REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

For a system of two particles 1 and 2 with coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) the potential energy of interaction between the particles is usually a function of only the relative coordinates $x_2 – x_1$, $y_2 – y_1$ and $z_2 – z_1$ of the particles. In this case the two-particle problem can be simplified to two separate one-particle problems

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

The Hamiltonian is $\hat{H} = \hat{T} + \hat{V}$

Kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right)$$

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

The Hamiltonian is $\hat{H} = \hat{T} + \hat{V}$

1) Potential energy operator for 2 charged particles (e.g. proton + electron, anion + cation)

$$V(x_1, y_1, z_1, x_2, y_2, z_2) = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

2) Potential energy operator for a 3D harmonic oscillator

$$V(x_1, y_1, z_1, x_2, y_2, z_2) = \frac{1}{2} k \left(\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2} - r_0 \right)^2$$

3) Potential energy operator for a 3D rigid rotor

$V(x_1, y_1, z_1, x_2, y_2, z_2) = 0$ (or in general $V = constant$)

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

We make a change of coordinates

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \qquad \mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}$$

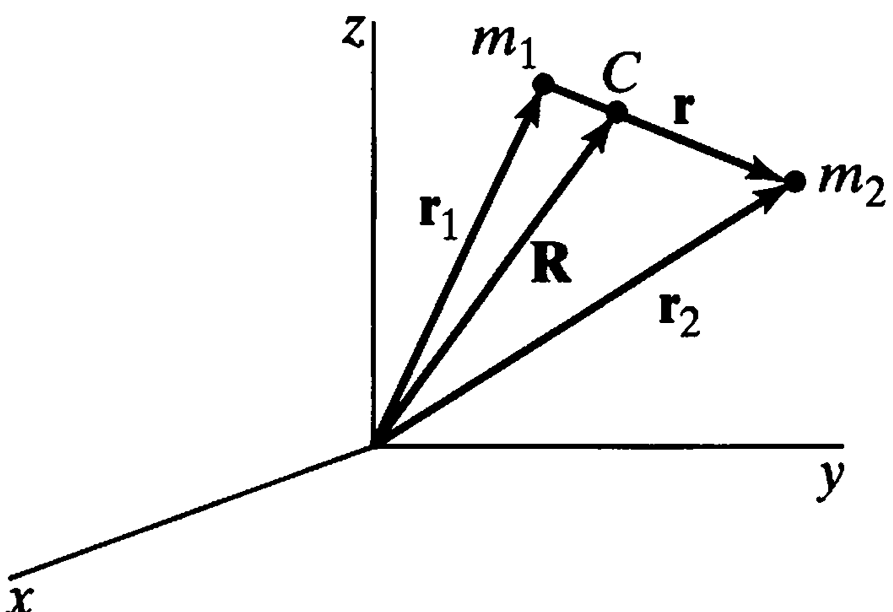
$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k} \qquad \mathbf{R} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}$$

where

$$\mathbf{r}_1 = x_1\mathbf{i} + y_1\mathbf{j} + z_1\mathbf{k}$$

$$\mathbf{r}_2 = x_2\mathbf{i} + y_2\mathbf{j} + z_2\mathbf{k}$$

$$M = m_1 + m_2$$



REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \qquad \mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}$$

These equations represent a **transformation of coordinates**

from $x_1 \ y_1 \ z_1 \ x_2 \ y_2 \ z_2$ to $X \ Y \ Z \ x \ y \ z$

The relations between the coordinates are

$$x = x_2 - x_1 \qquad X = (m_1x_1 + m_2x_2)/M$$

$$y = y_2 - y_1 \qquad Y = (m_1y_1 + m_2y_2)/M$$

$$z = z_2 - z_1 \qquad Z = (m_1z_1 + m_2z_2)/M$$

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

We will consider what happens to the Hamiltonian under this transformation of coordinates

The potential energy is simply a function of $\mathbf{r}$

$$V(x_1, y_1, z_1, x_2, y_2, z_2) = V(x, y, z)$$

For example, considering the electric potential energy, we have

$$V(x_1, y_1, z_1, x_2, y_2, z_2) = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

It can be easily written as a function of the new coordinates

$$\boxed{V(\mathrm{x}, \mathrm{y}, \mathrm{z}) = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{\sqrt{x^2 + y^2 + z^2}}}$$

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

We have seen that the kinetic energy of the 2 particles is

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right)$$

We need to transform the above partial derivatives in the following ones

$$\frac{\partial^2}{\partial x^2} \qquad \frac{\partial^2}{\partial y^2} \qquad \frac{\partial^2}{\partial z^2} \qquad \frac{\partial^2}{\partial X^2} \qquad \frac{\partial^2}{\partial Y^2} \qquad \frac{\partial^2}{\partial Z^2}$$

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

To this aim we exploit the chain rules

For coordinates x_1, y_1 and z_1, the rules are the following

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_1}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_1}\frac{\partial}{\partial z} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial Y}{\partial x_1}\frac{\partial}{\partial Y} + \frac{\partial Z}{\partial x_1}\frac{\partial}{\partial Z}$$

$$\frac{\partial}{\partial y_1} = \frac{\partial x}{\partial y_1}\frac{\partial}{\partial x} + \frac{\partial y}{\partial y_1}\frac{\partial}{\partial y} + \frac{\partial z}{\partial y_1}\frac{\partial}{\partial z} + \frac{\partial X}{\partial y_1}\frac{\partial}{\partial X} + \frac{\partial Y}{\partial y_1}\frac{\partial}{\partial Y} + \frac{\partial Z}{\partial y_1}\frac{\partial}{\partial Z}$$

$$\frac{\partial}{\partial z_1} = \frac{\partial x}{\partial z_1}\frac{\partial}{\partial x} + \frac{\partial y}{\partial z_1}\frac{\partial}{\partial y} + \frac{\partial z}{\partial z_1}\frac{\partial}{\partial z} + \frac{\partial X}{\partial z_1}\frac{\partial}{\partial X} + \frac{\partial Y}{\partial z_1}\frac{\partial}{\partial Y} + \frac{\partial Z}{\partial z_1}\frac{\partial}{\partial Z}$$

Analogous expressions can be written for the derivatives involving x_2, y_2 and z_2

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

After some algebra, we get

$$\frac{\partial}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{m_1}{M}\frac{\partial}{\partial X} \qquad \frac{\partial}{\partial x_2} = \frac{\partial}{\partial x} + \frac{m_2}{M}\frac{\partial}{\partial X}$$

$$\frac{\partial}{\partial y_1} = -\frac{\partial}{\partial y} + \frac{m_1}{M}\frac{\partial}{\partial Y} \qquad \frac{\partial}{\partial y_2} = \frac{\partial}{\partial y} + \frac{m_2}{M}\frac{\partial}{\partial Y}$$

$$\frac{\partial}{\partial z_1} = -\frac{\partial}{\partial z} + \frac{m_1}{M}\frac{\partial}{\partial Z} \qquad \frac{\partial}{\partial z_2} = \frac{\partial}{\partial z} + \frac{m_2}{M}\frac{\partial}{\partial Z}$$

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

Using the previous operators in the following kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right)$$

we obtain

$$\hat{T} = -\frac{\hbar^2}{2\mu}\overbrace{\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}^{\nabla_\mu^2} - \frac{\hbar^2}{2M}\overbrace{\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right)}^{\nabla_M^2}$$

$$\boxed{\hat{T} = -\frac{\hbar^2}{2\mu}\nabla_\mu^2 - \frac{\hbar^2}{2M}\nabla_M^2}$$

where $\mu = \dfrac{m_1 m_2}{M}$ Reduced Mass

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

$$\hat{T} = -\frac{\hbar^2}{2M}\nabla_M^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2$$

The first term can be viewed as the kinetic energy of a hypothetical particle of mass M moving with the coordinates of the center of mass (**translational motion**)

The second term can be viewed as the kinetic energy of internal (relative) motion of the 2 particles. This internal motion can be of two types. The distance r between the two particles can change (**vibration**), and the direction of the **r** vector can change (**rotation**)

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

With the new definitions of $\hat{V}$ and $\hat{T}$, the Hamiltonian operator becomes as follows

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_M^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2 + \hat{V}(x, y, z)$$

The Hamiltonian can be viewed as the sum of the Hamiltonians of two hypothetical noninteracting particles with masses M and μ, the latter being subject to the potential-energy function $V(x, y, z)$. We can apply the results obtained for two noninteracting particles

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS

Memo $$\hat{H} = -\frac{\hbar^2}{2M}\nabla_M^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2 + \hat{V}(x,y,z)$$

Total energy $$E = E_M + E_\mu$$

Eigenfunctions $$\psi = \psi_M\,\psi_\mu$$

where
$$\begin{cases} -\dfrac{\hbar^2}{2M}\nabla_M^2\psi_M = E_M\psi_M \\[2ex] -\dfrac{\hbar^2}{2\mu}\nabla_\mu^2\psi_\mu + V(x,y,z)\psi_\mu = E_\mu\psi_\mu \end{cases}$$

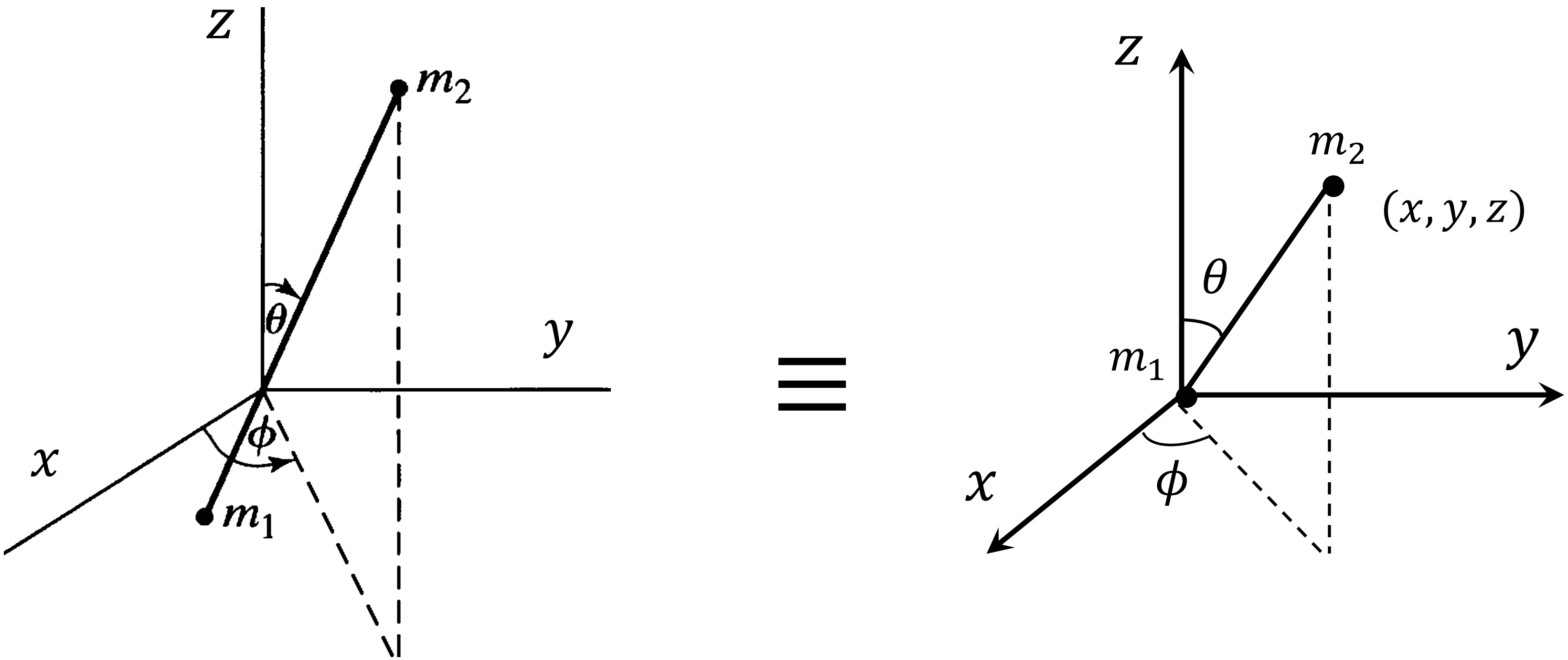
TWO-PARTICLE RIGID ROTOR

By **two-particle rigid rotor** we mean a two-particle system with the particles held at a fixed distance d from each other. The kinetic energy of internal motion is wholly rotational energy. The energy of the rotor is wholly kinetic, and $V(x, y, z) = 0$. The Schrödinger equation for the internal motion is

$$-\frac{\hbar^2}{2\mu}\nabla_\mu^2\psi_\mu = E_\mu\psi_\mu$$

Instead of the relative Cartesian coordinates x, y, z, it will prove more fruitful to use the relative spherical coordinates r, θ, ϕ

TWO-PARTICLE RIGID ROTOR



Coordinate system for the two-particle rigid rotor

TWO-PARTICLE RIGID ROTOR

In Cartesian coordinates the Schrödinger equation is

$$-\frac{\hbar^2}{2\mu}\nabla_\mu^2\psi(x,y,z) = E\,\psi(x,y,z)$$

To go from Cartesian to spherical coordinates, we exploit the results obtained from angular momentum. In particular, we use the chain rule

TWO-PARTICLE RIGID ROTOR

To perform the transformation to polar spherical coordinates, we use the **chain rule**

$$\frac{\partial}{\partial x} = \cancel{\left(\frac{\partial r}{\partial x}\right)_{y,z} \frac{\partial}{\partial r}} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z} \frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = \cancel{\left(\frac{\partial r}{\partial y}\right)_{x,z} \frac{\partial}{\partial r}} + \left(\frac{\partial \theta}{\partial y}\right)_{x,z} \frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \cancel{\left(\frac{\partial r}{\partial z}\right)_{x,y} \frac{\partial}{\partial r}} + \left(\frac{\partial \theta}{\partial z}\right)_{x,y} \frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} \frac{\partial}{\partial \phi}$$

Because the distance r is fixed (it does not depend on x, y, z). The distance r corresponds to the (fixed) bond length

TWO-PARTICLE RIGID ROTOR

After substitutions, we obtain

$$\frac{\partial}{\partial x} = \cancel{\sin\theta\cos\phi\frac{\partial}{\partial r}} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

Note that in these equations r is fixed

$$\frac{\partial}{\partial y} = \cancel{\sin\theta\sin\phi\frac{\partial}{\partial r}} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial z} = \cancel{\cos\theta\frac{\partial}{\partial r}} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$$

We use the operators above to determine the kinetic energy operator

$$-\frac{\hbar^2}{2\mu}\nabla_\mu^2 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

TWO-PARTICLE RIGID ROTOR

After algebra steps, the Schrödinger equation becomes as follows

The variable r is the distance between the 2 atoms (bond length). It has been replaced by d to outline that it is fixed

$$-\frac{\hbar^2}{2\,\mu\,d^2}\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\,\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi = E\psi$$

Recalling the definition of the square angular momentum operator

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\,\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

we can write

$$\boxed{\frac{1}{2\,\mu\,d^2}\hat{L}^2\psi = E\,\psi}$$

TWO-PARTICLE RIGID ROTOR

Memo $$\frac{1}{2\,\mu\,d^2}\hat{L}^2\psi = E\,\psi$$

We can rearrange as $\hat{L}^2\psi = 2\,\mu\,d^2 E\,\psi$

But, from the angular momentum solution, we know that

$$\hat{L}^2 Y_l^m(\theta,\phi) = l(l+1)\hbar^2\,Y_l^m(\theta,\phi)$$

This implies that the **wave-functions are the spherical harmonics**

$$\boxed{\psi(\theta,\phi) = Y_l^m(\theta,\phi)}$$

While the **energy** is
(we have replaced l with J)

$$\boxed{E = \frac{J(J+1)\hbar^2}{2\,\mu\,d^2}} \qquad J = 0, 1, 2, \ldots$$

TWO-PARTICLE RIGID ROTOR

The **moment of inertia** I of a system of n particles about some particular axis in space as defined as

$$I = \sum_{i=1}^{n} m_i r_i^2$$

where m_i is the mass of the ith atom and r_i is the perpendicular distance from this particle to the axis. The value of I depends on the choice of axis. For the two-particle rigid rotor, we choose our axis to be a line that passes through the center of mass and is perpendicular to the line joining m_1 and m_2

TWO-PARTICLE RIGID ROTOR

We assume to put the molecule along the x axis with the center of mass on the axis origin, we can write

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = 0 \quad \Rightarrow \quad m_1 x_1 + m_2 x_2 = 0 \qquad (1)$$

The bond length is $$d = x_2 - x_1 \qquad (2)$$

The moment of inertia is $$I = m_1 x_1^2 + m_2 x_2^2 \qquad (3)$$

Equations 1, 2 and 3 give $$\boxed{I = \mu\, d^2}$$

TWO-PARTICLE RIGID ROTOR

The energy of the two-particle rigid rotor is

$$\boxed{E = \frac{J(J+1)\hbar^2}{2I}} \qquad J = 0, 1, 2, \ldots$$

The energy depends on J only, but the wave function depends on J and m. For each value of J, there are $2J+1$ values of m, ranging from $-J$ to J. Hence the energy levels are $(2J+1)$-fold degenerate

The rotational levels of a diatomic molecule in gas phase can be well approximated by the two-particle rigid-rotor energies

TWO-PARTICLE RIGID ROTOR

When a diatomic molecule absorbs or emits radiation the allowed pure-rotational transitions are

$$\Delta J = \pm 1$$

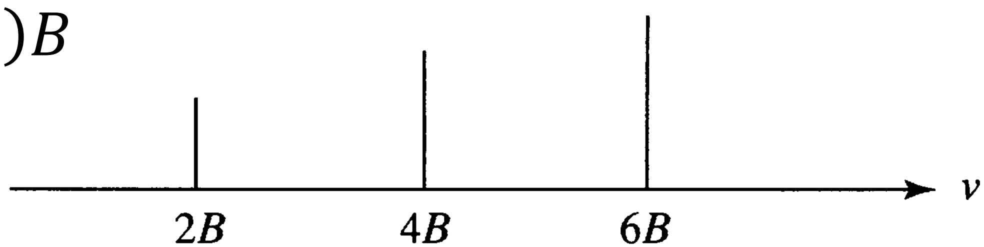
In addition, a molecule must have a nonzero dipole moment in order to show a pure-rotational spectrum. A pure-rotational transition is one where only the rotational quantum number changes. The pure-rotational spectrum falls in the microwave (or the far-infrared) region

$$J = 0, 1, 2, \ldots$$

$$\nu = \frac{E_{J+1} - E_J}{h} = 2(J+1)B$$

Rotational constant

$$B = \frac{h}{8\pi^2 I}$$



Rotational spectrum of a rigid rotor