Problem 4.27

Two particles (masses m_1 and m_2) are attached to the ends of a massless rigid rod of length a. The system is free to rotate in three dimensions about the (fixed) center of mass.

(a) Show that the allowed energies of this **rigid rotor** are

$$E_n = \frac{\hbar^2}{2I} n(n+1), \quad (n = 0,\, 1,\, 2,\, \ldots), \quad \text{where} \quad I = \frac{m_1 m_2}{(m_1 + m_2)} a^2$$

is the moment of inertia of the system. *Hint*: First express the (classical) energy in terms of the angular momentum.

(b) What are the normalized eigenfunctions for this system? (Let θ and ϕ define the orientation of the rotor axis.) What is the degeneracy of the nth energy level?

(c) What spectrum would you expect for this system? (Give a formula for the frequencies of the spectral lines.) *Answer:* $\nu_j = \hbar j / 2\pi I$, $j = 1,\, 2,\, 3,\, \ldots$.

(d) Figure 4.13 shows a portion of the rotational spectrum of carbon monoxide (CO). What is the frequency separation ($\Delta\nu$) between adjacent lines? Look up the masses of ^{12}C and ^{16}O, and from m_1, m_2, and $\Delta\nu$ determine the distance between the atoms.

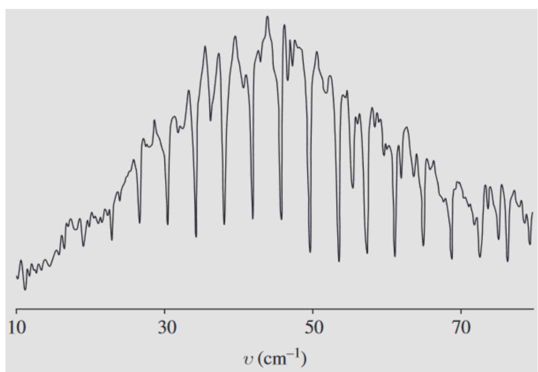


Figure 4.13: Rotation spectrum of CO. Note that the frequencies are in spectroscopist's units: inverse centimeters. To convert to Hertz, multiply by $c = 3.00 \times 10^{10}$ cm/s. Reproduced by permission from John M. Brown and Allan Carrington, *Rotational Spectroscopy of Diatomic Molecules*, Cambridge University Press, 2003, which in turn was adapted from E. V. Loewenstein, *Journal of the Optical Society of America*, **50**, 1163 (1960).

Solution

Assume the motion is purely rotational; according to classical mechanics, the total mechanical energy is

$$E = \frac{1}{2} I \omega^2,$$

where I and ω are the moment of inertia and angular velocity, respectively.

Since the rotation occurs about a fixed axis, the angular momentum is $L = I\omega$.

$$E = \frac{1}{2}(I\omega)\omega = \frac{1}{2}(L)\left(\frac{L}{I}\right) = \frac{L^2}{2I}$$

The operator L^2 satisfies the eigenvalue problem in Equation 4.118 on page 160.

$$L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m, \quad \begin{cases} \ell = 0,\, \frac{1}{2},\, 1,\, \frac{3}{2},\, \ldots \\ m = -\ell,\, -\ell+1,\, \ldots,\, \ell-1,\, \ell \end{cases} \tag{4.118}$$

As a result, the corresponding Hamiltonian operator for the rigid rotor in quantum mechanics satisfies

$$\frac{L^2}{2I} f_\ell^m = \frac{\hbar^2 \ell(\ell+1)}{2I} f_\ell^m.$$

Normalized eigenfunctions (the spherical harmonics) exist only for integer values of ℓ,

$$\boxed{f_\ell^m = Y_\ell^m(\theta, \phi), \quad \begin{cases} \ell = 0,\, 1,\, 2,\, \ldots \\ m = -\ell,\, -\ell+1,\, \ldots,\, \ell-1,\, \ell \end{cases},}$$

so the allowed eigenenergies of the rigid rotor are

$$\boxed{E_\ell = \frac{\hbar^2 \ell(\ell+1)}{2I}, \quad \ell = 0, 1, 2, \ldots.}$$

Each value of ℓ is associated with $2\ell+1$ values of m, which means the ℓth energy level has a degeneracy of $d = 2\ell+1$. Looking at the rotation spectrum of CO, there are roughly evenly spaced sharp dips, indicating that electromagnetic radiation is absorbed at specific frequencies. This absorption is due to the dipole of CO, resulting from C and O's electronegativities.

$$\Delta E = h\nu$$

$$E_f - E_i = 2\pi\hbar\nu$$

$$\nu = \frac{E_f - E_i}{2\pi\hbar}$$

$$= \frac{\frac{\hbar^2 \ell_f(\ell_f+1)}{2I} - \frac{\hbar^2 \ell_i(\ell_i+1)}{2I}}{2\pi\hbar}$$

$$= \frac{\hbar}{4\pi I}[\ell_f(\ell_f+1) - \ell_i(\ell_i+1)]$$

$\ell_f(\ell_f+1)$ is the product of an even number and an odd number, and $\ell_i(\ell_i+1)$ is the product of an even number and an odd number. Therefore, the quantity in parentheses is an even number.

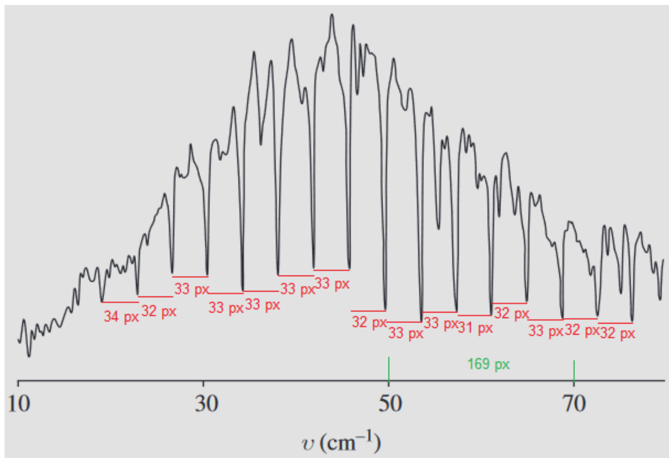
$$\nu_j = \frac{\hbar}{4\pi I}(2j), \quad j = 1, 2, 3, \ldots$$

Simplifying gives the desired result.

$$\boxed{\nu_j = \frac{\hbar}{2\pi I} j, \quad j = 1, 2, 3, \ldots}$$

Consequently, the theoretical frequency separation between adjacent lines is

$$\Delta\nu = \nu_{j+1} - \nu_j = \frac{\hbar}{2\pi I}(j+1) - \frac{\hbar}{2\pi I} j = \frac{\hbar}{2\pi I}.$$



Measure the distances between the absorption frequencies in pixels and take their average.

$$\bar{x} \approx \frac{(34+32+33+33+33+33+33+32+33+33+31+32+33+32+32)\text{ px}}{15} \approx 33\text{ px}$$

Use it to compute the experimental frequency separation between adjacent lines.

$$\boxed{\Delta\nu \approx 33\text{ px} \times \frac{20\text{ cm}^{-1}}{169\text{ px}} \times \frac{100\text{ cm}}{1\text{ m}} \times \frac{299\,792\,458\text{ m}}{1\text{ s}} \times \frac{1\text{ Hz}}{1\text{ s}^{-1}} \approx 1.2 \times 10^{11}\text{ Hz}}$$

^{12}C has 6 protons, 6 neutrons, and 6 electrons, so its mass is

$$\begin{aligned} m_1 &= 6m_p + 6m_n + 6m_e \\ &= 6(1.672621777 \times 10^{-27}\text{ kg}) + 6(1.674927351 \times 10^{-27}\text{ kg}) + 6(9.10938291 \times 10^{-31}\text{ kg}) \\ &\approx 2.00907604 \times 10^{-26}\text{ kg}. \end{aligned}$$

^{16}O has 8 protons, 8 neutrons, and 8 electrons, so its mass is

$$\begin{aligned} m_2 &= 8m_p + 8m_n + 8m_e \\ &= 8(1.672621777 \times 10^{-27}\text{ kg}) + 8(1.674927351 \times 10^{-27}\text{ kg}) + 8(9.10938291 \times 10^{-31}\text{ kg}) \\ &\approx 2.678768053 \times 10^{-26}\text{ kg}. \end{aligned}$$

Solve the frequency separation equation for I, substitute the formula for I, and solve for a^2.

$$\Delta\nu = \frac{\hbar}{2\pi I}$$

$$I = \frac{\hbar}{2\pi \Delta\nu}$$

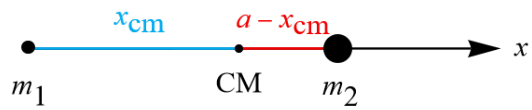
$$\frac{m_1 m_2}{m_1 + m_2} a^2 = \frac{\hbar}{2\pi \Delta\nu}$$

$$a^2 = \frac{\hbar}{2\pi \Delta\nu}\left(\frac{m_1 + m_2}{m_1 m_2}\right)$$

Take the square root of both sides to get a, the distance between the C and O atoms.

$$\boxed{a = \sqrt{\frac{\hbar}{2\pi \Delta\nu}\left(\frac{m_1 + m_2}{m_1 m_2}\right)} \approx 1.1 \times 10^{-10} \text{ m}}$$

The goal now is to derive the formula for I, the moment of inertia of the rigid rotor. Two masses, separated by a distance a, are rotating about a fixed axis through the center of mass.



Find the center of mass.

$$x_{\text{cm}} = \frac{\sum_{j=1}^{2} x_j m_j}{\sum_{j=1}^{2} m_j} = \frac{x_1 m_1 + x_2 m_2}{m_1 + m_2} = \frac{(0)m_1 + (a)m_2}{m_1 + m_2} = \frac{m_2 a}{m_1 + m_2}$$

Then find the moment of inertia.

$$\begin{aligned}
I = \sum_{j=1}^{2} m_j r_j^2 = m_1 r_1^2 + m_2 r_2^2 &= m_1 (x_{\text{cm}})^2 + m_2 (a - x_{\text{cm}})^2 \\
&= m_1 \left(\frac{m_2 a}{m_1 + m_2} \right)^2 + m_2 \left(a - \frac{m_2 a}{m_1 + m_2} \right)^2 \\
&= \frac{m_1 m_2^2 a^2}{(m_1 + m_2)^2} + m_2 \left(\frac{m_1 a}{m_1 + m_2} \right)^2 \\
&= \frac{m_1 m_2^2 a^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 a^2}{(m_1 + m_2)^2} \\
&= \frac{m_1 m_2 a^2}{(m_1 + m_2)^2} (m_2 + m_1) \\
&= \frac{m_1 m_2}{m_1 + m_2} a^2 \\
&= \mu a^2
\end{aligned}$$

μ is known as the reduced mass.