# Molecules

# 1 Types of Bonding

Here we make some very simple-minded estimates in order to understand the different types of bonding.

#### 1.1 Ionic Bonding

Consider sodium chloride. We want to argue that it is energetically favorable for sodium to give up an electron to chlorine, forming  $Na^+$  and  $Cl^-$ , and for these two ions to join to form a molecule. We first estimate the cost of removing an electron from sodium. Sodium has Z = 11. Its unfilled shell is 3s, containing one electron. We can estimate the binding energy of this electron by comparing with the hydrogen spectrum. We know that hydrogen energy levels go as:

$$E_n = \frac{Z^2}{n^2} \times (-13.6) \text{ eV}.$$
 (1)

The question is: what should we use for Z. When the outermost electron is far away from the nucleus, it sees Z = 1, but inside it can see much larger Z. As a guess, let's suppose that the average Z = 2. Then we obtain for the ionization energy:

$$E_{ion} = .4444 \times -13.6 = 6.04. \tag{2}$$

This is not too far off the measured value 5.14.

Now consider the energy released when chlorine captures the electron. Here the question is again the effective Z. Far away, the electron sees net charge zero. Inside the p level, it could see as much as 5. So again, let's guess 2. Again n = 3. So our guess for the capture energy is similar. In this case, though, we are further off. The capture energy is 3.62. (We have presumably overestimated the charge by a factor of about 1.2. Still not too bad). Now we can ask: what is the further energy gained by bringing the two ions close together. If the ions are too close, the inner electrons will overlap. We can ask the size of the two ions. Again, we can make an estimate, using the formula from hydrogen:

$$\langle r \rangle = \frac{a_o}{2Z} [3n^2 - \ell(\ell+1)]$$
 (3)

For sodium, n = 2,  $\ell = 1$  for the *p* shell, and *Z* is now larger; we might guess about 4. So we have  $\langle r \rangle \sim a_o$ . For the Chlorine, we might guess something larger. For the filled shell, taking Z = 2 again, we would have something like  $6a_o$  or about 3 angstroms. In fact, the actual separation is 2.36 angstroms. The associated energy is  $\frac{ke^2}{R} = 6.1eV$ , so the net binding energy is 5.144.

#### 1.2 Covalent bonds

A prototype for covalent bonds is provided by  $H_2$ . Here the electrons are not associated with one or the other nucleus but are shared between them. You should read the discussion in your text, which describes well what happens as one brings two hydrogen atoms together slowly. Starting with a wave function which is a product:

$$\psi(\vec{x}_1 - \vec{R}_1)\psi(\vec{x}_2 - \vec{R}_2) \tag{4}$$

one can consider the effects of the interactions between the two electrons and the two protons. One wants the attraction of the electrons for the protons to "beat" the repulsion of the electrons for each other and the protons for each other. This can occur if the electron wave function is large for the electrons in between the protons. Starting with our initial wave function, this requires that the wave function be symmetric in the coordinates  $\vec{x}_1$  and  $\vec{x}_2$ . Otherwise, when  $\vec{x}_1 = \vec{x}_2$ , the wave function will vanish. Because the spin and space wave function must be antisymmetric, this means that the spin wave function must be antisymmetric. This feature is characteristic of many covalent bonds.

When we are done, we are left with a system that looks much like a dumbell It has three types of excitations. One is associated with rotations; this leads to "rotational excitations" or "rotational modes." A second is associated with vibrations – small oscillations of the nuclei about their equilibrium position. The third are "electronic excitations" – excitations of the electrons into higher orbitals of the molecule.

### 2 The Rotor

The rotor: The energy (Hamiltonian) for a rotor is

$$H = E = \frac{\vec{L}^2}{2I}.$$
(5)

We know what the eigenvalues of  $\vec{L}^2$  are, so the energy levels are:

$$E_{\ell} = \frac{\hbar^2 \ell(\ell+1)}{2I}.\tag{6}$$

The degeneracy of each level is  $2\ell + 1$ .

#### 3 The Harmonic Oscillator

The Hamiltonian for the harmonic oscillator is probably the most important in physics. This is because any system, near the equilibrium point of its potential, experiences a linear force – not just springs.

The Hamiltonian for a harmonic oscillator is

$$H = E = \frac{p^2}{2m} + 1/2Kx^2 \tag{7}$$

The corresponding Schrodinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}Kx^2\psi = E\psi.$$
 (8)

The classical frequency of the oscillator is  $\omega_o = \sqrt{\frac{K}{m}}$ . As explained in your book the solutions have energy of a very simple form:

$$E_n = \hbar \omega_o (\frac{1}{2} + n). \tag{9}$$

The wave functions themselves are interesting. They are of the form:

$$\psi_n = H_n(x)e^{-\frac{\omega_o m x^2}{2\hbar}}.$$
(10)

The  $H_n$ 's are polynomials (of *n*'th degree) in x, known as the Hermite polynomials.

**Exercise**: Check the solution for n = 0. Then for n = 1, using the energy eigenvalue  $E = \frac{3}{2}\hbar\omega_o$ , find  $H_1$  (don't worry about the normalization of the wave function).

Solution:

This is a straightforward "plug in" problem. For the ground state,  $\psi = e^{-\omega_o m x^2/2\hbar}$ . Putting  $E = \hbar \omega_o/2$ , the Schrodinger equation becomes (remember  $\omega_o^2 = K/m$ ):

$$\frac{d^2\psi}{dx^2} - \frac{m^2\omega_o^2}{\hbar^2}\psi + \frac{m\omega_o}{\hbar}\psi = 0.$$
(11)

So now just evaluate the derivatives:

$$\frac{d\psi}{dx} = -\omega_o m x / \hbar e^{-\omega_o m x^2 / 2\hbar}$$
(12)

$$\frac{d^2\psi}{dx^2} = (-\omega_o m/\hbar + \omega_o^2 x^2/\hbar^2)e^{-\omega_o m x^2/2\hbar}$$
(13)

so the Schrodinger equation is satisfied.

For the first excited state, it is convenient to write the solution in a more general way. Calling  $\psi = H(x)e^{-\omega_o mx^2/2\hbar}$ , we plug in again. The new feature is that the derivatives act on H as well as the exponential, so there are more terms. The Schrödinger equation is (with  $E = 3/2\omega_o$ ):

$$\frac{d^2\psi}{dx^2} - \frac{m^2\omega_o^2}{\hbar^2}\psi + \frac{3m\omega_o}{\hbar}\psi = 0.$$
(14)

It is convenient also to write:

$$\psi = He^{-Ax^2} \tag{15}$$

so

$$\psi' = (-2xAH + H')e^{-Ax^2}.$$
(16)

$$\psi'' = (H'' - 4xAH' - 2AH + 4A^2x^2H)e^{-Ax^2}$$
(17)

Plugging in the Schrodinger equation gives:

$$H'' - \frac{2m\omega_o xH'}{\hbar} + 2\frac{m\omega_o}{\hbar}H = 0.$$
 (18)

This is solved, as in eqn. 6-58 in your text, by H = x (one can also work out the normalization but that is not necessary for this exercise.

#### 4 Molecules

What does this have to do with molecules?

We said that we can think of the following types of excitations in a molecule:

- Rotations a diatomic molecule like  $H_2$  rotates like a dumbell (rotor).
- Vibrations: If R is the distance between the two nuclei,

$$V(R) = V(R_o) + \frac{K}{2}(R - R_o)^2 \quad K = \frac{d^2 V}{dR^2}|_{R_o}.$$
(19)

Note that this is exactly a harmonic oscillator Hamiltonian.  $V(R_o)$  is just a constant in the energy, and doesn't matter; then call  $x = (R - R_o)$ .

• Electronic motions – so far we have been imagining that the nucleons are moving relatively slowly, so that the electrons are always in their ground state. It is possible to excite the electrons; these excitations will have energies of order a few electron volts, like atoms.

So the energy levels are given by

$$E_{n,\ell} = \hbar\omega_o(n+\frac{1}{2}) + \frac{\hbar^2\ell(\ell+1)}{2I}.$$
 (20)

The vibrational energies are typically an order of magnitude larger than the rotational energies, so one has two "bands." Transitions between the vibrational brands are typically in the infrared; those in the rotational bands in the microwave.

### 5 Thinking about the full Schrodinger Equation

We can derive these results by thinking about the Schrodinger equation directly. We focus on the motion of the nuclei. For a diatomic molecule, there are two nuclei. These are described by two vector positions (six coordinates overall). But three of these coordinates are just describe the overall motion of the center of mass. The three relative coordinates we call  $\vec{R}$ , the (vector) distance between the two nuclei ( $\vec{R} = \vec{x}_1 - \vec{x}_2$ ). The potential for a diatomic molecule is just a function of the distance between the nuclei,  $|\vec{R}|$ . So we can separate variables. We use spherical coordinates,  $\vec{R} = (R, \theta, \phi)$ . We get the same equations we had for hydrogen, except that  $r \to R$ , and the potential is different. The angular part is solved by the  $Y_{\ell,m}$ 's, and the radial part satisfies (remember that the radial part, if we divide by R, looks like the equation for a single particle in a potential with a centrifugal term):

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right)\chi = E\chi.$$
(21)

Now we Taylor series expand V and  $1/R^2$  about  $R_o$ . In the angular momentum term, the leading piece is just

$$\frac{\hbar^2 \ell(\ell+1)}{2\mu R_o^2} = \frac{\hbar^2 \ell(\ell+1)}{2I}$$
(22)

In the potential piece, we get just the harmonic oscillator potential, with K as before.

So again we can read off the spectrum right away. The energy is

$$E_{\ell,n} = \hbar\omega_o(n+1/2) + \frac{\hbar^2 \ell(\ell+1)}{2\mu R_o^2}$$
(23)

These are the same rotational and vibrational bands we wrote down above.

**Exercise:** Show that equation 11 follows from the Taylor expansion of Equation 9.

Solution: This is easy. Just write:

$$\frac{\hbar^2 \ell(\ell+1)}{2\mu R^2} \approx \frac{\hbar^2 \ell(\ell+1)}{2\mu R_o^2} + \text{ powers of } (R-R_o)$$
(24)

This is the Hamiltonian for a rotor with  $I\mu R_o^2$ .

$$V(R) = V(R_o) + V'(R_o)(R - R_o) + \frac{1}{2}V''(R_o)(R - R_o)^2.$$
(25)

The second term vanishes because  $R_o$  is the minimum of the potential. Calling  $K = V''(R_o)$ , gives the energy as the sum of a constant  $(V(R_o))$  plus a term for the harmonic oscillator, plus the rotor term.

## 6 Statistical Mechanics of Molecules

Let's see how, for high temperature, the equipartition theorem holds for the rotational states.

First, for sufficiently high temperatures (when  $e^{\alpha} \gg 1$ ), the velocities of the molecules obey the Maxwell-Boltzmann distribution. For each molecule, the  $\ell$ 's will be distributed according to the Bose-Einstein distribution (why?). So if we want to determine the average *rotational* energy, we need to evaluate  $(E_{rot} = \frac{\hbar^2}{2m})$ :

$$\sum_{\ell} \ell(\ell+1) E_{rot} \times \frac{2\ell+1}{e^{\beta\ell(\ell+1)E_{rot}} - 1}.$$
(26)

Note that we have included  $2\ell + 1$  to account for the degeneracy of the states.

For temperatures  $T \ll E_{rot}$ , only the term  $\ell = 1$  contributes, and the average energy is approximately zero. Once  $T \gg E_{rot}$ , however, we can approximate  $\sum_{\ell} \approx \int d\ell$ . So we need to evaluate the integral:

$$\langle E \rangle = \frac{\int_{o}^{\infty} d\ell \hbar^2 2\ell^3 E_{rot} e^{-\beta\ell^2 E_{rot}}}{\int_{o}^{\infty} d\ell 2\ell e^{-\beta\ell^2 E_{rot}}}$$
(27)

**Exercise:** Explain the factors in this expression. Note that we have simplified things by assuming that the temperature is large enough that we can use the Boltzmann distribution, and that  $\ell$  is large so that  $\ell^2 \gg \ell$ , for example. The denominator is there because we need to average over the distribution.

Solution: The  $2\ell$  in the denominator is an approximation, for large  $\ell$ , of  $2\ell + 1$ . The same factor appears in the numerator, along with an approximation for the energy,  $\hbar^2 \ell(\ell+1) \approx \hbar^2$ .

This integral can be evaluated by the following trick. Note that

$$\langle E \rangle = -\frac{d}{d\beta} \ln \left( \int_{o}^{\infty} d\ell 2\ell^{3} E_{rot} e^{-\beta\ell^{2} E_{rot}} \right)$$
(28)

Now because this is a derivative with respect to  $\beta$ , things simplify. The change of variables,  $\beta \ell^2 = x^2$  gives that the right hand side is of the form

$$\langle E \rangle = -\frac{d}{d\beta} \ln(\beta^{-1} \times C) = \frac{1}{\beta} = kT$$
 (29)

where C is a constant independent of T.

This is the equipartition theorem for two degrees of freedom, as promised.