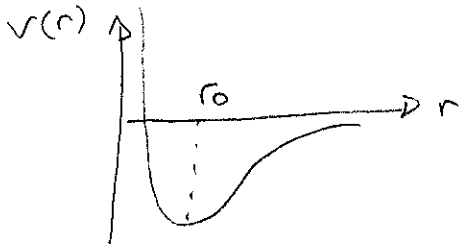
The diatomic molecule

The interaction potential between 2 atoms forming a diatomic molecule has, irrespective of the type of chemical bond, the following shape



This system is amenable to the treatment we did before concerning the 2-body problem with a central potential. We saw that the S-Eq

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi = E\psi \qquad (1)$$

could be written as

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = E\,u \qquad (2)$$

where

$$\psi = R(r)\,Y_\ell^m(\theta,\phi) \qquad (3)$$

$$R(r) = \frac{u(r)}{r}$$

the rigid rotor

Let us first suppose that the potential connecting the two atoms is very stiff, so that the relative position r between them is absolutely fixed. This is what we call a rigid rotor. In this case all the molecule can do is rotate.

In this case $R(r)$ will be a constant, as will $V(r)$. For simplicity we set $V(r_0) = 0$. This simply rescales the zero of energy. Eq (1) then becomes

$$\frac{\hbar^2}{2m}\frac{L^2}{r_0^2}\psi = E\psi$$

We already know that, since $R(r)$ is a constant,

$$\psi = Y_l^m$$

so that

$$E\,Y_l^m = \frac{\hbar^2}{2mr_0^2}\,l(l+1)\,Y_l^m$$

The energy levels of the rigid rotor are therefore

$$E_l = \frac{\hbar^2}{2I}\,l(l+1) \qquad (4)$$

where I defined the moment of inertia of the molecule as

$$I = m r_0^2 \qquad (5)$$

Also, recall that m is the reduced mass. Some people also call $B = \hbar^2/2I$ the rotational constant.

Rotations and vibrations

the potential $V(r)$, however, is not stiff. In fact, the molecule may also vibrate around r_0. Usually (but not always) this vibration is small. In this case we may approximate it by a harmonic oscillation

$$V(r) \approx \frac{1}{2} k (r-r_0)^2 \qquad (6)$$

where k is the spring constant. this is an important parameter because it gives information about the shape of the bonding energy for each molecule.

Eq (2) now becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{1}{2}k(r-r_0)^2 + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \qquad (7)$$

We may change variables to

$$\rho = r - r_0 \qquad (8)$$

this does not change the derivatives so that

$$-\frac{\hbar^2}{2m}\frac{d^2u}{d\rho^2} + \left[\frac{1}{2}k\rho^2 + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{(r_0+\rho)^2}\right]u = Eu \qquad (9)$$

But recall that we are assuming that the vibrations are small so that $r \approx r_0$. In other words, $\rho \ll r_0$.

Let

$$V_e = \frac{1}{2}k\rho^2 + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{(r_0+\rho)^2}$$

In this case we may expand

$$\frac{1}{(r_0+\rho)^2} = \frac{1}{r_0^2}\,\frac{1}{(1+\rho/r_0)^2} \approx \frac{1}{r_0^2}\left[1 - \frac{2\rho}{r_0} + \frac{3\rho^2}{r_0^2} + \dots\right]$$

the potential energy is, therefore, approximated to

$$e = \frac{1}{2}k\rho^2 + \frac{\hbar^2}{2m}\,\frac{\ell(\ell+1)}{(r_0+\rho)^2} \approx \frac{1}{2}k\rho^2 + \frac{\hbar^2}{2mr_0^2}\,\ell(\ell+1)\left[1 - \frac{2\rho}{r_0} + \frac{3\rho^2}{r_0^2} + \dots\right]$$

We now identify the same "rotational constant" B of before

$$B = \frac{\hbar^2}{2mr_0^2} \qquad (10)$$

So that, to 2^{nd} order in ρ,

$$V_e = \frac{1}{2}k\rho^2 + B\,\ell(\ell+1) - 2B\,\ell(\ell+1)\frac{\rho}{r_0} + 3B\,\ell(\ell+1)\frac{\rho^2}{r_0^2}$$

Apart from the constant term $B\cdot\ell(\ell+1)$, we have a quadratic polynomial in ρ:

$$\alpha\rho^2 + \beta\rho$$

where

$$\alpha = \frac{3B\,\ell(\ell+1)}{r_0^2} + \frac{1}{2}k \qquad (11a)$$

$$\beta = -\frac{2B\,\ell(\ell+1)}{r_0} \qquad (11b)$$

The trick now is to write this as

$$\alpha(\rho - a)^2 - \alpha a^2$$

Expanding

$$\alpha\rho^2 + \alpha a^2 - 2\alpha a\rho - \alpha a^2$$

Hence, by comparison we find

$$-2\alpha a = \beta$$

or

$$a = -\frac{\beta}{2\alpha} = \frac{B\ell(\ell+1)/r_0}{\frac{3B\ell(\ell+1)}{r_0^2} + \frac{1}{2}k}$$

$$\boxed{a = \frac{r_0 B\ell(\ell+1)}{3B\ell(\ell+1) + \frac{1}{2}k r_0^2}} \qquad (12)$$

Hence Ve becomes

$$V_e \approx B\ell(\ell+1) + \alpha(\rho - a)^2 - \alpha a^2 \qquad (13)$$

Plugging back on Eq (9) we find that

$$-\frac{\hbar^2}{2m}\frac{d^2u}{d\rho^2} + \left[B\ell(\ell+1) - \alpha a^2 + \alpha(\rho-a)^2\right]u = E\,u \qquad (14)$$

By a rescaling of the coordinates and the energy this can be transformed into the S-Eq of the harmonic oscillator. Let

$$\mathcal{E} = E - B\ell(\ell+1) + \alpha a^2 \qquad (15)$$

$$x = \rho - a \qquad (16)$$

and

$$\frac{1}{2}m\omega^2 = \alpha \qquad (17)$$

then we get

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}m\omega^2x^2u = \mathcal{E}\,u \qquad (18)$$

We already know the eigenvalues. They are

$$\mathcal{E}_n = \hbar\omega\,(n+1/2)\,, \qquad n = 0, 1, 2, \ldots$$

Hence the total energy is

$$E_{n,\ell} = \mathcal{E}_n + B\ell(\ell+1) - \alpha a^2$$

The only thing left to do is simplify. First:

$$\alpha a^2 = \frac{\alpha}{4\alpha^2}\beta^2 = \frac{\beta^2}{4\alpha}$$

$$\therefore \quad \alpha a^2 = \frac{\dfrac{4B^2[\ell(\ell+1)]^2}{r_0^2}\dfrac{1}{4}}{\dfrac{3B\ell(\ell+1)}{r_0^2} + \dfrac{1}{2}k}$$

$$\alpha a^2 = \frac{[B\ell(\ell+1)]^2}{3B\ell(\ell+1) + \frac{1}{2}kr_0^2} \qquad (14)$$

We can also find a formula for ω:

$$\omega^2 = \frac{2\alpha}{m} = \frac{2}{m}\left[\frac{3B\ell(\ell+1)}{r_0^2} + \frac{1}{2}k\right]$$

So

$$\omega_\ell = \sqrt{\frac{6B\ell(\ell+1) + kr_0^2}{mr_0^2}} \qquad (15)$$

The final formula for the energy is thus

$$\boxed{E_{n,\ell} = \hbar\omega_\ell(n+1/2) + B\ell(\ell+1) - \frac{[B\ell(\ell+1)]^2}{3B\ell(\ell+1) + \frac{1}{2}kr_0^2}} \qquad (16)$$

$n = 0, 1, 2, 3 \ldots$

$\ell = 0, 1, 2, 3, \ldots$

Eq (16) is called the ro-vibrational spectrum of the diatomic molecule. Note how rotations and vibrations are not independent processes. The first term is the energy of vibration but ω is actually a function of ℓ, so the frequency of vibration depends on the "intensity" of the rotation.

The 2nd term is a pure rotational energy, exactly like in the rigid rotor. Finally the third term may be viewed as a correction to the rotation due to the fact that the molecule is not actually rigid.

This Eq describes experimental data quite well. To obtain improvements we must consider more general shapes for the potential. A nice approach is that due to Morse, the so called Morse potential.