QUANTUM MECHANICS B PHY-413 Note Set No. 8

ROTATION-VIBRATION SPECTRA OF DIATOMIC MOLECULES.

(1) THE RIGID ROTATOR.

A diatomic molecule is made of two atoms bound together by an interatomic potential $V(r)$ when separated by a distance r. The quantum mechanics of this two-particle system is discussed in the Appendix, where we show that the dynamics of the system can be separated into two independent parts: an inessential centre-of-mass free motion of the system as a whole and an interaction between the two atoms described by a TISE in the relative coordinate $\mathbf{r}$ for a single 'particle' of reduced mass μ in a potential $V(r)$:

$$\{-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\}\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) \tag{1}$$

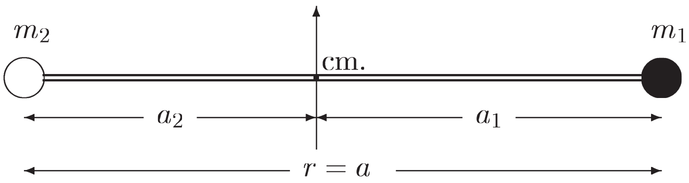

Figure 1: Diatomic molecule as rigid rotator.

This potential accounts for the forces between the two atoms. A very first approximation assumes the binding is so strong that the two atoms are held *rigidly* at a fixed distance, $r = a$, apart. Such a molecule can both travel as a free particle through space - a quantum mechanically uninteresting motion - and rotate about its centre-of-mass. It is this rotation which is described by the above equation. An improvement on this approximation would be to also take account of small vibrations about the equilibrium separation $r = a$ by using a simple harmonic oscillator potential. Our approximation procedure will be to assume that these two types of relative motion are *independent*, so that the total energy of relative motion is simply the sum of rotational and vibrational energies. The latter we already know from the harmonic oscillator, $E_{vib} = (n + 1/2)\hbar\omega_0$; the former we now proceed to calculate. A more realistic approximation would be to take account of both forms of motion simultaneously, including deviations from the harmonic oscillator potential and the effects of centrifugal forces due to rotation. For the rigid rotator the assumption that the distance r between the two atoms remains constant means that *the wave function only varies with the angular coordinates,* θ, φ, and not with r:

$$\psi(r,\theta,\varphi) = \psi(\theta,\varphi) \tag{2}$$

and that there is no potential; the condition $r = a =$*constant* plays the role of an effective potential keeping the atoms at a fixed distance apart. The result is that in spherical polar coordinates the derivatives with respect to r give zero contribution in the TISE (See equations

(68), (69) on p.8 of notes on 'ANGULAR MOMENTUM IN QUANTUM MECHANICS'.):

$$\begin{aligned}
\{-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\}\,\psi(r,\theta,\varphi) &= E\,\psi(r,\theta,\varphi), && (3)\\
\text{i.e.,}\qquad \left\{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\widehat{\mathbf{L}}^2}{2\mu\, r^2}+V(r)\right\}\psi(r,\theta,\varphi) &= E\,\psi(r,\theta,\varphi) && (4)\\
\text{which becomes, for the rigid rotator,}\qquad \frac{\widehat{\mathbf{L}}^2}{2\mu\, a^2}\,\psi(\theta,\varphi) &= E\,\psi(\theta,\varphi) && (5)
\end{aligned}$$

where we have used the assumption that $r = a$ and the fact that the angular momentum operator operates only on the angular variables. The final result is

$$\begin{aligned}
\widehat{\mathbf{L}}^2\,\psi(\theta,\varphi), &= 2\mu a^2 E\,\psi(\theta,\varphi) && (6)\\
&= 2IE\,\psi(\theta,\varphi);\quad I=\mu a^2 \text{ is the moment of inertia of the molecule.} && (7)
\end{aligned}$$

We immediately recognise this equation as an eigenvalue equation: it states that $\psi(\theta,\varphi)$ is an eigenfunction of the operator $\widehat{\mathbf{L}}^2$ with eigenvalue $2IE$. But we also know from the theory of angular momentum [1] that this operator has eigenfunctions $Y_{\ell,m}(\theta,\varphi)$ and eigenvalues $\hbar^2\ell(\ell+1), \ell = 0,1,2\ldots$. Hence the rigid rotator eigenfunctions are the spherical harmonics and the energy eigenvalues of the rigid rotator are quantised:

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1), \qquad \ell = 0,1,2\ldots \tag{8}$$

Typical values for these energies are very small, lying in the range $10^{-5} \to 10^{-4}\,$eV. For an astronomer this is particularly significant because the corresponding temperatures ($E = kT$) lie in the range $1 \to 10\,$K, comparable to interstellar cloud temperatures ($10 \to 100\,$K being typical), so that rotational excited states can easily be formed from collisions. The most abundant molecule in the interstellar medium after molecular hydrogen, H_2, is CO with $B = \hbar^2/2I = 2.4\times10^{-4}$ eV. A CO molecule finding itself in the $\ell-$th rotationally excited state, can de-excite by dropping down to one of the lower rotational levels, thereby emitting a photon. Since a photon has spin 1, it carries away angular momentum $1\hbar$ and therefore the only radiative transitions allowed are those which change ℓ by one unit and so conserve angular momentum; in addition the $z-$component, m may or may not change. This leads to the *selection rule for pure rotational transitions* which result in single photon emission or absorption,

$$\boxed{\Delta\ell = \pm1 \text{ for emission } (-) \text{ or absorption } (+) \text{ of 1 photon; with } \Delta m = 0,\pm1.}$$

Thus, for pure rotational transitions, the energy $h\nu = \Delta E$ of an *emitted photon* resulting from a transition from $\ell+1 \to \ell$ is [2]

$$\begin{aligned}
h\nu = \Delta E &= E_{\ell+1} - E_\ell && (9)\\
&= \frac{\hbar^2}{2I}(\ell+1)(\ell+2) - \frac{\hbar^2}{2I}\ell(\ell+1) && (10)\\
&= 2\left(\frac{\hbar^2}{2I}\right)(\ell+1) && (11)\\
&= 2B(\ell+1) \qquad \text{where } B \equiv \frac{\hbar^2}{2I} && (12)
\end{aligned}$$

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[1] See equation (71) on p.9 of notes on 'ANGULAR MOMENTUM IN QUANTUM MECHANICS'.

[2] Astronomers usually use the notation J instead of ℓ.

For CO the $\ell = 1 \rightarrow \ell = 0$ transition corresponds to the emission of a photon of frequency of 115 GHz and a wavelength of 2.6 mm.

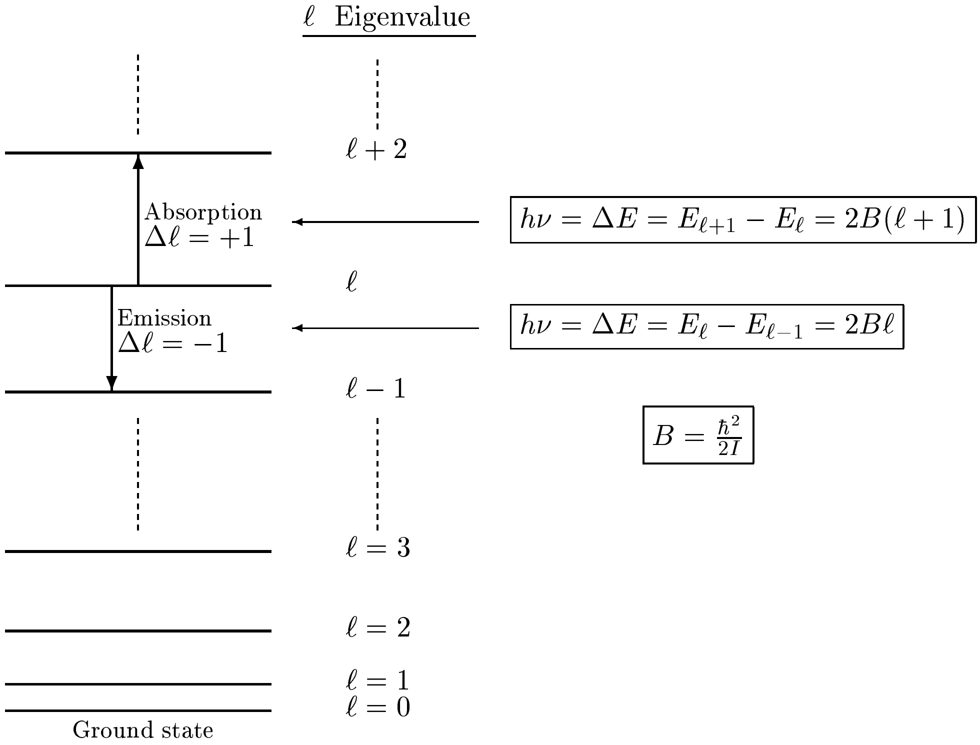

Figure 2: The rotational energy levels of a diatomic molecule modelled as a rigid rotator. Allowed pure rotational transitions with $\Delta\ell = \pm 1$ are shown together with expressions for the frequency of the photon emitted in downward transitions or absorbed in upward transitions.

Figure 3 shows an example of the rotational spectrum of HCl in absorption, $\Delta\ell = +1$, where the line frequencies correspond to the absorption minima. The first line seen is the $\ell = 1 \rightarrow 2$ transition at $\bar{\nu} = 4\bar{B} = 42.36\,\mathrm{cm}^{-1}$ corresponding to a wavelength of $236\,\mu$m in the infrared; succeeding lines arise from $\ell = 2 \rightarrow 3,\ 3 \rightarrow 4,\ 4 \rightarrow 5, \ldots$ transitions. The spacing of the lines is not *exactly* that of the rigid rotator model but decreases with ℓ. This is due to the effect of centrifugal forces, with larger angular momenta causing the interatomic spacing to increase: this increase in a then increases the moment of inertia, I, and hence decreases B.

PURE
ROTATIONAL
SPECTRUM
HCl.

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

$$h\nu_{\ell\to\ell+1} = \Delta E_{\ell\to\ell+1} = 2\left(\frac{\hbar^2}{2I}\right)(\ell+1)$$

$$= 2B(\ell+1) \quad ; \; B = 1.3\times10^{-4}\,\text{eV}$$

$$\begin{pmatrix}\Delta\ell = \pm1 \\ \Delta m = 0, \pm1\end{pmatrix}$$

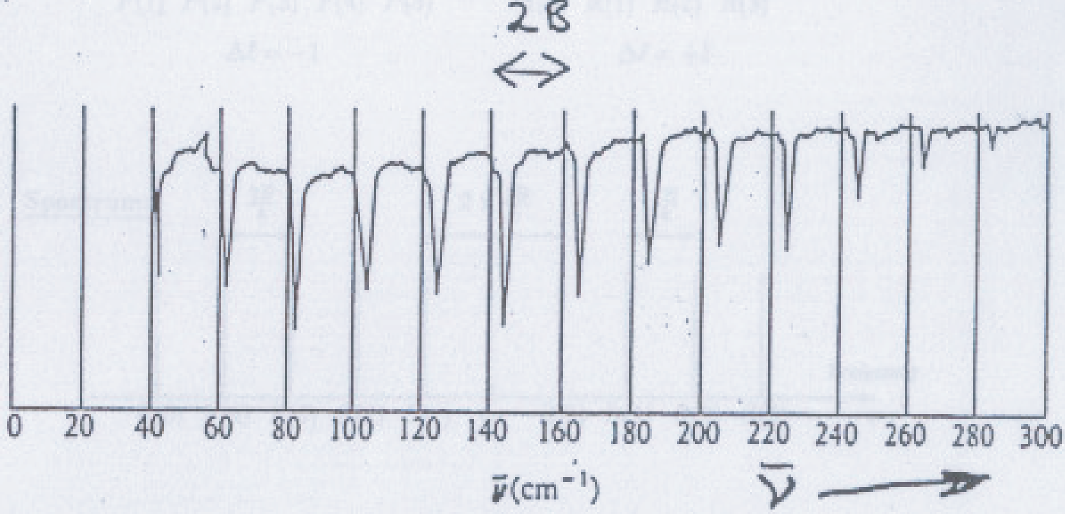

FIG3. The rotational absorption spectrum of gaseous HCl. The spacing i frequency between the absorption lines, (corresponding to transitions from $\ell\to\ell+1$), is constan and equal to $2B/h$. For HCl $\bar{B} = (B/hc) = 10.59\ \text{cm}^{-1}$ and the spacing in terms of the wav number $\bar{\nu}$ is $2\bar{B} = 21.18\ \text{cm}^{-1}$.

$$\bar{\nu} \equiv 1/\lambda.$$

(2) ROTATION-VIBRATION SPECTRA.

In the approximation that rotational and vibrational motion are independent we can write the total energy of a diatomic molecule in the vibrational state n and rotational state ℓ as[3]

$$\begin{aligned} E_{n,\ell} &= E_{vib} + E_{rot} && (13) \\ &= h\nu_0(n+\frac{1}{2}) + \frac{\hbar^2}{2I}\ell(\ell+1), \qquad n = 0,1,2\ldots,\ \ell = 0,1,2,\ldots && (14) \end{aligned}$$

For diatomic molecules $E_{vib} \approx 0.5\,\mathrm{eV} \gg E_{rot} \approx 10^{-4}\,\mathrm{eV}$; hence vibrational transitions will be in the infrared, rotational ones in the microwave to millimetre wavelength region. The key to understanding vibrational, rotational and combined rotational-vibrational transitions leading to the emission and absorption of photons is again the *selection rules.* In addition to the angular momentum selection rules already mentioned for pure rotational transitions there are also rules dictated by the photon's parity and that of the energy eigenstates of the harmonic oscillator. These require that the vibrational quantum number can change by *no more than one unit,* $\Delta n = 0, \pm 1$, while, because the photon carries one unit of angular momentum (photon spin $1\hbar$), we must *always* have $\Delta\ell = \pm 1$. Thus the full set of selection rules for pure rotational and rotational-vibrational transitions are:

$$\boxed{\Delta\ell = \pm 1 \qquad \text{with} \quad \Delta n = 0, \quad \text{or} \quad \Delta n = \pm 1}$$

Transitions with $\Delta n = 0$ are pure rotational transitions, which we have already discussed. Because the photon carries unit angular momentum there cannot be pure vibrational transitions: any transition leading to either single photon emission or absorption *must* be accompanied by a change of angular momentum; but when $\Delta n \neq 0$ this can be either an increase or a decrease $\Delta\ell = \pm 1$, whether the photon is emitted or absorbed: all that is required is that in emission the molecule's total energy decrease, while in absorption the energy increase. Figure 3 shows the allowed rotational-vibrational transitions in absorption for a diatomic molecule initially in the vibrational ground state $n = 0$. It is clear that the transitions break up into two distinct sets: the R-branch, with $\Delta\ell = +1$ and the P-branch with $\Delta\ell = -1$.

$$\boxed{\textbf{R-branch:} \qquad \Delta\ell = +1 \qquad \Delta n = +1}$$

$$\begin{aligned} \text{For} \quad n = 0 \to 1,\ \ell \to \ell+1 \quad \Delta E &= E_{n=1,\ell+1} - E_{n=0,\ell} \\ \text{i.e.} \quad h\nu &= h\nu_0 + 2\left(\frac{\hbar^2}{2I}\right)(\ell+1) && (15) \end{aligned}$$

$$\boxed{\textbf{P-branch:} \qquad \Delta\ell = -1 \qquad \Delta n = +1}$$

$$\begin{aligned} \text{For} \quad n = 0 \to 1,\ \ell \to \ell-1 \quad \Delta E &= E_{n=1,\ell-1} - E_{n=0,\ell} \\ \text{i.e.} \quad h\nu &= h\nu_0 - 2\left(\frac{\hbar^2}{2I}\right)\ell && (16) \end{aligned}$$

The pattern of allowed lines consists of two sets centred about a frequency ν_0, with the line at ν_0 being absent because it corresponds to the forbidden $\Delta\ell = 0$ transition ($\ell = 0 \to 0, 1 \to 1$, etc.). Figure 4 gives an example of the vibrational-rotational absorption spectrum of HCl showing clearly the central missing line at ν_0 with the P-branch lines extending to lower frequencies and the R-branch to higher frequencies.

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[3] A more frequently used notation is J instead of ℓ and v instead of n. I use ℓ, n because these are the symbols we used in discussing orbital angular momentum and the SHO. Note also that $\hbar\omega_0 = h\nu_0$.

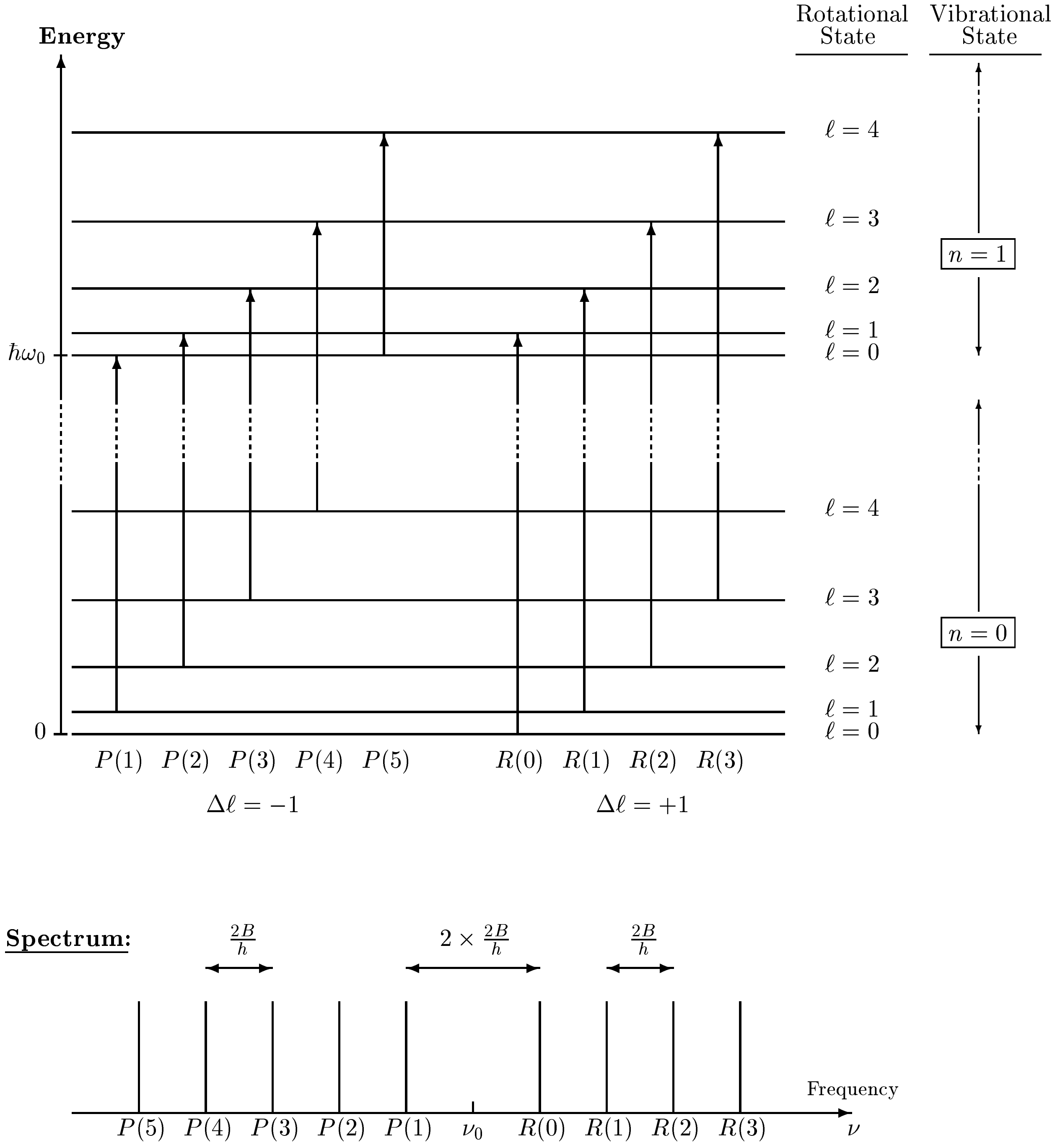

Figure 4: The rotation-vibration energy levels of a diatomic molecule modelled as independent rigid rotator and harmonic oscillator. Allowed vibrational-rotational absorption transitions with $\Delta n = +1$ are shown: the R-branch corresponds to $\Delta\ell = +1$, the P-branch to $\Delta\ell = -1$. The missing line at the centre of the spectrum occurs at the frequency ν_0 correponding to the forbidden $\Delta\ell = 0, \Delta n = +1$ transitions. Note that the energy separation of the vibrational states, $\hbar\omega_0 = h\nu_0$, is not shown accurately here: in practice it is some 10^4 times greater than the separation of the lowest two rotational levels.

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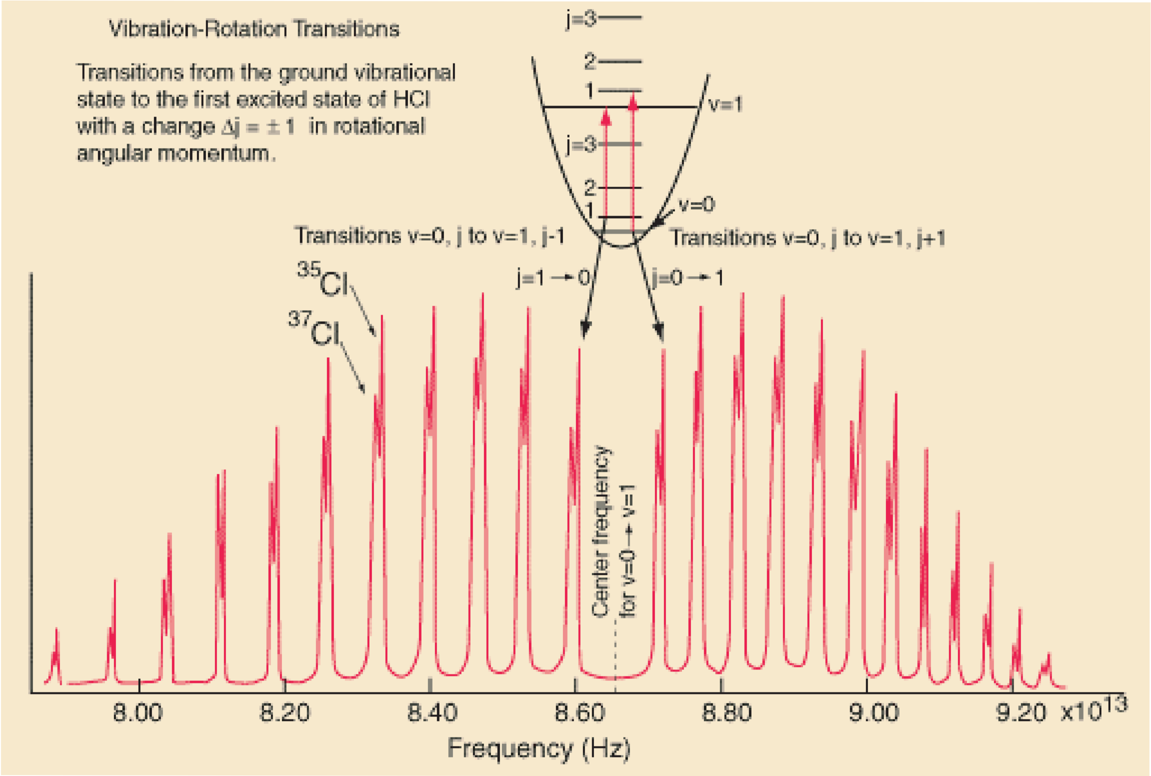

Analysis of the lines of the vibrational-rotational spectrum leads to estimates of both the interatomic separation and the strength of the interatomic potential. I append the spectrum of CO we obtained in the laboratory together with the solution to Problems 9, Q.1 showing how this analysis is carried out.

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APPENDIX: THE 2-BODY SCHRÖDINGER EQUATION.

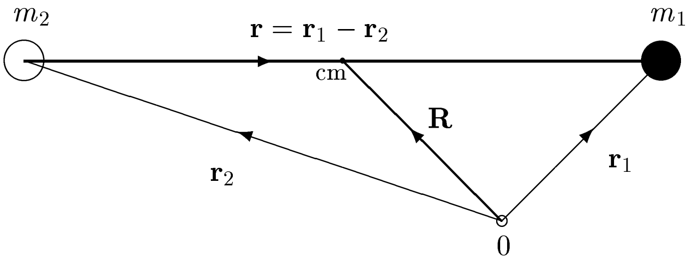

Figure: Coordinate system for 2-particles.

Consider the general problem of two particles interacting through a time-independent potential depending on their separation. The TDSE for the two-particle system is,

$$\widehat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2; t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2; t)}{\partial t} \tag{17}$$

where the two-particle Hamiltonian is

$$\widehat{H} = \frac{\widehat{\mathbf{p}}_1^2}{2m_1} + \frac{\widehat{\mathbf{p}}_2^2}{2m_2} + V(\mathbf{r}_1 - \mathbf{r}_2) \tag{18}$$

$$= -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1 - \mathbf{r}_2) \tag{19}$$

As usual for time-independent potentials we may separate out the time-dependence, obtaining:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; t) = \psi(\mathbf{r}_1, \mathbf{r}_2) e^{-iE_{tot}t/\hbar} \tag{20}$$

where $\psi(\mathbf{r}_1, \mathbf{r}_2)$ obeys the TISE with two-particle energy E_{tot},

$$\{-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1 - \mathbf{r}_2)\}\,\psi(\mathbf{r}_1, \mathbf{r}_2) = E_{tot}\,\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{21}$$

This complicated looking equation can easily be simplified using our physical intuition gained from classical mechanics. The two-particle system has two distinct kinds of motion: the motion of the system 'as a whole', by which we mean the motion of the centre of mass (denoted cm. in the figure); and the motion of the particles relative to one another. The former corresponds to the centre of mass vector $\mathbf{R}$ changing; the latter to the relative coordinate vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ changing. The former should be free motion of a system with mass $M = m_1 + m_2$; the latter relative motion in a potential $V(\mathbf{r})$. To see how this happens in QM we transform the TISE from the coordinates $(\mathbf{r}_1, \mathbf{r}_2)$ to new coordinates $(\mathbf{R},\ \mathbf{r})$:[4]

$$\mathbf{r} = (x, y, z) = \mathbf{r}_1 - \mathbf{r}_2 \tag{22}$$

$$\mathbf{R} = (X, Y, Z) = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{23}$$

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[4] The coordinates of the centre of mass are obtained by noting that the sum of the moments of the two separate masses about the origin is $m_1\mathbf{r}_1 + m_2\mathbf{r}_2$ and should equal the moment of the total mass $M = m_1 + m_2$ acting at the centre of mass, $M\mathbf{R}$. This gives the equation for $\mathbf{R}$.

These are very simple linear transformations, with $x = x(x_1, x_2)$ and $X = X(x_1, x_2)$, so that there is no mixing of x, y and z coordinates, and partial differentiation enables us to transform the differentials without difficulty:

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} = \frac{m_1}{m_1+m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial x} \tag{24}$$

$$\frac{\partial}{\partial x_2} = \frac{\partial X}{\partial x_2}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} = \frac{m_2}{m_1+m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x} \tag{25}$$

Since the coefficients of the differentials on the right are just constants the second differentials are easily obtained by ‘squaring’,

$$\frac{\partial^2}{\partial x_1^2} = \frac{m_1^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x^2} + 2\frac{m_1}{m_1+m_2}\frac{\partial^2}{\partial X \partial x} \tag{26}$$

$$\frac{\partial^2}{\partial x_2^2} = \frac{m_2^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x^2} - 2\frac{m_2}{m_1+m_2}\frac{\partial^2}{\partial X \partial x} \tag{27}$$

Exactly similar expressions can be found for the y and z components. These two expressions are very similar except for the interchange $m_1 \leftrightarrow m_2$ and the crucial sign difference in the cross terms, which therefore cancel:

$$-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} = -\frac{\hbar^2}{2(m_1+m_2)}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} \tag{28}$$

$$= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} \tag{29}$$

where M is the total mass and μ is the **reduced mass** of the two-particle system:

$$\frac{1}{\mu} = \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \quad \text{ie.} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{30}$$

$$M = m_1 + m_2 \tag{31}$$

The same cancellations occur for the y and z components, leading to a TISE involving only the variables $\mathbf{R}$ and $\mathbf{r}$:

$$\left\{-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right\}\psi = E_{tot}\,\psi \tag{32}$$

which is obviously separable by making the substitution

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \Phi(\mathbf{R})\,\psi(\mathbf{r}) \tag{33}$$

Dividing, as usual by $\Phi(\mathbf{R})\,\psi(\mathbf{r})$ and rearranging we find

$$\frac{\hbar^2}{2M}\frac{1}{\Phi(\mathbf{R})}\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) + E_{tot} = -\frac{\hbar^2}{2\mu}\frac{1}{\psi(\mathbf{r})}\nabla^2_{\mathbf{r}}\frac{1}{\psi(\mathbf{r})} + V(\mathbf{r}) \tag{34}$$

$$= E, \quad \text{a constant,} \tag{35}$$

where, since each side of the equation depends on a *different and independent* variable, they must equal some constant, whose name is chosen as E since it has the dimensions of energy. Writing $E_{tot} - E = E_{cm}$ we obtain the promised equations,

$$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) = E_{cm}\Phi(\mathbf{R}) \tag{36}$$

$$\left\{-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right\}\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) \tag{37}$$

The first equation is a TISE for a free 'particle' of mass M and energy E_{cm}; the second for a 'particle' of mass μ in a potential $V(\mathbf{r})$ with an energy E. The whole two-particle system's energy E_{tot} is the sum of these energies,

$$E_{tot} = E_{cm} + E \tag{38}$$

The first equation obviously has the solution

$$\Phi(\mathbf{R}) = e^{\pm i\mathbf{P}.\mathbf{R}/\hbar}, \quad \text{where } \mathbf{P} \text{ is the momentum vector,} \quad \mathbf{P}^2 = 2ME_{cm} \tag{39}$$

which is a plane wave momentum eigenstate representing the free motion of the two-particle system as a whole.

The second equation is the one that concerns us here: for the the rotations of a diatomic molecule we would use as our first approximation the *rigid rotator* - a rigid weightless rod joining the two masses with the magnitude of the vector $\mathbf{r}$ remaining fixed, $r = a$, and no interaction between the particles, $V = 0$; for the vibrations of a diatomic molecule we would approximate with a one-dimensional SHO potential, $V(x) = \mu\omega_0^2x^2/2$. In both cases the mass used would be the reduced mass μ. In a first approximation we will assume these two relative motions, rotation and vibration, are independent.