

## 7: Molecular structure and spectra

### Objectives

In this chapter we shall discuss the question about the internal structure and the energy of molecules, which depend not only on the distribution of the electrons like in atoms, but also on the location and motion of atomic nuclei. Although the different possible mechanisms responsible for the molecular spectra are interrelated, there are three kinds of motions that can be distinguished in practice, because the differences in their typical energies allow their characterization to be examined independently. The three main mechanisms determining the spectra of the molecules are their **electronic**, **vibrational** and **rotational** excitations.

### Prerequisites

Chapters 2, 4-5-6. Molecules and valence in chemistry. Rotation of rigid bodies, the harmonic oscillator.

### Introduction

For simplicity, and in order to grasp the essence of this topic, we shall consider diatomic molecules. In particular, the interaction between two neutral atoms and its dependence on their distance  $R$  from each other will give us better insight into the nature of chemical bond. Also, the model of atomic orbitals, which gives an intuitive picture of the spatial electron distribution and plays an important role in chemistry, can be explained more readily for diatomic molecules. Since the energy levels of molecules are not only determined by electronic excitation but also by vibrations of the nuclei, or the rotation of the whole molecule around an axis through its centre of mass, the spectra of molecules are much more complex than those of atoms, but on the other hand they also give more detailed information about the internal structure and dynamics of molecules. First we come to the simplest discussion of the electronic states, and explain why two neutral atoms tend to form a molecule.

### Molecular orbitals of diatomic molecules.

We shall consider a specific problem, the neutral  $\text{H}_2$  molecule, where electron-electron interaction is also present, and this example explains also why two electrically neutral H atoms tend to form a stable molecule, instead of remaining separated. This is the long standing problem of valence, that can be explained only by quantum theory. In considering the  $\text{H}_2$  molecule we shall assume in this section that the two protons are at **fixed positions** in space, and we will try to determine the two-electron wavefunction of the system in its ground state. The resulting energy will depend on the distance between the nuclei, and then the dynamics of that degree of freedom can be investigated further.

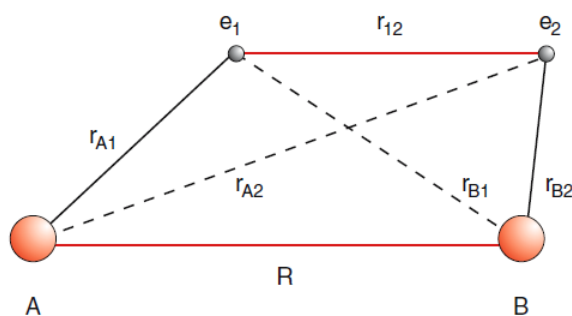


Figure 7.1:  $\text{H}_2$  molecule.

The Hamiltonian of the system, which does not contain nuclear motion (with  $e_0^2 = q_0^2/4\pi\epsilon_0$ ) is

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_A|} - \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_B|} - \frac{e_0^2}{|\mathbf{R}_2 - \mathbf{R}_A|} - \frac{e_0^2}{|\mathbf{R}_2 - \mathbf{R}_B|} + \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} + \frac{e_0^2}{R} \quad (7.1)$$

# Problem 7.1

Explain the terms in this Hamiltonian.

One of the methods to find the energy eigenvalues is the following. We try to build a molecular wave function, called a molecular orbital as a linear combination of atomic orbitals, abbreviated as the MO LCAO method. Let us assume that in the ground state of the molecule the molecular orbital of one of the electrons can be written as the linear combination of normalized  $1s$  ground state hydrogenic orbitals, which are centered at the nuclear positions:

$$\phi(\mathbf{r}) = c_A \phi_A(\mathbf{r}) + c_B \phi_B(\mathbf{r}) \quad (7.2)$$

where

$$\phi_A(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(\mathbf{r}-\mathbf{R}_A)/a_0}, \quad \phi_B(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(\mathbf{r}-\mathbf{R}_B)/a_0} \quad (7.3)$$

Due to the symmetry of the problem we choose  $c_B = \pm c_A$  which leads after normalization to the following two wavefunctions for a single electron in the field of the two nuclei:

$$\phi_+(\mathbf{r}) = \frac{\phi_A(\mathbf{r}) + \phi_B(\mathbf{r})}{\sqrt{2+2S(R)}} \quad \phi_-(\mathbf{r}) = \frac{\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})}{\sqrt{2-2S(R)}} \quad (7.4)$$

where  $S(R) := \int \phi_A^*(\mathbf{r}) \phi_B(\mathbf{r}) d^3\mathbf{r}$  is a real constant, as the  $1s$  functions above are real.  $S(R)$  is called the overlap integral of the functions centred at the two nuclei. It will be a function of the distance  $R = |\mathbf{R}_A - \mathbf{R}_B|$  between the nuclei, and it is diminishing with increasing  $R$ . Note that  $\phi_+(\mathbf{r})$  in (7.4) is a symmetric while  $\phi_-(\mathbf{r})$  is an antisymmetric function with respect to the exchange of the two identical nuclei. The question which of the two is to be used to describe the electrons will be discussed below, when also the electron spin is to be taken into account.

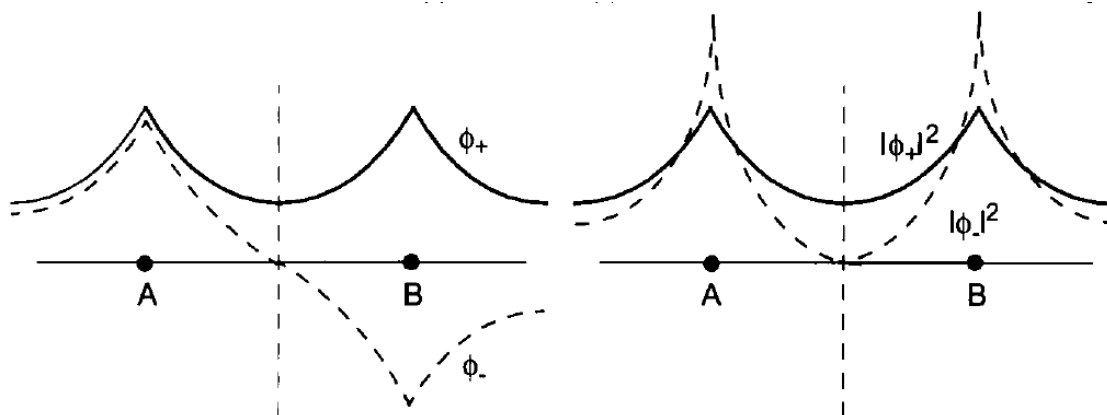


Figure 7.2: Wavefunctions and their absolute value square for a single electron in the field of the two nuclei. See Eqn.(7.4).

Now we assume that each of the two electrons is in one of the states  $\phi_+(\mathbf{r})$ , or  $\phi_-(\mathbf{r})$  above, and look for the two-particle wave function as their product.

## The singlet state

First we consider the possibility, when both of the electrons are in the  $\phi_+(\mathbf{r})$  states:

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \phi_+(\mathbf{r}_1) \phi_+(\mathbf{r}_2) \quad (7.5)$$

Obviously this is symmetric with respect to the exchange of the two electrons, and therefore according to the postulate that requires the antisymmetry of the wave functions for fermions, it cannot be a true wave function. But as we know, this is not the total state, because the electrons possess a the spin degree of freedom, which – though not contained in the Hamiltonian – influences the symmetry properties of the state. We can complete the symmetric spatial wave function by an antisymmetric spin part by forming the Slater determinant:

$$\psi_s(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_+(\mathbf{r}_1) \chi^+(1) & \phi_+(\mathbf{r}_2) \chi^+(2) \\ \phi_+(\mathbf{r}_1) \chi^-(1) & \phi_+(\mathbf{r}_2) \chi^-(2) \end{vmatrix} \quad (7.6)$$

where  $\chi^+(i)$  and  $\chi^-(i)$  are the two different and orthogonal eigenstates of the  $S_z$  operator (spin up +, spin down -, according to the common usage (5.2)) for the  $i$ -th particle.

By expanding the determinant we get

$$\begin{aligned}\psi_s(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2) &= \frac{1}{\sqrt{2}} \phi_+(\mathbf{r}_1) \phi_+(\mathbf{r}_2) \{ \chi^+(1) \chi^-(2) - \chi^+(2) \chi^-(1) \} = \\ &= \frac{1}{2\sqrt{1+S(R)}} \{ \phi_A(\mathbf{r}_1) + \phi_B(\mathbf{r}_1) \} \{ \phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_2) \} \{ \chi^+(1) \chi^-(2) - \chi^+(2) \chi^-(1) \} \quad (7.7)\end{aligned}$$

In view of the last, spin dependent factor in (7.7) one sometimes simply says that in this state the two electrons have antiparallel spins. As the antisymmetric spin state  $\{ \chi^+(1) \chi^-(2) - \chi^+(2) \chi^-(1) \} / \sqrt{2}$  is called a **spin singlet**, the more correct statement is that the total  $\psi_s$  state is a spin singlet state.

### The triplet state

From (7.4) we can also construct a spatial wave function which is antisymmetric with respect to the interchange of the electrons. In contrast to the symmetric  $\psi_s$  we take the combination

$$\psi_a(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \phi_+(\mathbf{r}_1) \phi_-(\mathbf{r}_2) - \phi_-(\mathbf{r}_1) \phi_+(\mathbf{r}_2) \} \quad (7.8)$$

which is antisymmetric if we change the electrons. This must be again completed by spin dependent parts, which must be then symmetric, so that the total state is antisymmetric. There are three different and orthogonal symmetric spin functions of the two particles, which are the following:

$$\chi^+(1) \chi^+(2), \quad \frac{1}{\sqrt{2}} \{ \chi^+(1) \chi^-(2) + \chi^-(1) \chi^+(2) \}, \quad \chi^-(1) \chi^-(2) \quad (7.9)$$

Multiplying  $\psi_a$  with any of these we get again an allowed wave function  $\psi_a(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2)$ . One loosely says, that the two spins are parallel in these states. As there are three of them, we call these three spin states, as well as the total wave function as a **triplet**.

#### Problem 7.3

Multiply  $\psi_a$  by the second of these symmetric spin states and write the result as a Slater determinant.

### The energy expectation values of the states

One can now find the energies in the states  $\psi_s$  and  $\psi_a$  by calculating  $\varepsilon_s = \int \psi_s^* H \psi_s d^3\mathbf{r}_1 d^3\mathbf{r}_2$  and  $\varepsilon_a = \int \psi_a^* H \psi_a d^3\mathbf{r}_1 d^3\mathbf{r}_2$ , where  $H$  is the Hamilton operator (7.1). In the calculations there appears the ground state energy  $\varepsilon_1$  of an isolated H:  $\frac{P_i^2}{2m} - \frac{e_0^2}{|R_i - R_{A(B)}|}$ . In addition the result will contain the Coulomb energy

$$Q = \int \phi_A^2(\mathbf{r}_1) \phi_B^2(\mathbf{r}_2) \left( \frac{e_0^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e_0^2}{|\mathbf{r}_1 - R_B|} - \frac{e_0^2}{|\mathbf{r}_2 - R_A|} \right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \frac{e_0^2}{R} \quad (7.10)$$

and the so called exchange energy  $A$ :

$$A = \int \phi_A(\mathbf{r}_1) \phi_B(\mathbf{r}_2) \phi_A(\mathbf{r}_2) \phi_B(\mathbf{r}_1) \left( \frac{e_0^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e_0^2}{|\mathbf{r}_1 - R_B|} - \frac{e_0^2}{|\mathbf{r}_2 - R_A|} \right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 + S^2(R) \frac{e_0^2}{R} \quad (7.11)$$

which is the measure of the overlap of the two electronic wave functions weighted by the potential energy, and results from the interplay of the Pauli principle and the Coulomb interaction. The result is

$$\varepsilon_s = 2\varepsilon_1 + \frac{Q+A}{1+S^2}, \quad \varepsilon_a = 2\varepsilon_1 + \frac{Q-A}{1-S^2} \quad (7.12)$$

Here both  $Q$  and  $A$  depend on the nuclear distance  $R$ . The Coulomb energy  $Q$  is positive, while apart from very small  $R$ -s  $A$  is negative and  $|A| > Q$ . This results in the dependence of the energy values of  $\varepsilon_s$  as shown in Fig. 7.3

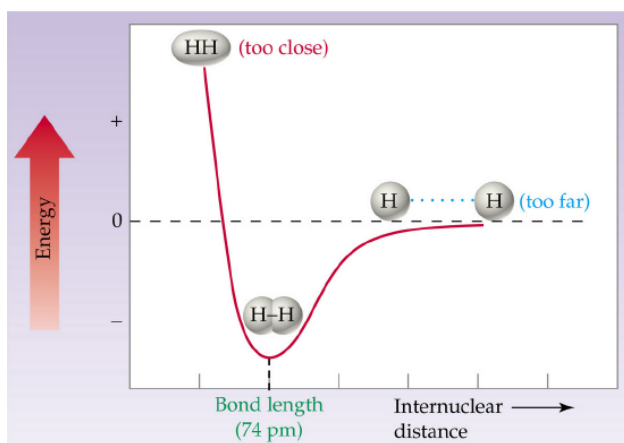


Figure 7.3: Dependence of the energy values of  $\epsilon_s$  on the nuclear distance  $R$ .

This means that the singlet state (antiparallel spins in the sense of the last factor in (7.7)) is stable around an equilibrium distance  $R = R_e$ . The calculated value from this simple model is  $R_e = 0.8\text{nm}$ , while the measured value is  $0.74\text{nm}$ . The state  $\psi_s$  is called therefore a **bonding state**, and it is denoted by  $\sigma$ . The other, triplet state, which is antisymmetric in space but the spins of the two electrons are parallel in the sense of (7.9) is not stable, there is no minimum in the energy, it is called an **antibonding state**, and it is denoted by  $\sigma^*$ . See figure 7.4 and the animation below.

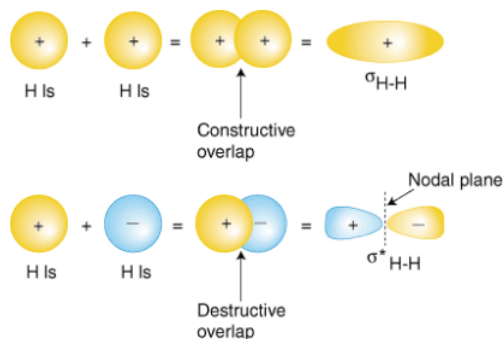
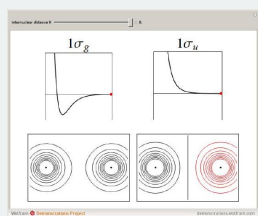


Figure 7.4: Schematic drawing of bonding and antibonding states.

<http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.rhtml>

#### Note



The lowest-energy bonding and antibonding molecular orbitals (MO) for a homonuclear diatomic molecule are shown, as the internuclear distance is varied. The red contours designate negative values of the wavefunction.

<http://demonstrations.wolfram.com/BondingAndAntibondingMolecularOrbitals/>

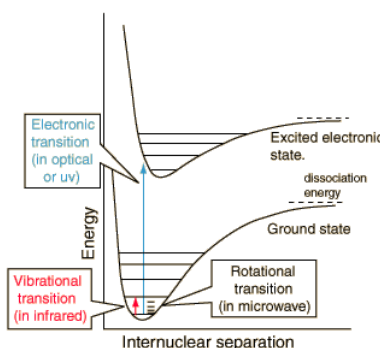
The  $\text{H}_2$  molecule is a **homonuclear** diatomic molecule, where homonuclear means that the two nuclei are identical. In some of the heteronuclear diatomic molecules (different atoms) there is another effect besides the one we discussed here. In  $\text{HCl}$  for instance the electron cloud will be asymmetric along the molecular axis, the electron from the  $\text{H}$  atom tends to get closer to the  $\text{Cl}$  and simply the attraction of the proton by the negatively charged  $\text{Cl}$  ion will stabilize this molecule.

The example we considered above was one of the simplest ones. The calculation of the **electronic structure** of very complicated large molecules have become possible in the second half of the 20th century due to the technical development of fast electronic

computers, as well as to the evolution of sophisticated algorithms and program packages, which are the subject of the science called quantum chemistry.

## Molecular spectra

In the atomic system, our consideration of radiative transitions was limited to the problem of electronic transitions between states. In the molecules, the internal structure allows also for transitions involving **rotational and vibrational excitations** of the constituent nuclei. As with atoms, electronic transitions are typically of the order of eV, corresponding to wavelengths in or near the optical region. However, it is unlikely that an electronic transition will occur without inducing motion of the nuclei, as well, because the equilibrium distances between the nuclei will be different in the initial and final electron states. The typical energies of rotational states of molecules are much smaller than those of electronic excited states, of order  $\hbar^2/2\Theta$ , where  $\Theta$  is the molecular moment of inertia. Substituting typical values for the interatomic spacing and atomic masses, one finds that rotational energies are of the order of  $10^{-4}$  eV corresponding to the far infra-red or microwave regions. Typical energies for vibrational excitations of molecules are around  $10^{-1}$  eV corresponding to the infra-red waveband. All of these types of transitions can occur radiatively, i.e. through the emission or absorption of a photon of the appropriate frequency  $\nu = \Delta\epsilon/h$ . As in the case of atoms, the most probable radiative transitions are usually electric dipole transitions. In an electric dipole transition, the photon carries away or brings in one unit of angular momentum and negative parity, so there will be the usual selection rule for the change in the total angular momentum quantum number of the molecule:  $\Delta J = 0, \pm 1$ , but not  $0 \rightarrow 0$ , accompanied by a change in the parity of the molecular state (which may impose further restrictions on  $\Delta J$ ).



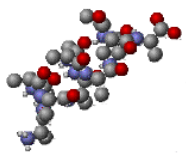
**Figure 7.5:** This figure visualizes the difference in orders of magnitude for the different type of transitions (electronic, vibrational and rotational).

<http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/molec.html>

In a gas or a liquid, transitions can also be produced by collisions between their molecules. The appropriate energy change can be provided by excitation or de-excitation of the other molecule, or as part of the kinetic energy of the collision. Such non-radiative transitions do not have to obey the selection rules above. Thus, for example, a molecule in a metastable state, i.e. one that cannot return to the ground state via an allowed radiative transition, can be de-excited by a collision. In the absence of any incident radiation or other non-thermal sources of excitation, collisions will bring about a thermal distribution of molecular energy levels, with the number of molecules in state  $i$  being given by  $N_i = \frac{N}{Z} g_i e^{-\epsilon_i/k_B T}$ , where  $g_i$  is the degeneracy and  $\epsilon_i$  the energy. At room temperature  $k_B T = 2 \times 10^{-2}$  eV, so typically many rotational states of molecules are excited, but not electronic or vibrational.

In a rotating and vibrating molecule the kinetic energy of the nuclei is small compared to the energy of the molecular state. This is because the nuclear masses are large, and therefore their motion is slow compared to the motion of the electrons. This allows the separation of the total wave function  $\Phi(\mathbf{R}, \mathbf{r})$  into a product  $\Phi(\mathbf{R}, \mathbf{r}) = \phi(\mathbf{R})\psi(\mathbf{R}, \mathbf{r})$  of a nuclear wave function  $\phi(\mathbf{R})$  and an electronic function  $\psi(\mathbf{R}, \mathbf{r})$  which depends on the electron coordinates  $\mathbf{r}$  and contains the nuclear positions  $\mathbf{R}$  as parameters. This approximation is called the adiabatic or Born-Oppenheimer approximation. Within this approximation the total energy of a molecular level can be written as a sum of the electronic, vibrational and rotational energies.

 Animation



Shown here is the thermal motion of a segment of protein alpha helix. Molecules have various internal vibrational and rotational degrees of freedom. This is because molecules are complex objects; they are a population of atoms that can move about within a molecule in different ways. This makes molecules distinct from the noble gases such as helium and argon, which are monatomic (consisting of individual atoms).

[http://upload.wikimedia.org/Wikipedia/commons/2/23/Thermally\\_Agitated\\_Molecule.gif](http://upload.wikimedia.org/Wikipedia/commons/2/23/Thermally_Agitated_Molecule.gif)

## Molecular rotation

### The model of a rigid diatomic molecule

In general, the Schrödinger equation for the nuclear motion has many solutions, which give the various molecular energy levels for a given electronic configuration. The simplest case is that of a diatomic molecule where the molecule can be characterized by its moment of inertia with respect to its centre of mass. If we assume in the first approximation that the molecule is rigid, and we consider the problem in the system fixed to the centre of mass of the molecule, then the translational kinetic energy can be separated. From the point of view of rotations, the molecule is characterized by its moment of inertia  $\Theta = \mu r_0^2$  about an axis through the centre of mass orthogonal to the bond, where  $r_0$  is the equilibrium bond length, and  $\mu$  is the reduced mass of the two atoms. The rotational kinetic energy can be expressed by the angular momentum  $\mathcal{L} = \Theta\omega$  as

$$\frac{1}{2}\Theta\omega^2 = \frac{\mathcal{L}^2}{2\Theta} \quad (7.13)$$

and if we replace the classical  $\mathcal{L}$  by the operator of the angular momentum we get the Hamilton operator of the pure rotational motion:

$$H = \frac{L^2}{2\Theta} \quad (7.14)$$

The stationary states are the solutions of the eigenvalue equation

$$\frac{L^2}{2\Theta}\Phi = \varepsilon_J\Phi \quad (7.15)$$

As  $L^2$  is a square of an angular momentum belonging to an orbital motion its eigenvalues are of the form  $\hbar^2 J(J+1)$ , (in molecular spectroscopy instead of the notation  $\ell$ , we use  $J$ ) where  $J=0, 1, \dots$ , and its projection  $m_J$  takes the values  $J, J-1, \dots, -J$ ). The rotational energy eigenvalues are therefore

$$\varepsilon_J = \frac{\hbar^2}{2\Theta} J(J+1) \quad (7.16)$$

while the eigenfunctions will be the spherical harmonic functions  $\Phi = Y_J^{m_J}$ . As mentioned earlier, the typical energies of rotational states of molecules are much smaller than those of electronic excited states. Since molecular dimensions are determined by the electronic wavefunction, their scale is set by the Bohr radius  $a_0$ . Thus moments of inertia are of order  $m_N a_0^2$  and the scale of rotational energies is  $\hbar^2/m_N a_0^2$ . For the electronic states, the Heisenberg inequality implies momenta of order  $\hbar/a_0$  and hence electron energies around  $\hbar^2/(m_e a_0^2)$ , a factor of  $m_N/m_e \simeq 10^4$  greater. To bring about a radiative rotational transition, an emitted or absorbed photon must interact with the electric dipole moment of the molecule. In a pure rotational transition the initial and final electronic states are the same, therefore the state needs to have a permanent electric dipole moment. Thus we can have purely rotational radiative transitions in heteronuclear diatomic molecules like HCl and CO, which have permanent dipole moments, but not in homonuclear ones like  $\text{H}_2$  and  $\text{O}_2$ .

The usual electric dipole selection rules apply:  $\Delta J = \pm 1, 0$  with a parity change. In a rotational state with angular momentum quantum numbers  $J$  and  $m_J$ , the nuclear wavefunction is proportional to the spherical harmonic  $Y_J^{m_J}$ , which has parity  $(-1)^J$ . (For simplicity, we consider only molecular states in which the electronic wavefunction has zero angular momentum and even parity). Then the fact that the parity must change in a radiative transition excludes the possibility  $\Delta J = 0$ . Therefore the possible energy changes in emission ( $J+1 \rightarrow J$ ;  $J=0, 1, 2, \dots$ ) are given by:

$$\Delta\varepsilon = \frac{\hbar^2}{2\Theta} [(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{\Theta} (J+1) \quad (7.17)$$

Accordingly the spectrum is expected to consist of lines with increasing frequencies.

To specify a spectral line in practical molecular spectroscopy one uses the wavenumber  $\bar{\nu} = 1/\lambda = \nu/c$ , which is obtained according the Bohr rule ( $\bar{\nu} = \Delta\varepsilon/hc$ ) as a difference of terms:

$$F_J = \frac{\varepsilon_J}{hc} \quad (7.18)$$

Here the word **term** is the standard terminology for the expression in (7.18). So the wavenumbers corresponding to the energy differences, i. e. to the transition, are obtained from (7.17) as:

$$\bar{\nu}_{\text{rot}}(J) = 2B(J+1) \quad (7.19)$$

where the **rotational constant**  $B = \hbar/4\pi c\mu R_e^2$ , is expressed here with the reduced mass  $\mu$ . Rotational transitions fall into the THz-GHz domain, i.e. in the far infrared or microwave range. In fact, the rate for spontaneous emission between rotational states is very small, because of the small energy release. The spontaneous emission rate varies as  $\omega^3$ , and so rotational transitions are more conveniently studied by absorption spectroscopy. The same formula for the transition energies clearly applies to the  $J \rightarrow (J+1)$  absorption case, as well. Observation of this spacing can be used to determine the moment of inertia and hence the bond length of the molecule.

The intensities of rotational spectral lines show some interesting features. Although the transition matrix element depends on the quantum numbers, the dominant factor is usually the population of the initial state. As mentioned earlier, non-radiative transitions due to molecular collisions bring about a thermal distribution,

$$(7.20)$$

This increases with  $J$  up to some value, which depends on the temperature, and then decreases. Thus successive spectral lines increase and then decrease in intensity.

### Centrifugal Distortion

A real molecule is not rigid. When it rotates, the centrifugal force acts on the atoms and the internuclear distance increases to a value  $R$  where this force  $F_c = -M\omega^2 R$  is compensated by the restoring force  $F_r = -dE_{\text{pot}}(R)/dR$  holding the two atoms together, which depends on the slope of the potential energy function  $E_{\text{pot}}(R)$ . In the vicinity of the equilibrium distance  $R_e$  the potential can be approximated by a parabolic function. This leads to a linear restoring force

$$F_r = -k(R - R_e) \quad (7.21)$$

From the relation  $J^2 = \Theta^2\omega^2 = M^2 R^4\omega^2$  we obtain:

$$M\omega^2 R = \frac{J(J+1)}{MR^3} \hbar^2 = k(R - R_e) \quad (7.22)$$

which leads to

$$R = R_e + \frac{J(J+1)\hbar^2}{MkR_e^3} \quad (7.23)$$

This means that the internuclear distance  $R$  is increased by the molecular rotation. Since the potential energy  $E_{\text{pot}}(R)$  has a minimum for  $R = R_e$ , in case of  $\text{Req}R_e$  we have an additional energy  $\Delta E_{\text{pot}} = \frac{k}{2}(R - R_e)^2$  in the case of a nonrigid rotor. The total energy of the nonrigid rotor is then

$$\varepsilon_{\text{rot}} = \frac{J(J+1)\hbar^2}{MR^2} + \frac{1}{2}k(R - R_e)^2 \quad (7.24)$$

If we express RR on the right side of (7.23) by  $R_e$  and  $k$  with the help of (7.22) we obtain

$$R = R_e \left( 1 + \frac{J(J+1)\hbar^2}{MkR_e^4} \right) \quad (7.25)$$

where the second term is  $\ll 1$ . This allows us to expand  $1/R^2$  into the power series

$$\frac{1}{R^2} = \frac{1}{R_e^2} \left( 1 - \frac{2J(J+1)\hbar^2}{MkR_e^4} + \frac{3J^2(J+1)^2\hbar^4}{M^2k^2R_e^8} \mp \dots \right) \quad (7.26)$$

and the rotational energy becomes up to third order in  $\hbar^2$

$$\varepsilon_{\text{rot}} = \frac{J(J+1)\hbar^2}{2MR_e^2} - \frac{J^2(J+1)^2\hbar^4}{2M^2kR_e^6} + \frac{3J^3(J+1)^3\hbar^6}{2M^3k^2R_e^{10}} \quad (7.27)$$

This means that for a given value of the rotational quantum number  $J$  the centrifugal force makes the moment of inertia larger and therefore the rotational energy smaller. This effect overcompensates the increase in potential energy.

Using the term-values again instead of the energies, (7.27) becomes

$$F_{rot}(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \quad (7.28)$$

with the rotational constants:

$$B_e = \frac{h^2}{8\pi^2 I_e}, \quad D_e = \frac{h^4}{64\pi^4 I_e^3}, \quad H_e = \frac{h^6}{32768\pi^6 I_e^5} \quad (7.29)$$

The experimental spectroscopic accuracy is nowadays sufficiently high to measure even the higher order constant  $H_e$ .

## Vibrational transitions

### Harmonic approximation

Another important type of molecular motion is vibration, in which the nuclei oscillate around their equilibrium positions. For a diatomic molecule, we can make a Taylor expansion of the molecular potential  $E_0(R)$  around the equilibrium nuclear separation  $R_0$  to obtain

$$E_0(R) = E_0(R_0) + \frac{1}{2} (R - R_0)^2 \left. \frac{\partial^2 E_0(R)}{\partial R^2} \right|_{R=R_0} + \dots \quad (7.30)$$

The first derivative vanishes, because  $E_0(R)$  has a minimum at  $R_0$ .  $E_0(R_0)$  is a constant, and the second term on the right-hand side can be written as , which is the potential for a simple linear harmonic oscillator with  $X = R - R_0$  , and classical frequency

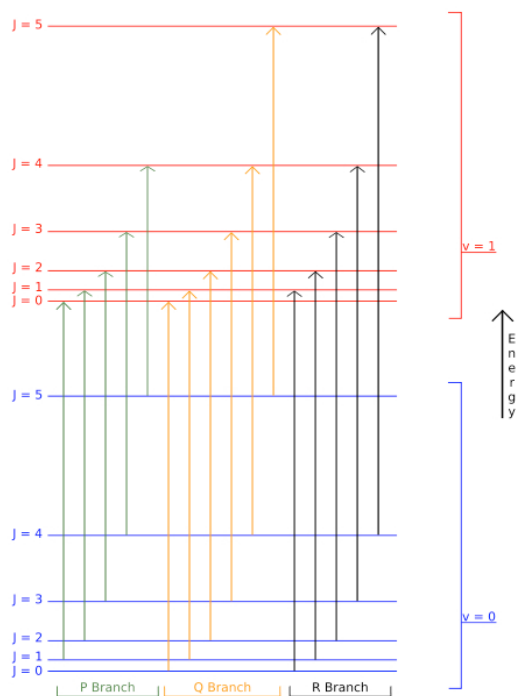
$$\omega = \left[ \frac{1}{\mu} \left. \frac{\partial^2 E_0}{\partial R^2} \right|_{R=R_0} \right]^{1/2} \quad (7.31)$$

where  $\mu$  is the reduced mass. According to the quantum theory of the harmonic oscillator the energy levels including nuclear vibration is given by

$$\varepsilon(v) = E_0(R_0) + \hbar\omega(v + 1/2), \quad v = 0, 1, 2 \dots \quad (7.32)$$

The excitation energies of molecular vibrational states are typically larger than those of rotational states by a factor of about  $(m_N/m_e)^{1/2}$  and smaller than electronic excitation energies by a factor of about  $(m_e/m_N)^{1/2}$ . As we discussed earlier,  $E_0(R_0)$  will be of the same order of magnitude as atomic energies, i.e. of the order of  $\hbar^2/m_e a_0^2$ , where  $a_0$  is the Bohr radius. Thus, on dimensional grounds,  $\left. \frac{\partial^2 E_0}{\partial R^2} \right|_{R_0}$  will be of order  $\hbar^2/m_e a_0^4$ , and  $\hbar\omega \sim \hbar^2/\sqrt{m_e m_N} a_0^2$ . Therefore the vibrational energy is smaller than the electronic by a factor of order  $\sqrt{m_e/m_N}$ . This puts vibrational spectra in the wavelength region around  $10\mu\text{m}$ , which is in the infra-red.





**Figure 7.6:** Generally vibrational transitions occur in conjunction with rotational transitions. Consequently, it is possible to observe both rotational and vibrational transitions in the vibrational spectrum. The top figure shows an energy level diagram demonstrating some of the transitions involved in the IR vibrational-rotational spectrum of a linear molecule: P branch (where  $\Delta J = -1$ ), Q branch (not always allowed,  $\Delta J = 0$ ) and R branch ( $\Delta J = +1$ ).

<http://en.Wikipedia.org/wiki/File:Vibrationrotationenergy.svg>

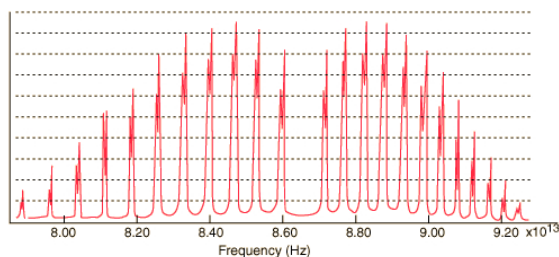


Figure 7.7: The vibration-rotation spectrum of HCl. The left hand branch of the spectrum represents the P branch and the right the R. The Q branch is not allowed. The splitting of the lines is associated with the two isotopes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ .

We can now check explicitly that the Born-Oppenheimer approximation is valid for nuclear vibrational states, as follows. The mean square nuclear vibrational momentum is of order  $m_N \hbar \omega \sim \sqrt{m_N/m_e} (\hbar/a_0)^2$ , which means that  $\nabla_N^2 \phi_k \sim \sqrt{m_N/m_e} \phi_k/a_0^2$ , where  $\phi_k$  is the nuclear part of the wavefunction. On the other hand  $\nabla_N^2 \psi \sim \psi/a_0^2$ , where  $\psi$  is the electronic part. Thus  $\phi \nabla_N^2 \psi$  is smaller than  $\psi \nabla_N^2 \phi$  by a factor of  $\sqrt{m_e/m_N}$ , and it is legitimate to neglect the former.

For vibrational transitions we have the selection rule  $\Delta v = \pm 1$ . This implies only a single energy in the spectrum

$$\Delta \varepsilon = (\varepsilon_{v+1} - \varepsilon_v) = \hbar \omega \quad (7.33)$$

corresponding to the classical frequency of oscillation.

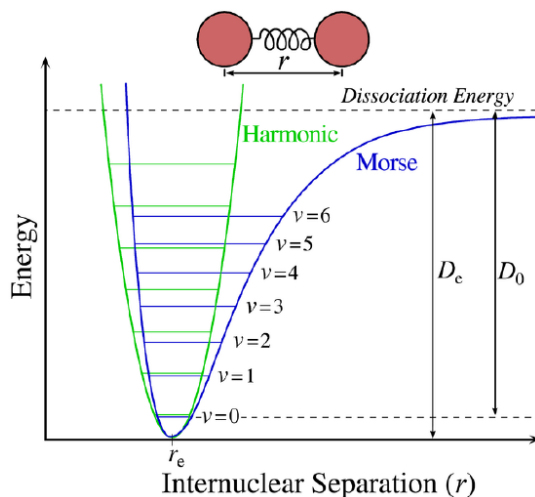
### Anharmonic effects

In practice the Taylor expansion around  $R = R_0$  has non-negligible terms of higher than second order and the harmonic oscillator approximation is not very reliable: there is anharmonicity. The flattening of the molecular potential energy curve at larger separations has the effect of bringing the energy levels closer together. Thus transitions at larger  $v$  have lower energies than that given above. Also, since the true stationary state wavefunctions are not precisely harmonic oscillator eigenfunctions, our selection rule is not exactly valid, and transitions with  $|v| > 1$  become possible. A good approximation of the potential that includes anharmonic effects is the so called **Morse potential** having the form:

$$E_0(R) = D_e (1 - e^{-a(R-R_e)})^2 \quad (7.34)$$

where  $D_e$  is the dissociation energy, the limit to which the potential converges at  $R \rightarrow \infty$ . The minimum of the potential is at the equilibrium value  $R_e$  of the distance between the atoms. The definition in (7.31) yields:

$$\omega = a\sqrt{2D_e/\mu} \quad (7.35)$$



**Figure 7.8:** The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by  $|\langle \hbar\omega \rangle|$ , the Morse potential level spacing decreases as the energy approaches the dissociation energy.

<http://en.Wikipedia.org/wiki/File:Morse-potential.png>

The eigenvalue equation of the corresponding vibrational Hamiltonian  $\frac{p^2}{2\mu} + D_e (1 - e^{-a(R-R_e)})^2$  in one dimension can be solved in closed form yielding the exact eigenvalues:

$$\varepsilon(v) = E_0(R_0) + \hbar\omega \left(v + \frac{1}{2}\right) - \frac{\hbar^2\omega^2}{4D_e} \left(v + \frac{1}{2}\right)^2, \quad v = 0, 1, 2, \dots \quad (7.36)$$

This provides the energy separation

$$\Delta\varepsilon(v) = \hbar\omega \left(1 - \frac{\hbar\omega}{2D_e} (v+1)\right) \quad (7.37)$$

which means that the transition frequencies are decreasing, with increasing vibrational quantum numbers. In contrast to the harmonic case the number of bound states is finite  $[s] + 1$ , where  $s = \frac{\sqrt{2\mu D_e}}{\hbar\alpha} - 1/2$ , and  $[s]$  denotes the integer part of  $s$ .

Vibrational modes for polyatomic molecules can be quite complicated. If there are  $N$  atoms, in general there are  $3N - 6$  normal modes ( $3N$  coordinates minus 3 to define the overall position of the centre of mass, and minus 3 to define the overall orientation of the molecule) or  $3N - 5$  in the case of a diatomic molecule. Thus, in the simple case of the linear  $\text{CO}_2$  molecule, there are four modes, two with the atoms remaining collinear (one with the two O atoms moving in antiphase with the C stationary, and one with the O atoms moving in phase in the opposite direction to the C atom) and two degenerate orthogonal bending modes. The more detailed classification of the possible vibrational modes of polyatomic molecules relies strongly on their symmetry properties and needs the mathematical method called group theory.

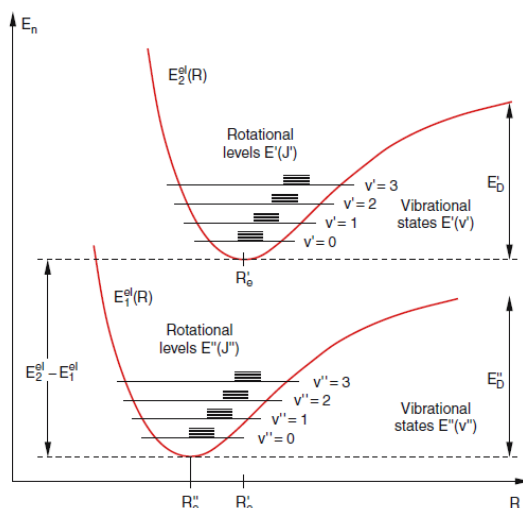


Figure 7.9: The combined electronic vibrational and rotational levels of a molecule. We see that the largest energy difference is between the electronic states. The electronic spectrum consists of a system of vibrational bands, while each vibrational band includes many rotational lines.

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