quad (6.5)$$

which is symmetric in  $r_A$  and  $r_B$ , and the “ungerade molecule orbital”,

$$\chi_u(\mathbf{r}; \mathbf{R}) = \psi_{1s}(r_A) - \psi_{1s}(r_B), \quad (6.6)$$

which is antisymmetric. (As defined, the wave functions  $\chi_g(\mathbf{r}; \mathbf{R})$  and  $\chi_u(\mathbf{r}; \mathbf{R})$  are not normalized to unity; however the normalization is not important here.) This method of constructing molecular orbitals is called the LCAO method (LCAO for Linear Combination of Atomic Orbitals). It is used widely in Molecular Physics and in Solid State Physics.

Note 1: For homonuclear diatomic molecules such as  $\text{H}_2^+$  and molecular hydrogen,  $\text{H}_2$ , i.e., molecules formed by two atoms with identical nuclei, the centre of mass of the nuclei is exactly half way between them and is a centre of symmetry. For instance, one notes that Eq. (6.3) remains the same if  $\mathbf{r}$  is changed into  $-\mathbf{r}$ , which is a reflection about the centre of mass. The upshot is that the solutions of this equation are either even or odd for  $\mathbf{r} \rightarrow -\mathbf{r}$ ; i.e., either  $\chi(-\mathbf{r}; \mathbf{R}) = \chi(\mathbf{r}; \mathbf{R})$  or  $\chi(-\mathbf{r}; \mathbf{R}) = -\chi(\mathbf{r}; \mathbf{R})$ , depending on the state. The states that are of even parity are said to be gerade states (the German word gerade means even) and the others (of odd parity) are said to be ungerade states.

Gerade states must be symmetric in  $r_A$  and  $r_B$ , since changing  $\mathbf{r}$  into  $-\mathbf{r}$  transforms  $r_A$  into  $r_B$  and  $r_B$  into  $r_A$ . Hence, the symmetric combination of the two atomic orbitals  $\psi_{1s}(r_A)$  and  $\psi_{1s}(r_B)$ , i.e., the wave function  $\chi_g(\mathbf{r}; \mathbf{R})$  defined by Eq. (6.5), represents a gerade state. For the same reason, the antisymmetric combination represents an ungerade state.

Clearly, the molecular orbitals thus constructed are not exact solutions of Eq. (6.3). However, when  $\chi_g(\mathbf{r}; \mathbf{R})$  is plugged into the energy functional of the variational method, this function yields potential energy curves of sufficient accuracy to understand why the two protons form a bound state. One finds that in this gerade state, the potential energy curve is a minimum at a certain internuclear distance  $R_0$  ( $R_0$  is approximately 0.1 nm in  $\text{H}_2^+$ ). This potential energy curve effectively forms a potential well, and the bound states supported by this well describe states of the molecule in which the two nuclei are bound to each other through their interaction with the electron. The internuclear distance  $R_0$  at which this minimum occurs is the equilibrium position of the nuclei in the ground electronic state of this molecule. ( $R_0$  is typically of the order of one angstrom, 0.1 nm, in the ground electronic state of diatomic molecules).

The potential energy is approximately quadratic in  $R - R_0$  in the vicinity of this minimum, with the consequence that for  $R \approx R_0$  Eq. (6.4) is effectively the Schrödinger equation of a harmonic oscillator. The resulting energy levels are the vibrational energy levels mentioned at the beginning. One says that the gerade molecular orbital is a bonding orbital. (The motion is not perfectly harmonic, particularly in the excited vibrational states, because the potential well formed by  $E_{\text{el}}(\mathbf{R})$  is not exactly quadratic.)

By contrast to  $\chi_g(\mathbf{r}; \mathbf{R})$ , the ungerade molecular orbital  $\chi_u(\mathbf{r}; \mathbf{R})$  gives a potential energy curve which has no minimum and varies from large positive values for small internuclear distances to 0 for  $R \rightarrow \infty$ . The exact ungerade solutions of Eq. (6.3) have the same behaviour. Clearly, the two protons cannot form a bound molecule in the ungerade electronic symmetry. The molecular orbital  $\chi_u(\mathbf{r}; \mathbf{R})$  is said to be antibonding.

Why the symmetric (gerade) orbital is bonding while the antisymmetric (ungerade) orbital is antibonding can be understood by comparing  $|\chi_g(\mathbf{r}; \mathbf{R})|^2$  to  $|\chi_u(\mathbf{r}; \mathbf{R})|^2$ . In the antisymmetric orbital, the contributions of  $\psi_{1s}(r_A)$  and  $\psi_{1s}(r_B)$  exactly cancel each other at the mid point between the two protons, while they add to each other in the symmetric orbital. Thus  $|\chi_u(\mathbf{r}; \mathbf{R})|^2$  is smaller between the two protons than on either side of them, while  $|\chi_g(\mathbf{r}; \mathbf{R})|^2$  is larger. This means that in the gerade state each proton “sees” an excess of negative charges around the centre of the molecule: each proton is attracted by the electron “sitting” in between them, which binds them into a molecule. In the ungerade state, on the other hand, the excess of negative charges is on the other side of each proton and pulls the two protons apart.

It is worth noting that the spin of the electron plays no role here, contrary to the case of molecules containing more than one electron such as  $\text{H}_2$ .