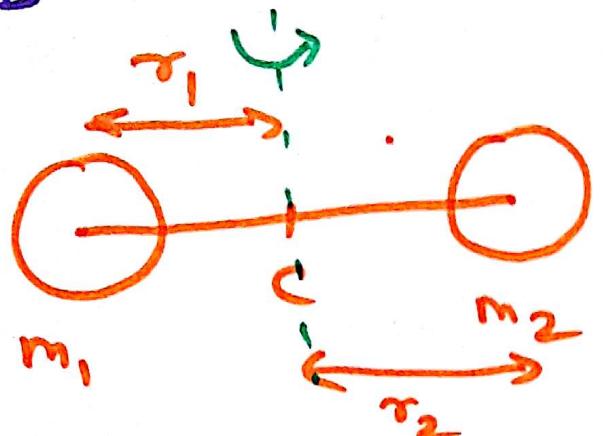


ROTATIONAL SPECTROSCOPY

- RIGID DIATOMIC MOLECULE



$$\tau_1 + \tau_2 = \tau_0$$

→ MOMENT OF INERTIA : $I = m_1 \tau_1^2 + m_2 \tau_2^2$

→ ROTATIONAL ENERGY

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$J = 0, 1, 2, \dots$
ROTATIONAL QUANTUM NUMBER

• WE KNOW THAT

$$m_1 \tau_1 = m_2 \tau_2 = m_2 (\tau_0 - \tau_1)$$

$$\Rightarrow I = (m_1 \tau_1) \tau_1 + (m_2 \tau_2) \tau_2$$

$$\tau_1 = \frac{m_2 \tau_0}{m_1 + m_2}$$

$$= m_2 \tau_2 \tau_1 + m_1 \tau_1 \tau_2$$

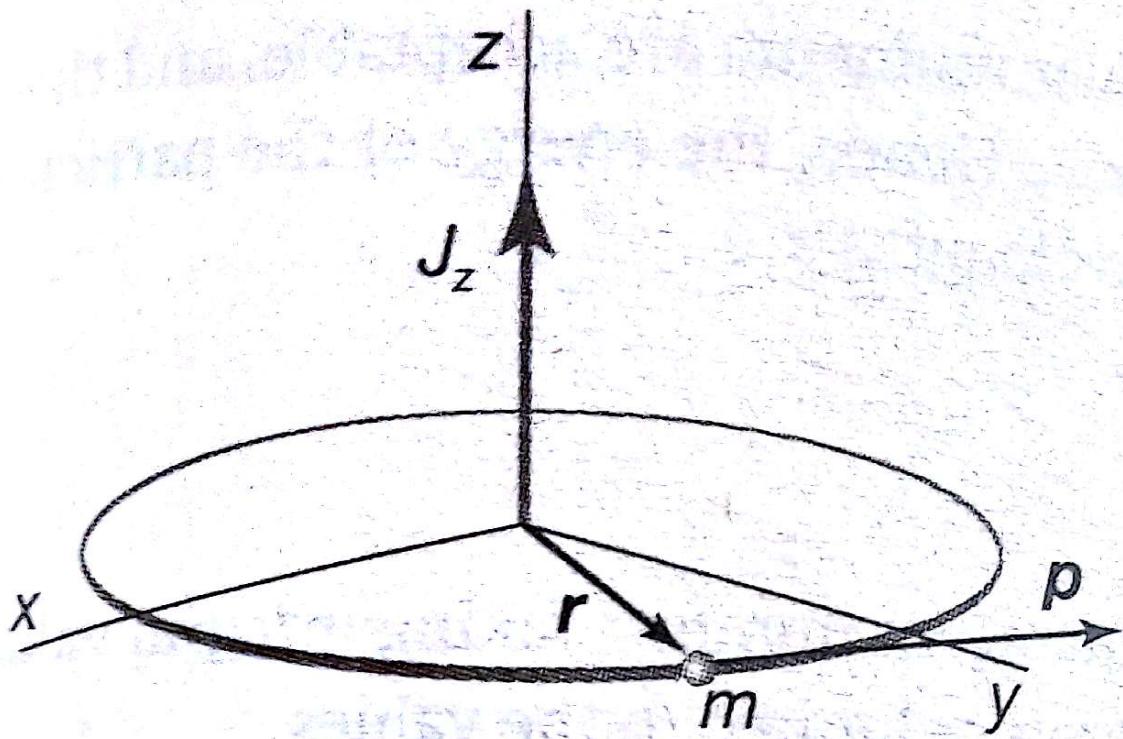
$$\tau_2 = \frac{m_1 \tau_0}{m_1 + m_2}$$

$$I = \tau_1 \tau_2 (m_1 + m_2)$$

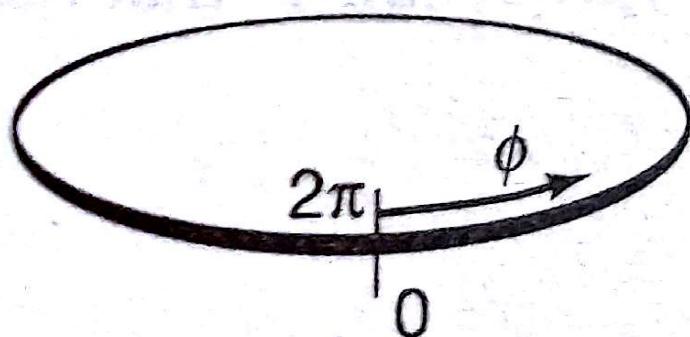


$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) \tau_0^2 = \mu \tau_0^2$$

REDUCED MASS



12.23 The angular momentum of a particle of mass m on a circular path of radius r in the xy -plane is represented by a vector J with the single nonzero component J_z of magnitude pr perpendicular to the plane.



The hamiltonian for a particle of mass m in a plane (with $V = 0$) is the same as that given in eqn 16:

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

and the Schrödinger equation is $H\psi = E\psi$, with the wavefunction a function of the angle ϕ . It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates r and ϕ (Fig. 12.26), where $x = r \cos \phi$ and $y = r \sin \phi$. By standard manipulations (see *Further reading*) we can write

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \quad (12.51)$$

5. The value $m_1 = 0$ corresponds to $\lambda = \infty$; a 'wave' of infinite wavelength has a constant height at all values of ϕ . See *Further information 1*.

However, because the radius of the path is fixed, the derivative with respect to r can be discarded. The hamiltonian then becomes

$$H = -\frac{\hbar^2}{2mr^2} \frac{d^2}{d\phi^2}$$

The moment of inertia $I = mr^2$ has appeared automatically, so H may be written

$$H = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \quad (12.52)$$

and the Schrödinger equation is

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi \quad (12.53)$$

The normalized general solutions of the equation are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \quad m_l = \pm \frac{(2IE)^{1/2}}{\hbar}$$

The quantity m_l is just a dimensionless number at this stage.

We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction ψ must satisfy a **cyclic boundary condition**, and match at points separated by a complete revolution: $\psi(\phi + 2\pi) = \psi(\phi)$. On substituting the general wavefunction into this condition, we find

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{e^{im_l\phi} e^{2\pi im_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi) e^{2\pi im_l}$$

As $e^{i\pi} = -1$, this relation is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l} \psi(\phi) \quad (12.54)$$

Because we require $(-1)^{2m_l} = 1$, $2m_l$ must be a positive or a negative even integer (including 0), and therefore m_l must be an integer: $m_l = 0, \pm 1, \pm 2, \dots$

In the discussion of translational motion in one dimension, we saw that the opposite signs in the wavefunctions e^{ikx} and e^{-ikx} correspond to opposite directions of travel, and that the linear momentum is given by the eigenvalue of the linear momentum operator. The same conclusions can be drawn here, but now we need the eigenvalues of the angular momentum operator. In classical mechanics the orbital angular momentum l_z about the z-axis is defined as⁷

$$l_z = xp_y - yp_x \quad [12.55]$$

where p_x is the component of linear motion parallel to the x-axis and p_y is the component parallel to the y-axis. The operators for the two linear momentum components are given in eqn 11.32, so the operator for angular momentum about the z-axis, which we denote l_z , is

$$l_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (12.56)$$

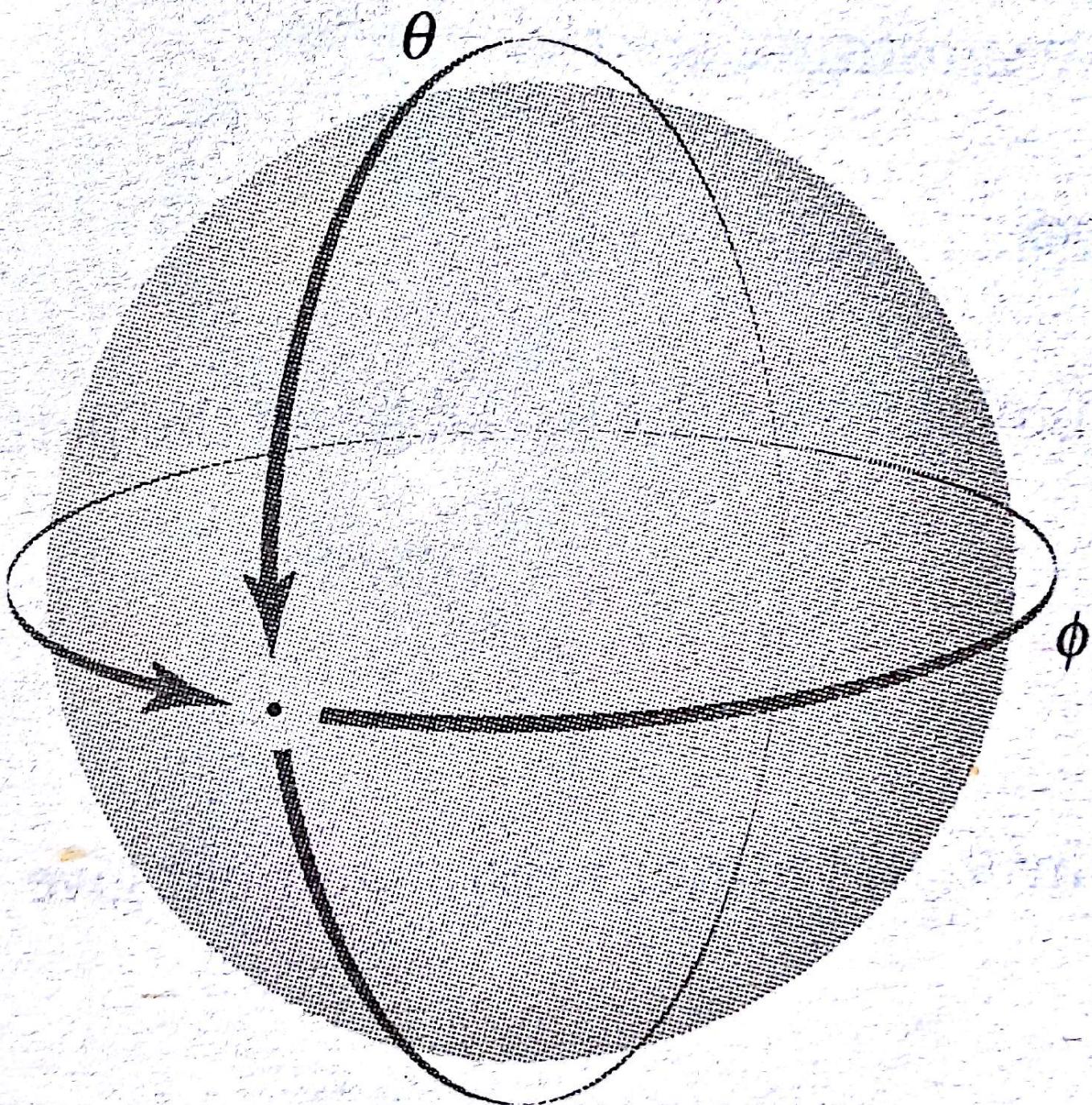
When expressed in terms of the coordinates r and ϕ , by standard manipulations this equation becomes

$$l_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad (12.57)$$

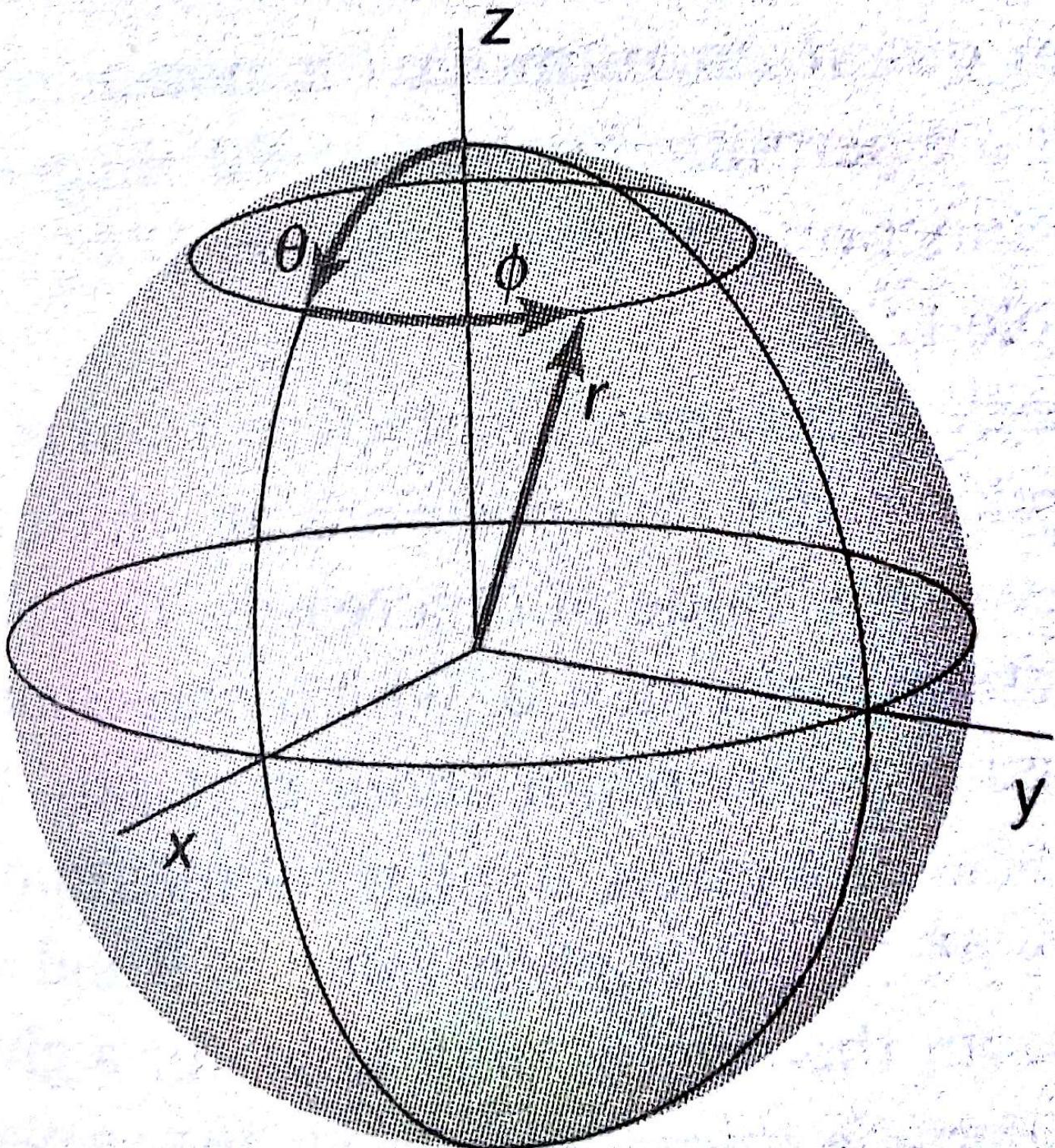
With the angular momentum operator available, we can test the wavefunction in eqn 50. Disregarding the normalization constant, we find

$$l_z \psi_{m_l} = \frac{\hbar}{i} \frac{d\psi_{m_l}}{d\phi} = im_l \frac{\hbar}{i} e^{im_l \phi} = m_l \hbar \psi_{m_l} \quad (12.58)$$

That is, ψ_{m_l} is an eigenfunction of l_z , and corresponds to an angular momentum $m_l \hbar$. When m_l is positive, the angular momentum is positive (clockwise when seen from below); when m_l is negative, the angular momentum is negative (counterclockwise when seen from below). These features are the origin of the vector representation of angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation (Fig. 12.28).



12.30 The wavefunction of a particle on the surface of a sphere must satisfy two cyclic boundary conditions; this requirement leads to two quantum numbers for its state of angular momentum.



12.31 Spherical polar coordinates. For a particle confined to the surface of a sphere, only the colatitude, θ , and the azimuth, ϕ , can change.

12.7 Rotation in three dimensions: the particle on a sphere

We now consider a particle of mass m that is free to move anywhere on the surface of a sphere of radius r . We shall need the results of this calculation when we come to describe the states of electrons in atoms (Chapter 13) and of rotating molecules (Chapter 16). The requirement that the wavefunction should match as a path is traced over the poles as well as round the equator of the sphere surrounding the central point introduces a second cyclic boundary condition and therefore a second quantum number (Fig. 12.30).

(a) The Schrödinger equation

The hamiltonian for motion in three dimensions (Table 11.1) is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (12.59)$$

The symbol ∇^2 is a convenient abbreviation for the sum of the three second derivatives; it is called the **laplacian**, and read either ‘del squared’ or ‘nabla squared’. For the particle confined to a spherical surface, $V=0$ wherever it is free to travel, and the radius r is a constant. The wavefunction is therefore a function of the **colatitude**, θ , and the **azimuth**, ϕ (Fig. 12.31), and we write it $\psi(\theta, \phi)$. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad (12.60)$$

As shown in the following *Justification*, this partial differential equation can be simplified by the separation of variables procedure by expressing the wavefunction (for constant r) as the product

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad (12.61)$$

where Θ is a function only of θ and Φ is a function only of ϕ .

JUSTIFICATION 12.0

The laplacian in spherical polar coordinates is (see *Further reading*)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{2}{r^2} \Lambda^2 \quad (12.6)$$

where the legendrian, Λ^2 , is

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \quad (12.6)$$

Because r is constant, we can discard the part of the laplacian that involves differentiation with respect to r , and so write the Schrödinger equation as

$$\frac{1}{r^2} \Lambda^2 \psi = -\frac{2mE}{\hbar^2} \psi$$

or, because $I = mr^2$, as

$$\Lambda^2 \psi = -\varepsilon \psi \quad \varepsilon = \frac{2IE}{\hbar^2}$$

To verify that this expression is separable, we substitute $\psi = \Theta\Phi$:

$$\frac{1}{\sin^2\theta} \frac{\partial^2(\Theta\Phi)}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial(\Theta\Phi)}{\partial\theta} = -\varepsilon\Theta\Phi$$

We now use the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta} \frac{d^2\Phi}{d\phi^2} + \frac{\Phi}{\sin\theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} = -\varepsilon\Theta\Phi$$

Division through by $\Theta\Phi$, multiplication by $\sin^2\theta$, and minor rearrangement give

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} + \varepsilon \sin^2\theta = 0$$

The first term on the left depends only on ϕ and the remaining two terms depend only on θ . We met a similar situation when discussing a particle on a rectangular surface (Justification 12.2) and, by the same argument, the complete equation can be separated. Thus, if we set the first term equal to the numerical constant $-m_l^2$ (a constant clearly chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2 \quad \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} + \varepsilon \sin^2\theta = m_l^2$$

The first of these two equations is the same as in Justification 12.4, so it has the same solutions (eqn 50). The second is much more complicated to solve, but the solutions are tabulated as the *associated Legendre functions*. The cyclic boundary conditions on θ result in the introduction of a second quantum number, l , which identifies the acceptable solutions. The presence of the quantum number m_l in the second equation implies, as we see below, that the range of acceptable values of m_l is restricted by the value of l .

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$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2 \quad \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \sin \theta \frac{d\Theta}{d\theta} + \epsilon \sin^2 \theta = m_l^2$$

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As indicated in Justification 12.6, solution of the Schrödinger equation shows that the acceptable wavefunctions are specified by two quantum numbers l and m_l which are restricted to the values

$$l = 0, 1, 2, \dots \quad m_l = l, l-1, \dots, -l \quad (12.64)$$

Note that the orbital angular momentum quantum number l is non-negative and that, for a given value of l , there are $2l+1$ permitted values of the magnetic quantum number, m_l . The normalized wavefunctions are usually denoted $Y_{l,m_l}(\theta, \phi)$ and are called the **spherical harmonics** (Table 12.3).

Figure 12.32 is a representation of the spherical harmonics for $l=0$ to 4 and $m_l=0$ which emphasizes how the number of angular nodes (the positions at which the wavefunction passes through zero) increases as the value of l increases. There are no angular nodes around the z-axis for functions with $m_l=0$, which corresponds to there being no component of orbital angular momentum about that axis. Figure 12.33 shows the distribution of the particle of a given angular momentum in more detail. In this representation, the value of $|Y_{l,m_l}|^2$ at each value of θ and ϕ is proportional to the distance of the surface from the origin. Note how, for a given value of l , the most probable location of the particle migrates towards the xy -plane as the value of $|m_l|$ increases.⁸

8. The real and imaginary components of the ϕ component of the wavefunctions, $e^{im_l\phi} = \cos m_l \phi + i \sin m_l \phi$, each have $|m_l|$ angular nodes, but these nodes are not seen when we plot the probability density, because $|e^{im_l\phi}|^2 = 1$.

Table 12.3 The spherical harmonics $Y_{l,m_l}(\theta, \phi)$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
	1	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
	± 1	$\mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$
	± 1	$\mp \left(\frac{15}{8\pi}\right)^{1/2} \cos \theta \sin \theta e^{\pm i\phi}$
	± 2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$
	± 1	$\mp \left(\frac{21}{64\pi}\right)^{1/2} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi}$
	± 2	$\left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
± 3		$\mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$

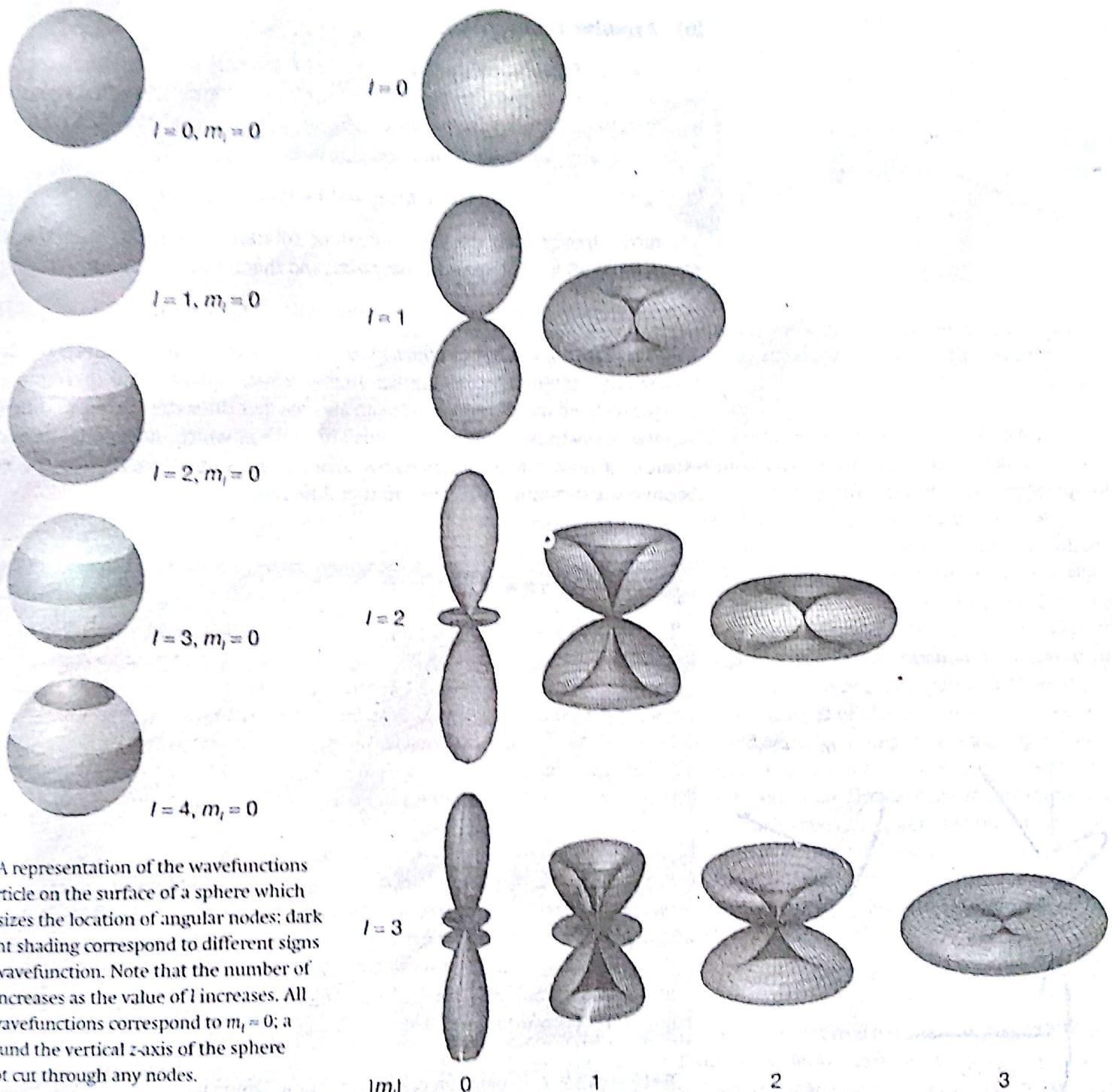
The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^\pi \int_0^{2\pi} Y_{l',m'}^*(\theta, \phi) Y_{l,m}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{l'l} \delta_{m'm}$$

An important 'triple integral' is

$$\int_0^\pi \int_0^{2\pi} Y_{l'',m''}^*(\theta, \phi) Y_{l',m'}(\theta, \phi) Y_{l,m}(\theta, \phi) \sin \theta d\theta d\phi$$

= 0 unless $m'' = m' + m_l$ and l'', l' , and l can form a triangle.



12.32 A representation of the wavefunctions of a particle on the surface of a sphere which emphasizes the location of angular nodes; dark and light shading correspond to different signs of the wavefunction. Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to $m_l = 0$; a path round the vertical z -axis of the sphere does not cut through any nodes.



12.33 A more complete representation of the wavefunctions for $l = 0, 1, 2$, and 3 . The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wavefunction at that point.

It also follows from the solution of the Schrödinger equation that the energy E of the particle is restricted to the values

$$E = l(l+1) \frac{\hbar^2}{2I} \quad l = 0, 1, 2, \dots \quad (12.65)$$

We see that the energy is quantized, and that it is independent of m_l . Because there are $2l + 1$ different wavefunctions (one for each value of m_l) that correspond to the same energy, it follows that a level with quantum number l is $(2l + 1)$ -fold degenerate.

(b) Angular momentum

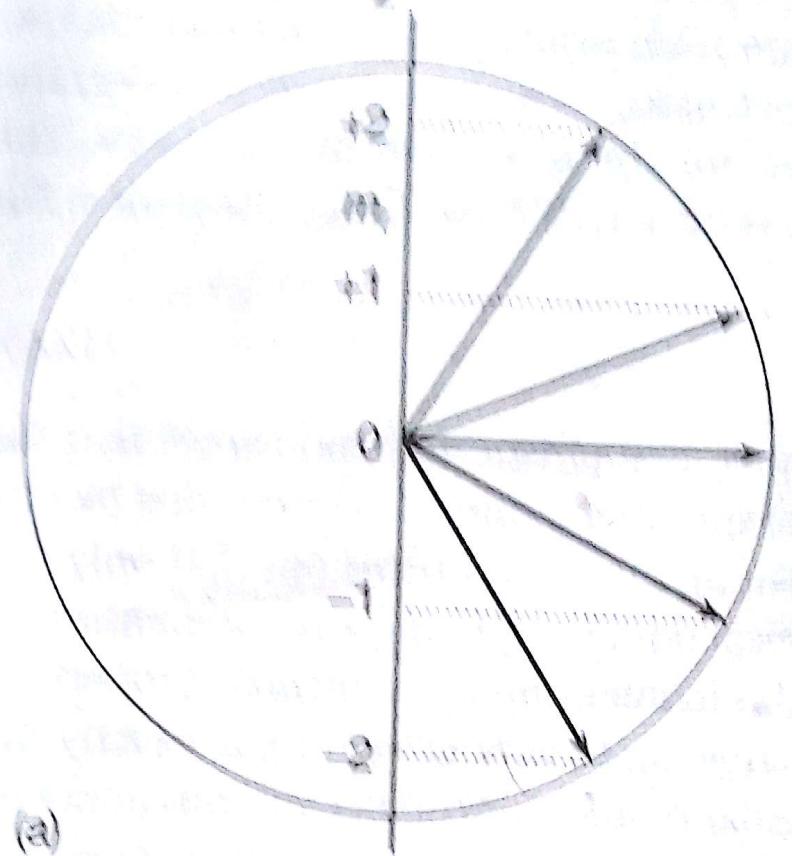
The energy of a rotating particle is related classically to its angular momentum J by $E = J^2/2I$ (see *Further information 2*). Therefore, by comparing this equation with eqn 65, we can deduce that, because the energy is quantized, then so too is the magnitude of the angular momentum, and confined to the values

$$\text{Magnitude of angular momentum} = \{l(l+1)\}^{1/2}\hbar \quad l = 0, 1, 2, \dots \quad (12.66a)$$

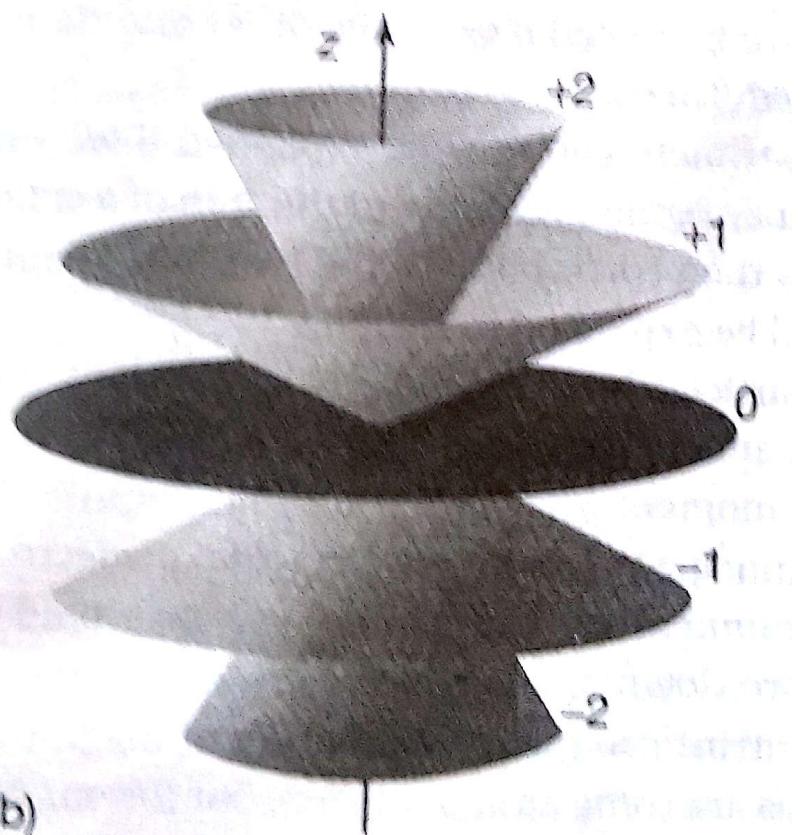
We have already seen (in the context of rotation in a plane) that the angular momentum about the z -axis is quantized, and that it has the values

$$z\text{-component of angular momentum} = m_l\hbar \quad m_l = l, l-1, \dots, -l \quad (12.66b)$$

The fact that the number of nodes in $\psi_{l,m_l}(\theta, \phi)$ increases with l reflects the fact that higher angular momentum implies higher kinetic energy, and therefore a more sharply buckled wavefunction. We can also see that the states corresponding to high angular momentum around the z -axis are those in which most nodal lines cut the equator: a high kinetic energy now arises from motion parallel to the equator, because the curvature is greatest in that direction.

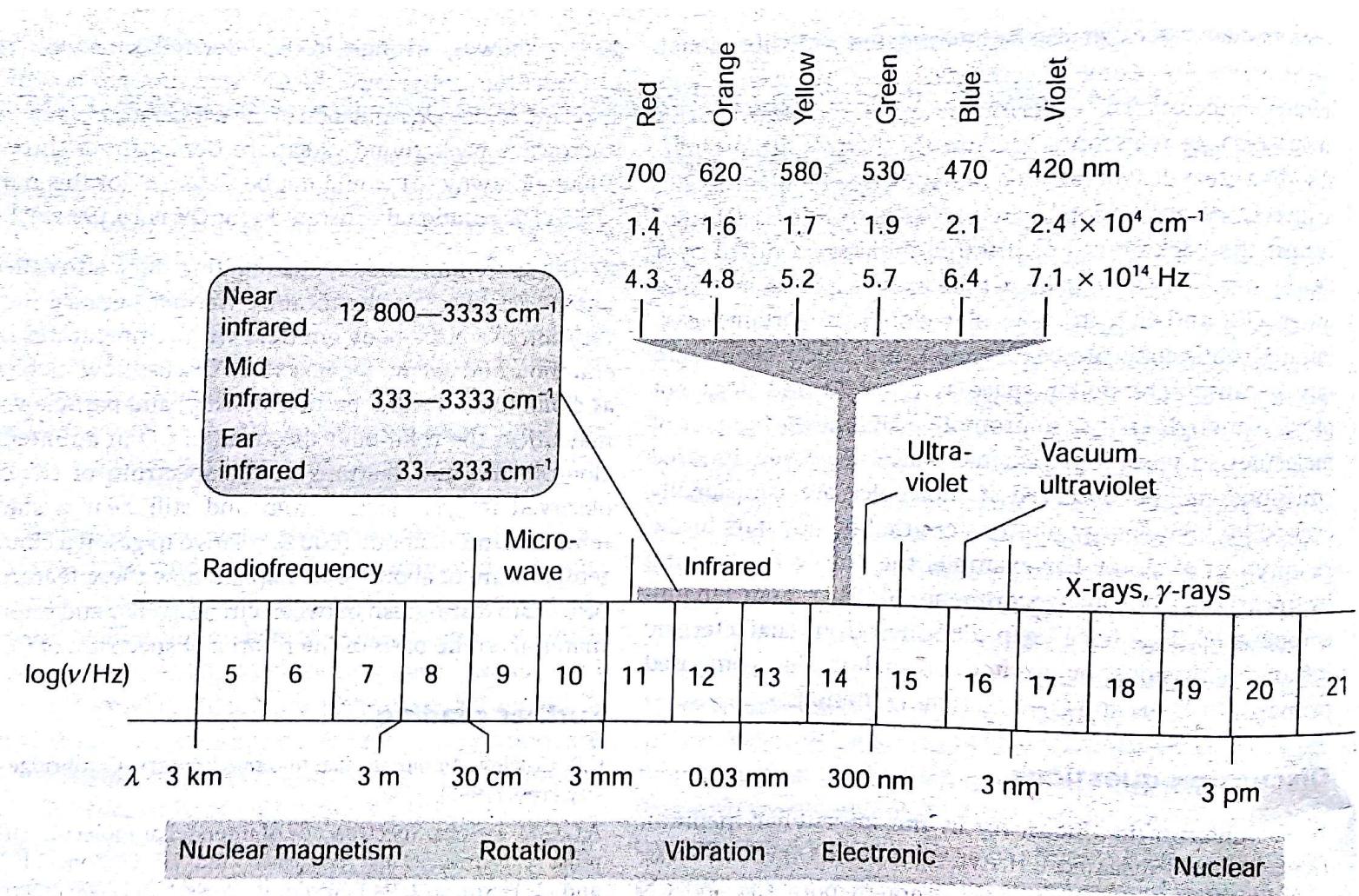


(a)

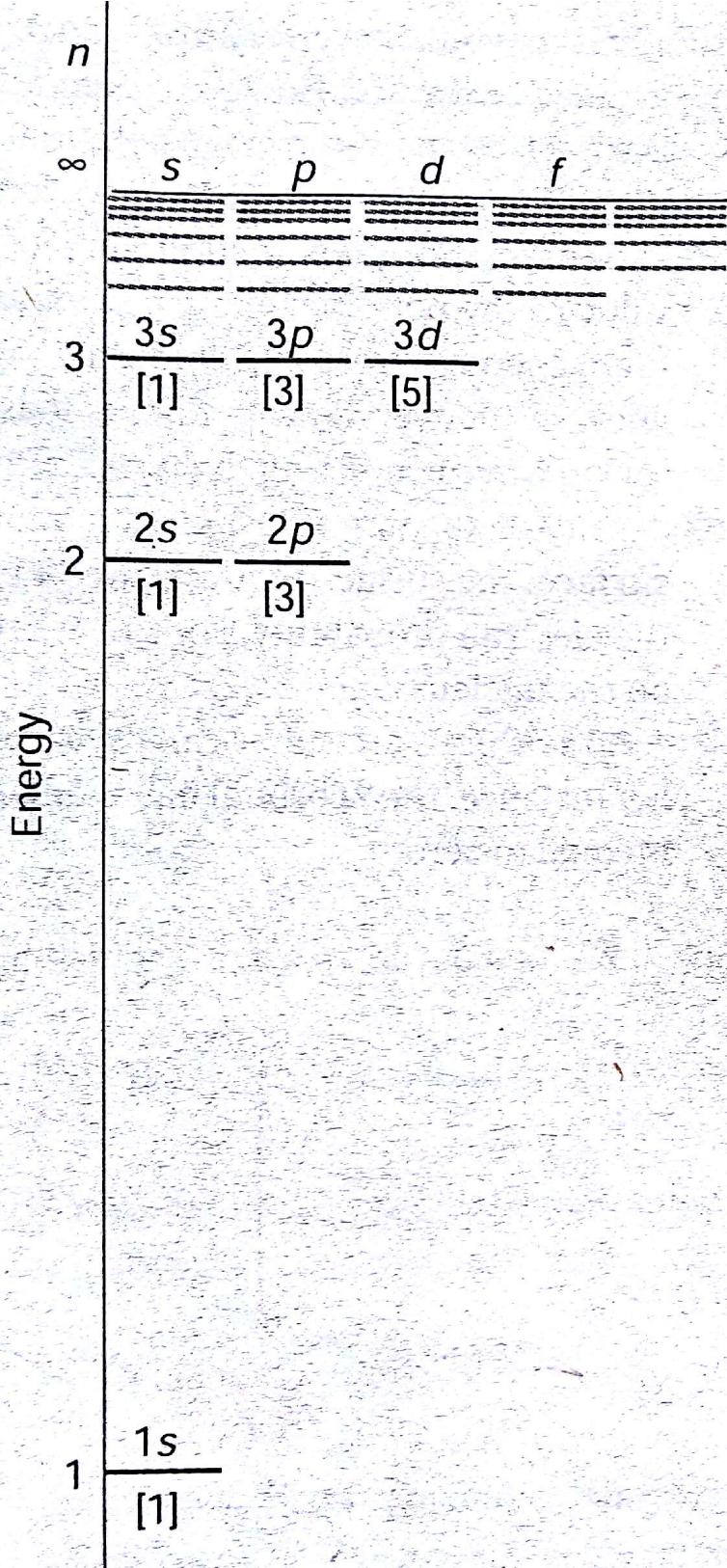


(b)

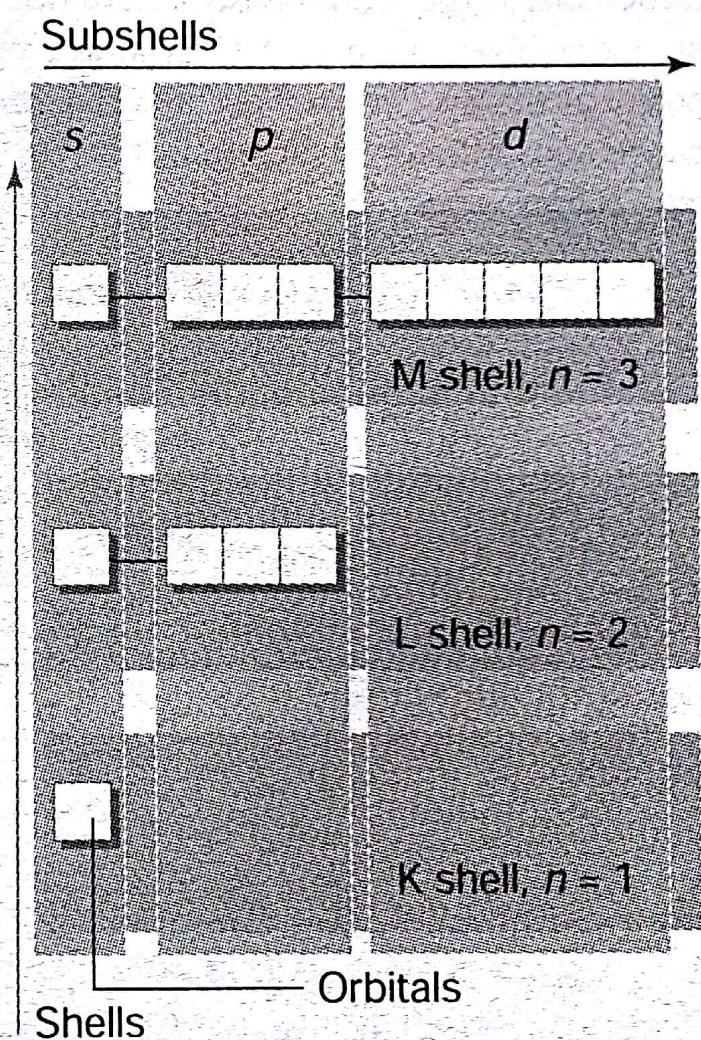
12.36 (a) A summary of Fig. 12.34. However, because the azimuthal angle of the vector around the z -axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.



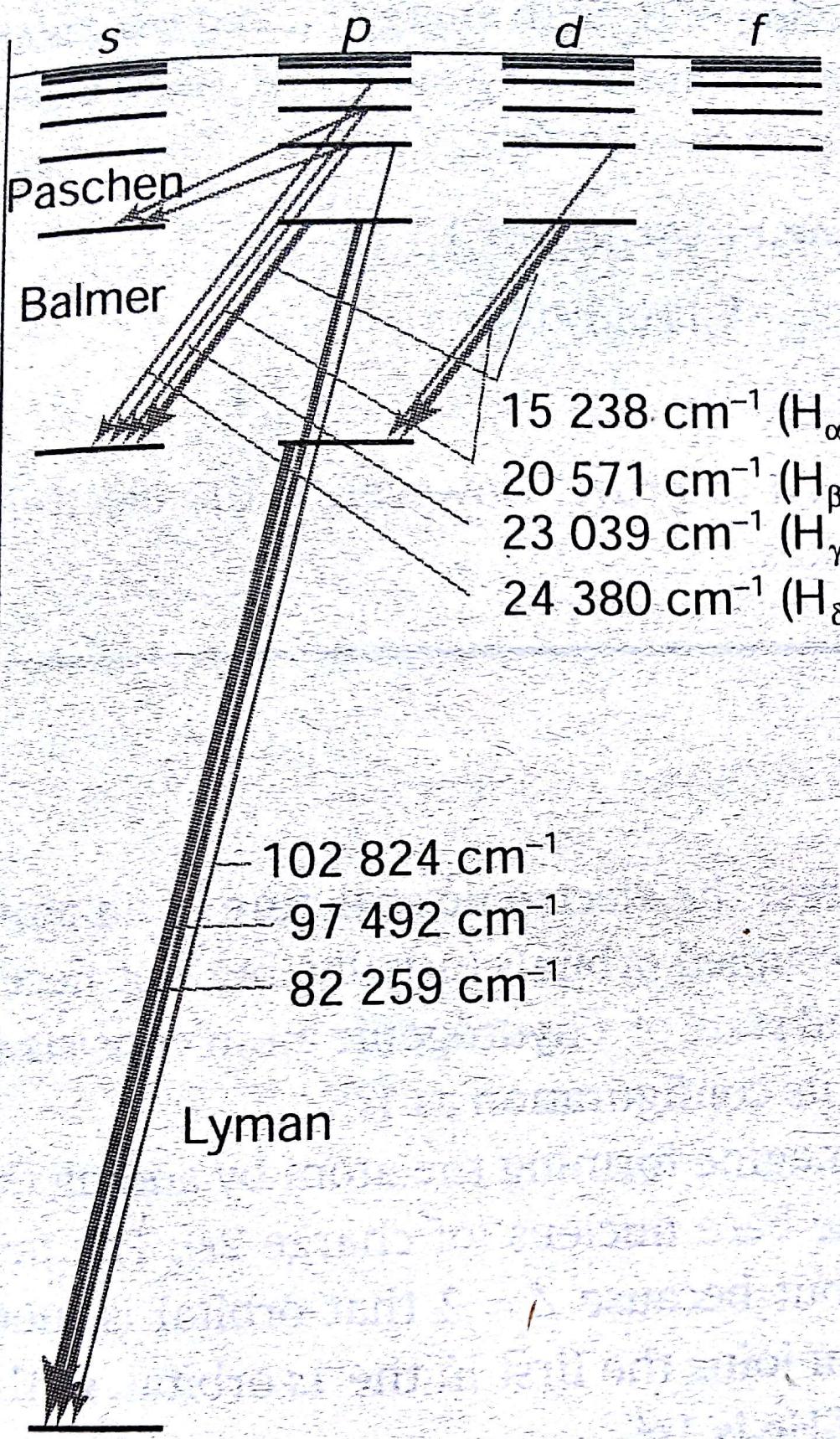
16.1 The electromagnetic spectrum and the classification of the spectral regions. The band at the bottom of the illustration indicates the types of transitions that absorb or emit in the various regions. ('Nuclear magnetism' refers to the types of transitions discussed in Chapter 18; 'nuclear' refers to transitions within the nucleus.)



13.8 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy .



13.9 The organization of orbitals (white squares) into subshells (characterized by l) and shells (characterized by n).



13.19 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition.

We saw in Section 12.10 that the rate of transition between two states is proportional to the square of the transition dipole moment, μ_{fi} , between the initial and final states, where

$$\mu_{fi} = \langle f | \mu | i \rangle \quad [13.28]$$

and μ is the electric dipole moment operator. For a one-electron atom μ is multiplication by $-e\mathbf{r}$ with components $\mu_x = -ex$, $\mu_y = -ey$, and $\mu_z = -ez$. If the transition dipole moment is zero, the transition is forbidden; the transition is allowed if the transition moment is nonzero. Physically, the transition dipole moment is a measure of the dipolar ‘kick’ that the electron gives to or receives from the electromagnetic field.

To evaluate a transition dipole moment, we consider each component in turn. For example, for the z-component,

$$\mu_{z,fi} = -e\langle f | z | i \rangle = -e \int \psi_f^* z \psi_i d\tau \quad [13.29]$$

To evaluate the integral, we note from Table 12.3 that $z = (4\pi/3)^{1/2}rY_{1,0}$, so

$$\int \psi_f^* z \psi_i d\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty R_{n_f, l_f} r R_{n_i, l_i} r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* Y_{1,0} Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi$$

It follows from the properties of the spherical harmonics (Section 12.7) that the integral

$$\int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* Y_{1,0} Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi$$

is zero unless $l_f = l_i \pm 1$ and $m_{l,f} = m_{l,i} + m$. Because $m = 0$ in the present case, the angular integral, and hence the z -component of the transition dipole moment, is zero unless $\Delta l = \pm 1$ and $\Delta m_l = 0$, which is a part of the set of selection rules. The same procedure, but considering the x - and y -components, results in the complete set of rules.

Illustration 13.3

To identify the orbitals to which a $4d$ electron may make radiative transitions, we first identify the value of l and then apply the selection rule for this quantum number. Because $l = 2$, the final orbital must have $l = 1$ or 3 . Thus, an electron may make a transition from a $4d$ orbital to any np orbital (subject to $\Delta m_l = 0, \pm 1$) and to any nf orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any ns orbital or to another nd orbital is forbidden.

Self-test 13.6 To what orbitals may a $4s$ -electron make radiative transitions?
[to np orbitals only]

TIME DEPENDENT PERTURBATION THEORY

- CONSIDER TWO QUANTUM STATES i AND f
- IN THE ABSENCE OF LIGHT (AT $t = 0$)

$$\Psi_i^D(\vec{r}, t=0) \quad D \rightarrow \text{DARK}$$

$$\Psi_f^D(\vec{r}, t=0)$$

HAMILTONIAN

$$\hat{H} = \hat{H}_0$$

TIME EVOLUTION OF Ψ_i^D AND Ψ_f^D

$$\Psi_i^D(\vec{r}, t) = \Psi_i^D(\vec{r}, 0) e^{-i \frac{E_i t}{\hbar}}$$

$$\Psi_f^D(\vec{r}, t) = \Psi_f^D(\vec{r}, 0) e^{-i \frac{E_f t}{\hbar}}$$

- IN THE PRESENCE OF LIGHT

HAMILTONIAN $\hat{H} = \hat{H}_0 + \hat{H}^{(1)}$

$$\Psi^B(\vec{r}, t) = C_i \Psi_i^D(\vec{r}, t) + C_f \Psi_f^D(\vec{r}, t)$$

AT $t=0$: $C_i = 1$; $C_f = 0$

C_i AND C_f DEPEND ON TIME

$C_i^2 \rightarrow$ PROBABILITY OF FINDING THE given SYSTEM IN STATE i (at a time)

$C_f^2 \rightarrow$ PROBABILITY OF FINDING THE SYSTEM IN STATE f

$$C_i^2 + C_f^2 = 1 \quad \text{CORRELATED}$$

$$\cdot \hat{H}^{(1)} = -\vec{\mu} \cdot \vec{E} \xrightarrow{\text{DIPOLE MOMENT}} \text{ELECTRIC FIELD}$$

$$= -\mu_x E_x - \mu_y E_y - \mu_z E_z$$

CONSIDER A POLARIZED LIGHT
($E_x = E_y = 0; E_z \neq 0$)

$$\hat{H}^{(1)} = -\mu_z E_z$$

$$= -\mu_z (2E_z^0 \cos(2\pi\omega t))$$

$$= -\mu_z (E_z^0 (e^{-i2\pi\omega t} + e^{i2\pi\omega t}))$$

$$\cdot (\hat{H}_0 + \hat{H}^{(1)}) (c_i \Psi_i^D(\vec{r}, t) + c_f \Psi_f^D(\vec{r}, t))$$

$$= -\frac{\hbar}{i} \frac{\partial}{\partial t} (c_i \Psi_i^D(\vec{r}, t) + c_f \Psi_f^D(\vec{r}, t))$$

$$\cdot c_i \cancel{H_0} \Psi_i^D(\vec{r}, t) + c_f \cancel{H_0} \Psi_f^D(\vec{r}, t)$$

$$+ c_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + c_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t)$$

$$= -\frac{\hbar}{i} \left[c_i \frac{\partial \Psi_i^D(\vec{r}, t)}{\partial t} + c_f \frac{\partial \Psi_f^D(\vec{r}, t)}{\partial t} \right]$$

$$+ \Psi_i^D(\vec{r}, t) \frac{\partial c_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial c_f}{\partial t}$$

$$\cdot c_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + c_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t)$$

$$= -\frac{\hbar}{i} \left[\Psi_i^D(\vec{r}, t) \frac{\partial c_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial c_f}{\partial t} \right]$$

$\times \Psi_f^D(\vec{r}, t)$ AND INTEGRATE AND USE
THE FACT $\int_{\vec{r}} \Psi_f^D(\vec{r}, t) \Psi_i^D(\vec{r}, t) d\vec{r} = 0$
 $= 1; i=f$

$$\Rightarrow C_i \int_{\vec{r}} \Psi_f^D(\vec{r}, t) H^{(1)} \Psi_i^D(\vec{r}, t) d\vec{r} + C_f \int_{\vec{r}} \Psi_f^D(\vec{r}, t) H^{(1)} \Psi_f^D(\vec{r}, t) d\vec{r} = -\frac{i}{\hbar} \frac{\partial C_f}{\partial t}$$

\Rightarrow APPROXIMATION: SMALL PERTURBATION
(FIRST- ORDER)

$$C_i \rightarrow 1 ; C_f \rightarrow 0$$

$$\frac{\partial C_f}{\partial t} \approx -\frac{i}{\hbar} \int_{\vec{r}} \Psi_f^D(\vec{r}, t) H^{(1)} \Psi_i^D(\vec{r}, t) d\vec{r}$$

$$\frac{\partial C_f}{\partial t} = \frac{-i}{\hbar} \sum_i \frac{(E_f - E_i)}{\hbar} t \int_{\vec{r}} \Psi_f^D(\vec{r}, 0) H^{(1)} \Psi_i^D(\vec{r}, 0) d\vec{r}$$

RATE OF CHANGE OF PROBABILITY
INTEGRATE: TIME EVOLUTION OF C_f

IF $\frac{\partial C_f}{\partial t} = 0 \Rightarrow$ NO CHANGE IN C_f
NO TRANSITION

$C_f^2 \Rightarrow$ PROBABILITY

$H^{(1)}$ \Rightarrow TRANSITION DIPOLE
MOMENT INTEGRAL

\Rightarrow SUBSTITUTE