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Physical Chemistry 2

Lecture 7. The Harmonic Oscillator (2) and the Rigid Rotor (1)

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Topics in Lecture 7

Harmonic oscillator wavefunctions

Spherical coordinates

Rigid rotor model

Connection to spectroscopy

In Atkins' *Physical Chemistry* (11th ed.),

7E Vibrational motion
7F Rotational motion

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IR spectrum

The vibrational energy levels are given by

$$E_n = \hbar\omega(n + \frac{1}{2}) \quad (n = 1,2,\ldots)$$

Transitions between vibrational levels

$$\Delta E = \hbar\omega = \hbar \left(\frac{k}{\mu}\right)^{1/2} \implies k = (2\pi c\tilde{\nu})^2 \mu$$

We can calculate spring constant of a diatomic molecule!

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Hermite polynomials

The wavefunctions corresponding to the E_n for a harmonic oscillator are nondegenerate and are given by

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2} \text{ where } \alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$$

$H_n(x)$ are *Hermite polynomials*.

TABLE 5.2
The first few Hermite polynomials.

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

TABLE 5.3
The first few harmonic-oscillator wave functions, Equation 5.35. The parameter $\alpha = (k\mu)^{1/2}/\hbar$.

$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$	$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}$
$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$	$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x)e^{-\alpha x^2/2}$

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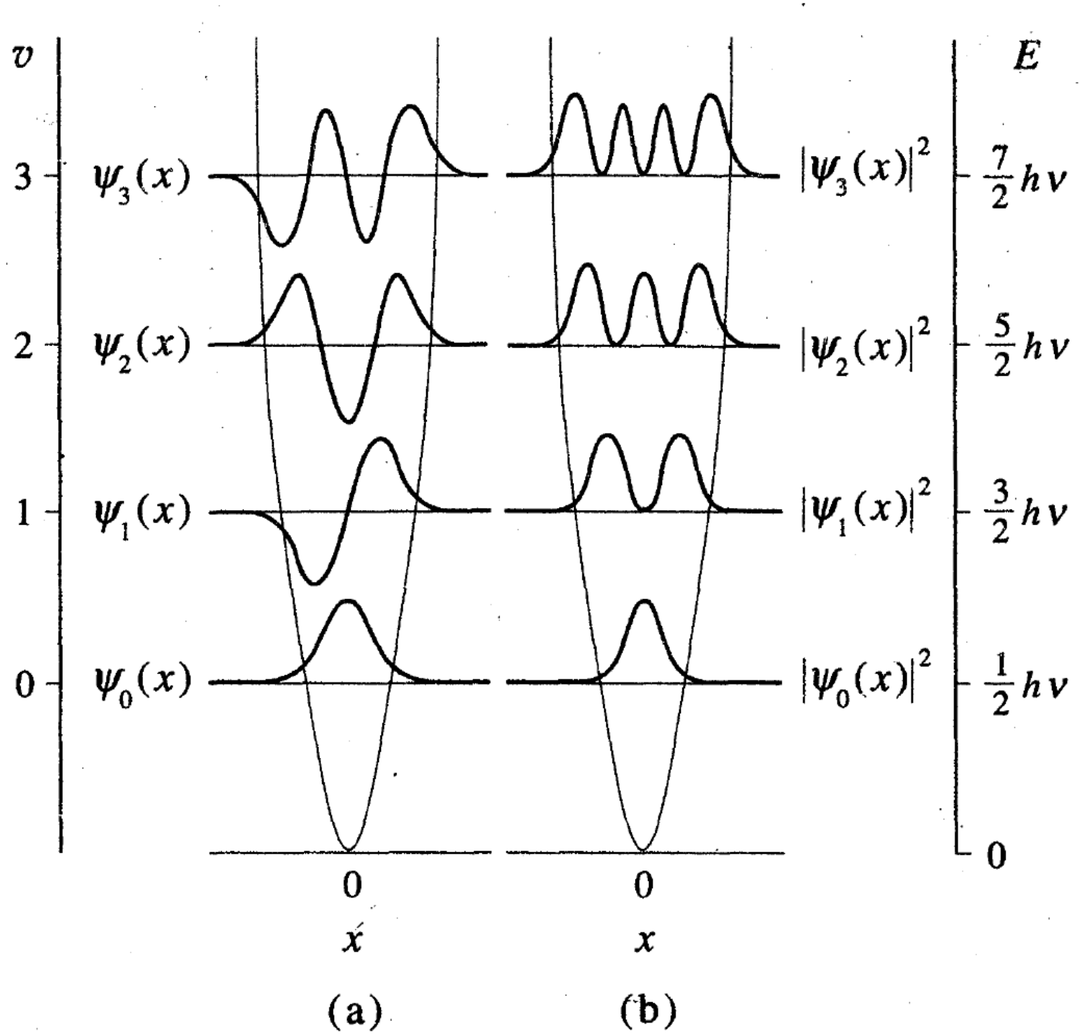
Hermite polynomials



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Hermite polynomials

We can easily find that HO Hamiltonian is hermitian: therefore eigenfunctions are orthonormal.

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x)\,dx = N_n N_m \int_{-\infty}^{\infty} H_n(\alpha^{1/2}x)H_m(\alpha^{1/2}x)e^{-\alpha x^2}\,dx = \delta_{nm}$$

Hermite polynomials are either even or odd, alternatingly.

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Spherical coordinates

We **should** be familiar with *spherical coordinates*, in order to deal with centrosymmetric systems.

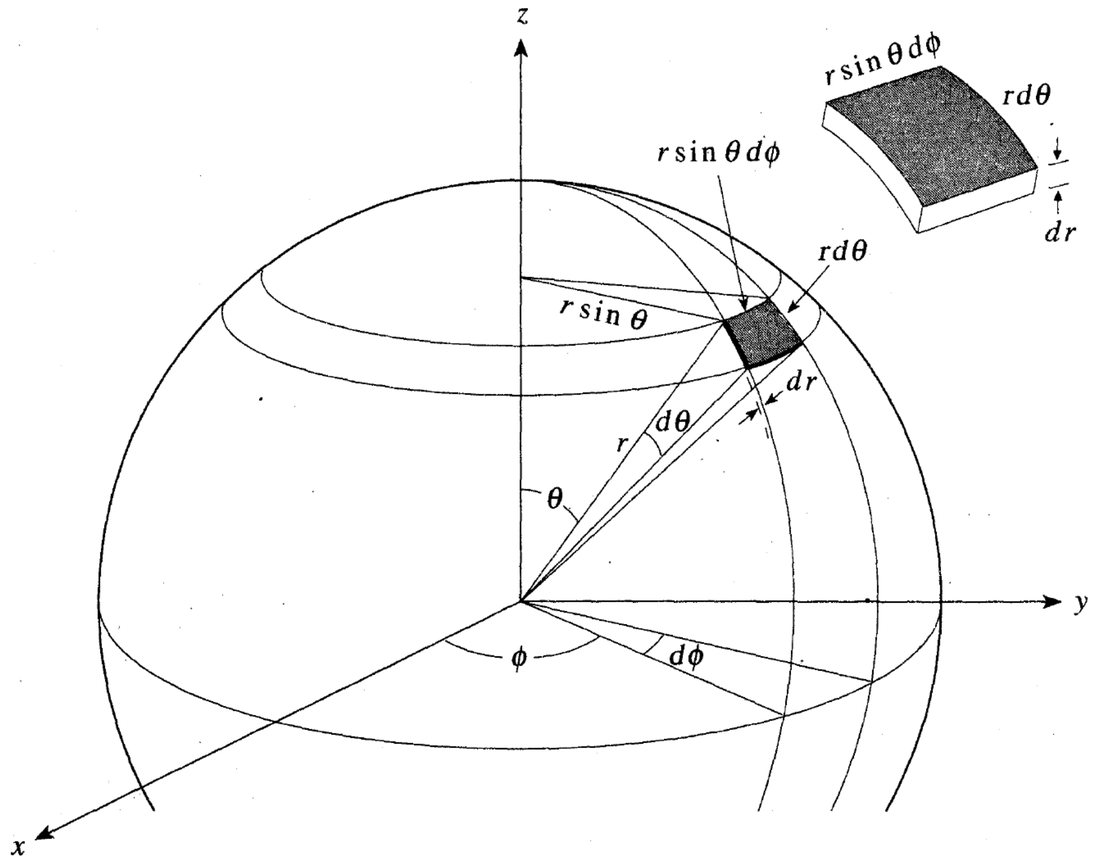

FIGURE D.2
A geometrical construction of the differential volume element in spherical coordinates.

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Spherical coordinates

Area element and *volume element* of cartesian coordinates are very simple.

$$dA = dxdy, \quad dV = dxdydz$$

For spherical coordinates,

$$dA = r^2 \sin\theta \, d\theta d\phi, \quad dV = r^2 \sin\theta \, dr d\theta d\phi$$

Elementary exercise. Calculate the surface area and volume of sphere.

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Spherical coordinates

Gradient and *Laplacian* of cartesian coordinates are very simple.

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right), \quad \nabla^2 = \nabla \cdot \nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \cdot \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For spherical coordinates, situation is way more bad.

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

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Rigid Rotator

Now, we will discuss a simple model for a rotating diatomic molecule. The most simple approximation for rotating molecule, is assuming the distance between the two masses is fixed. This model is referred to as the *rigid rotator* model.

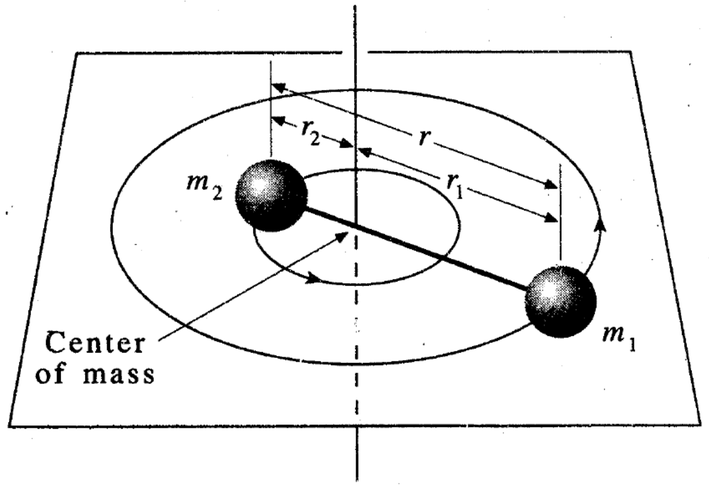

FIGURE 5.9
Two masses m_1 and m_2 shown rotating about their center of mass.

With harmonic oscillator model, RR is conventional model for diatomic molecules. Usually we use two models simultaneously: **RRHO model of diatomic molecules**.

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Rigid Rotator

Kinetic energy of the rigid rotator is

$$K = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = \frac{1}{2}(m_1 r_1^2 + m_2 r^2)\omega^2 = \frac{1}{2}I\omega^2$$

Where *I* is the moment of inertia. By using reduced mass and interatomic distance,

$$I = \mu r^2$$

By introducing angular momentum,

$$L = I\omega, \quad K = \frac{L^2}{2I}$$

Hamiltonian for RR has no potential energy: therefore

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2$$

Since *r* is fixed in RR model, $\partial/\partial r$ is identical to zero.

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Rigid Rotator

Full Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Therefore, we can derive $\hat{L}^2$ operator from the relation

$$\hat{H} = \frac{\hat{L}^2}{2I}, \quad \hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The equation is fully *angular*. It depends to only angular variables.

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