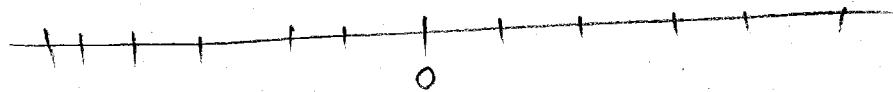


# States of Physical Systems

## Classical Mechanics

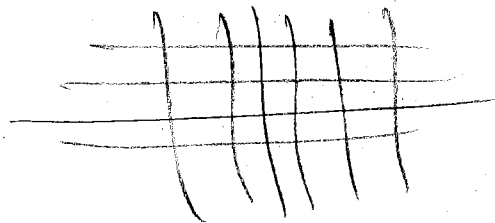
Particle in discrete space

(1) one-dimensional, straight line



States:  
positions  $0, \pm 1, \pm 2, \dots$

(2) two-dimensional, plane

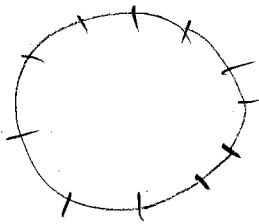


state =  $(n, m)$

$n = 0, \pm 1, \pm 2, \dots$

$m = 0, \pm 1, \pm 2, \dots$

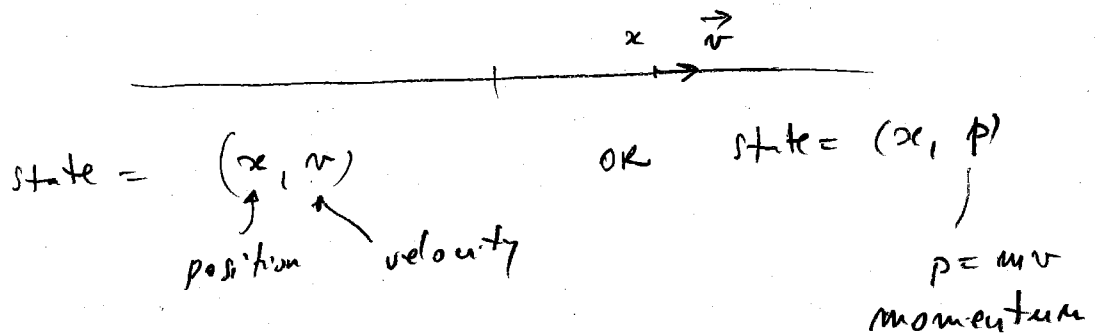
(3) one-dimensional, circle



$n = 0, 1, 2, \dots, N$

# Particle in continuous space

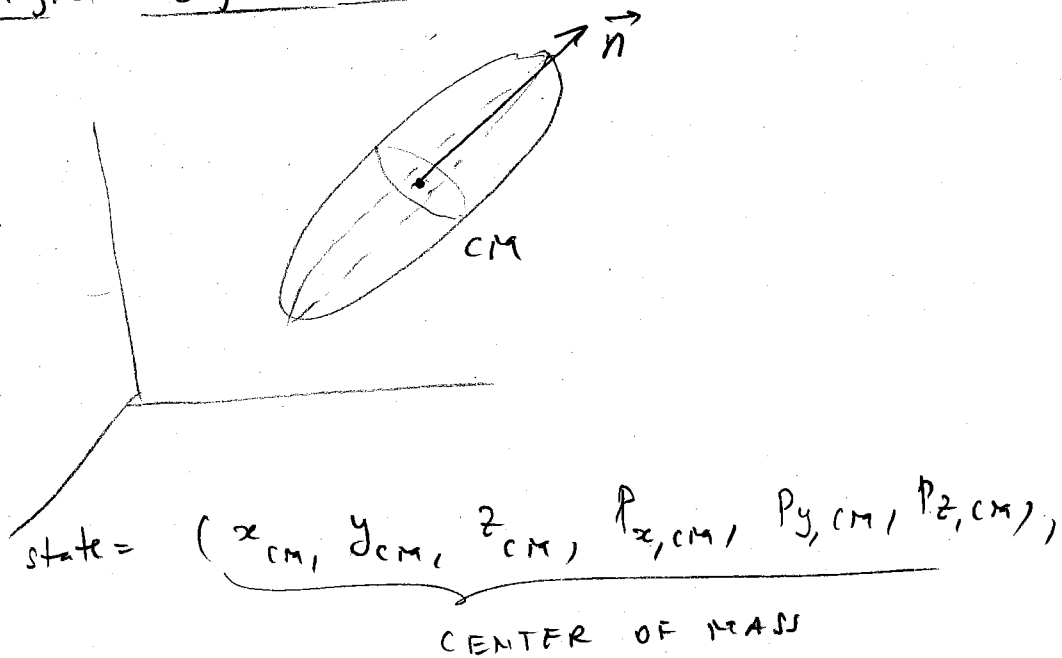
(1) one-dimensional



(2) three-dimensional

$$\text{state} = (x, y, z, p_x, p_y, p_z).$$

# Rigid object in three-dimensions



$$(\pi_x, \pi_y, \pi_z, \omega_x, \omega_y, \omega_z)$$

ORIENTATION

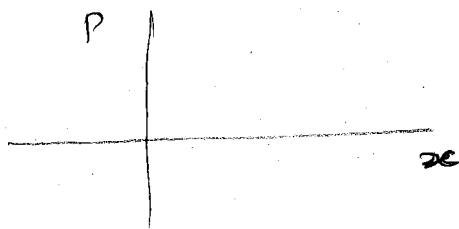
## Quantum harmonic oscillator

States =  $n$

$n = 0, 1, 2, \dots$

$$E_n = \hbar \omega \left( n + \frac{1}{2} \right)$$

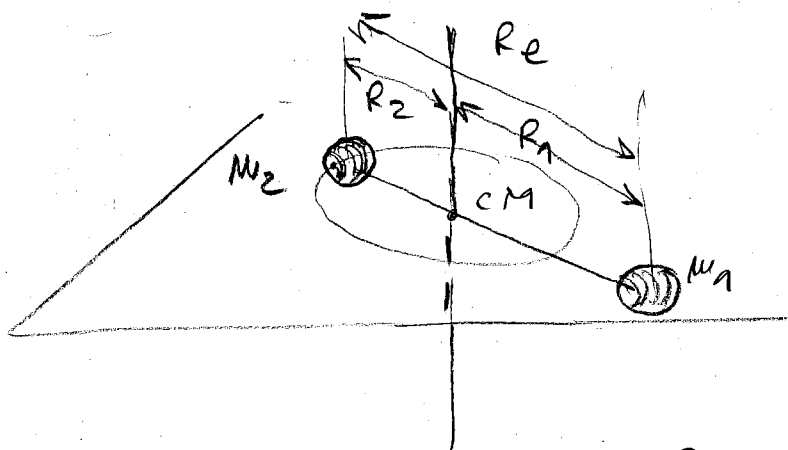
## Classical harmonic oscillator



State =  $(x, P)$

$$E = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

## Quantum rigid rotator



$$K = \frac{1}{2} I \omega^2$$

$$I = m_1 R_1^2 + m_2 R_2^2$$

$$v_1 = R_1 \omega$$

$$v_2 = R_2 \omega$$

States =  $(J, m)$   $J = 0, 1, 2, \dots$

$m = -J \dots J$

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

# Quantum mechanics

Free particle state  $(n_1, n_2, n_3)$  with  $n_1 = 0, \pm 1, \pm 2, \dots$   
 $n_2 = 0, \pm 1, \pm 2, \dots$   
 $n_3 = 0, \pm 1, \pm 2, \dots$

Remember that

$$E_{\text{state}} = \frac{2^2 \pi^2}{m} \left[ \left( \frac{n_1}{L_1} \right)^2 + \left( \frac{n_2}{L_2} \right)^2 + \left( \frac{n_3}{L_3} \right)^2 \right]$$

$$p_{\text{state}, 1} = \hbar k_1 = \hbar \frac{2\pi}{L_1} n_1$$

$$p_{\text{state}, 2} = \hbar \frac{2\pi}{L_2} n_2$$

$$p_{\text{state}, 3} = \hbar \frac{2\pi}{L_3} n_3$$

Remark

$$\hbar = \frac{h}{2\pi} \rightarrow \text{Planck's constant}$$

$$h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$

The quantum mechanical Hamiltonian operator is

$$\hat{H} = \frac{\hat{L}^2}{2I} \quad (9.47)$$

and the time-independent Schrödinger equation for this system appears as

$$\hat{H}\varphi = \left( \frac{\hat{L}^2}{2I} \right) \varphi = E\varphi \quad (9.48)$$

The eigenvalues of  $\hat{H}$  are the same as those of the square angular momentum operator  $\hat{L}^2$ . With the results obtained we may rewrite the equation above with the  $l, m$  indices.

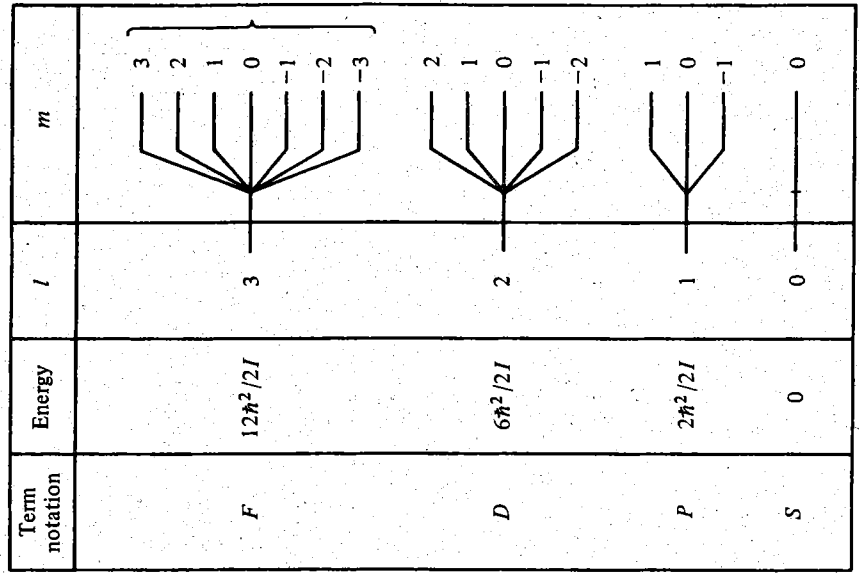


FIGURE 9.8 Term diagram for the rigid rotator of moment of inertia,  $I$ . The  $l$ th eigen-

$$\begin{aligned}
 \hat{L}^2 \varphi_{lm} &= \hbar^2 l(l+1) \varphi_{lm} \\
 \hat{L}_z \varphi_{lm} &= \hbar m \varphi_{lm} \quad (m = -l, \dots, +l) \\
 \hat{L}_+ \varphi_{lm} &= \varphi_{l, m+1} \quad (\hat{L}_+ = \hat{L}_x + i \hat{L}_y) \\
 \hat{L}_- \varphi_{lm} &= \varphi_{l, m-1} \quad (\hat{L}_- = \hat{L}_x - i \hat{L}_y)
 \end{aligned}
 \tag{9.44}$$

Since  $m = l$  is the maximum value of  $m$  and  $m = -l$  is the minimum value of  $m$ ,

$$\begin{aligned}
 L_+ \varphi_{ll} &= 0 \\
 L_- \varphi_{l, -l} &= 0
 \end{aligned}
 \tag{9.45}$$

These equations will be used in the next section for the derivation of the  $\varphi_{lm}$  eigenfunctions.

### The Rigid Rotator/Dumbbell Molecule

As an application of the preceding results relevant to the eigenvalues of  $\hat{L}^2$  and  $\hat{L}_z$ , let us consider the problem of the energy spectrum of a rigid rotator, or, equivalently, a dumbbell molecule (at sufficiently low temperature<sup>2</sup>). The rotator has two particles each of mass  $M$  separated by a weightless rigid rod of length  $2a$ . The midpoint of the rotator is fixed in space (Fig. 9.7). The moment of inertia of the rotator, about an axis of rotation through this point, is

$$I = 2Ma^2$$

Let the rotator be far removed from any force fields so that its energy is purely kinetic.

$$E = \frac{L^2}{2I} \tag{9.46}$$

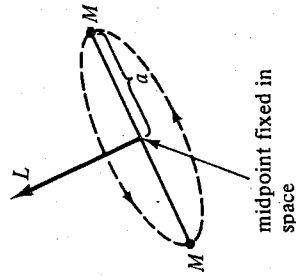


FIGURE 9.7 Rigid rotator with fixed midpoint. Moment of inertia about an axis of rotation through the midpoint is  $I = 2Ma^2$ .

<sup>2</sup>See footnote, p. 626.

$$\left(\frac{L}{2I}\right) \varphi_{lm} = E_l \varphi_{lm} \quad (9.49)$$

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

This energy is  $(2l+1)$ -fold degenerate. For any value of  $l$ , there are  $(2l+1)$  eigenfunctions

$$\varphi_{l, l}, \dots, \varphi_{l, -l} = \{\varphi_{lm}\} \quad (9.50)$$

all corresponding to the same eigenenergy, (9.49). The energy of the rotator does not depend on the projection of  $L$  into the  $z$  axis or onto any other prescribed direction. The energy-level diagram for this system is sketched in Fig. 9.8, together with the "term notation" of levels. This notation is common to atomic spectroscopy and will be used in the next three chapters. When a particle is in a state of definite orbital angular momentum, characterized by the quantum number  $l = 0, 1, 2, \dots$ , one speaks of the particle being, respectively, in an  $S, P, D, F, \dots$  state.

## PROBLEMS

9.5 Show that the frequencies of photons due to energy decays between successive levels of a rotator with moment of inertia  $I$  are given by

$$\hbar\omega = \left(\frac{\hbar^2}{I}\right) l(l+1), \quad \text{or} \quad \left(\frac{\hbar^2}{I}\right) l$$

9.6 An HCl molecule may rotate as well as vibrate. Discuss the difference in emission frequencies associated with these two modes of excitation. Assume that only  $l \rightarrow l \pm 1$  transitions between rotational states are allowed. Assume the same for vibrational levels. For rotational levels assume  $l \lesssim 50$ . Spring constant and moment of inertia may be inferred from the equivalent temperature values for HCl:  $\hbar\omega_0/k_B = 4150$  K;  $\hbar^2/2Ik_B = 15.2$  K.

9.7 Show that

$$(a) [\hat{L}_x, \hat{x}] = 0$$

$$(b) [\hat{L}_x, \hat{y}] = i\hbar\hat{z}$$

$$(c) [\hat{L}_y, \hat{z}] = i\hbar\hat{x}$$

$$(d) [\hat{L}_z, \hat{x}] = i\hbar\hat{y}$$

$$(e) [\hat{L}_y, \hat{z}] = [\hat{y}, \hat{L}_z]$$

$$(f) [\hat{p}_x, \hat{L}_x] = 0$$

$$(g) [\hat{p}_x, \hat{L}_y] = i\hbar\hat{p}_z$$

$$(h) [\hat{p}_y, \hat{L}_z] = i\hbar\hat{p}_x$$

$$(i) [\hat{p}_z, \hat{L}_x] = i\hbar\hat{p}_y$$

$$(j) [\hat{L}_y, \hat{p}_z] = [\hat{p}_y, \hat{L}_z]$$

9.8 Calculate

$$(a) \hat{L}_z^2 kr$$

$$(b) \hat{L}_z \sin kr$$

$$(c) \hat{L}_z f(kr)$$