4.1 Rotational Motion and the Rigid Rotor

Consider a particle of mass *m* moving in the 3D physical space in the absence of forces, but under the constraint that its distance, *r,* from a fixed point *O* is constant, $r=R_0$ (Figure 4.1). Such a particle has only two degrees of freedom because its distance from the center is never changing. The physical motion of the particle is rotation about the point *O*. We will call this type of rotation in which $r=R_0$ is fixed as "rigid" rotation in order to distinguish it from the more general "nonrigid" rotation in which *r* may also be changing during the rotation. A particle executing rigid rotation is called a "rigid rotor". To describe its motion we set up a Cartesian axis system that is fixed in space with origin at the point *O*. Cartesian type variables (*x*, *y*, *z*) are not suitable for this problem because of the constraint: $x^2+y^2+z^2=R_0^2$. Instead, spherical polar variables are ideal here since then we can simply set $r=R_0$, and take the two angles θ and ϕ as our independent variables.

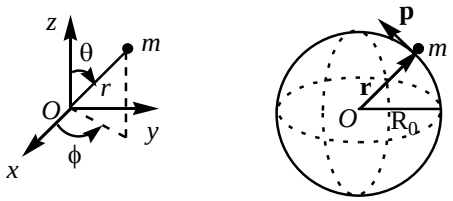

Figure 4.1 A "rigid rotor" is a particle of mass *m* constrained to move on the surface of a fictitious sphere with radius $r=R_0$.

4.2 Angular Momentum

"Angular momentum" is an important concept in both the classical and quantum descriptions of the rotational motion of a particle. The angular momentum, $\vec{L}$, of a classical particle about the point *O* is a vector quantity defined by

$$\vec{L} = \vec{r} \times \vec{p} \qquad \text{eq 4.1}$$

The direction of $\vec{L}$ is perpendicular to the plane formed by the position vector $\vec{r}$ and the linear momentum vector $\vec{p}$. Its magnitude is, $L= rp \sin(\alpha)$, where *r* and *p* are the magnitudes of the position and linear momentum vectors, respectively, and α is the angle between them. For the classical rigid rotor, $r=R_0$, and you should convince yourself that α =90˚; hence, $p=L/R_0$, and the kinetic energy, $p^2/2m$, of the rigid rotor can be written as

$$T= \frac{L^2}{2I} \qquad \text{Kinetic energy of a rigid rotor (Classical)} \qquad \text{eq 4.2}$$

where

$$I=mR_0^2 \qquad \text{eq 4.3}$$

is the moment of inertia of the particle; it is a characteristic property of the rigid rotor. There are no forces, and we take V=0. Hence, the classical Hamiltonian of the rotor is

$H=\frac{L^2}{2I}$ eq 4.4

Classically, H=E, and the energy E is conserved during the motion. This means that *L* is also a constant of motion. Classically allowed values of *L* follow from those of E; i.e. all values from 0 to infinity.

The quantum mechanical Hamiltonian operator is

$\hat{H}=\frac{\hat{L}^2}{2I}$ Hamiltonian operator of the rigid rotor eq 4.5

We need to find an explicit expression for the operator $\hat{L}^2$ in terms of the independent variables θ and ϕ. This is accomplished in two steps: First, one writes the components of classical $\vec{L}$ in eq 4.1 in terms of Cartesian variables:

$L_x = yp_z - zp_y$ eq 4.6a

$L_y = zp_x - xp_z$ eq 4.6b

$L_z = xp_y - yp_x$ eq 4.6c

The reason is: the operator replacement $p_q \rightarrow \hat{p}_q = -i\hbar\,\partial/\partial q$ works only in Cartesian variables. The quantum mechanical operators corresponding to those in eqs 4.6a-c are thus

$\hat{L}_x = y\hat{p}_z - z\hat{p}_y$ eq 4.7a

$\hat{L}_y = z\hat{p}_x - x\hat{p}_z$ eq 4.7b

$\hat{L}_z = x\hat{p}_y - y\hat{p}_x$ eq 4.7c

In the second step, the Cartesian variables in these expressions are converted into spherical polar variables (*r*, θ, ϕ) using standard rules of calculus. The results are

$\hat{L}_x = i\hbar\left(sin\,\phi\frac{\partial}{\partial\theta} + cot\,\theta\,cos\,\phi\frac{\partial}{\partial\phi}\right)$ eq 4.8a

$\hat{L}_y = -i\hbar\left(cos\,\phi\frac{\partial}{\partial\theta} - cot\,\theta\,sin\,\phi\frac{\partial}{\partial\phi}\right)$ eq 4.8a

$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ eq 4.8c

In a similar way it is found that

$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + cot\,\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$ eq 4.9

In obtaining these expressions from eqs 4.7a-c, it is not assumed that *r* is a constant; i.e. the full set of (*r*, θ, ϕ) variables are used. It is interesting that the variable *r* cancels out in the transformation from

Cartesian to polar variables so that the operators above are functions of only the two independent angle variables θ and ϕ. Expressions in eqs 4.8a-c and 4.9 are valid for rigid as well as nonrigid rotation.

It can be shown that the components (eqs 4.8a-c) of the angular momentum operator do not commute with each other, but all three components do commute with $\hat{L}^2$. This means that we can take $\hat{L}^2$ with only one of the three components as a set of commuting operators; it is conventional to take $\hat{L}^2$ and $\hat{L}_z$. When there are several operators as in here, it is important to identify the set of commuting operators among them because of the general principle that commuting operators have the same set of eigenfunctions. This principle helps in solving the Schrödinger equation.

The eigenvalue-eigenfunction equation for $\hat{L}_z$ is a simple one, and we can readily solve it. Let us denote the eigenfunctions and the associated eigenvalues by the (scalar) symbols Φ and L_z, respectively. Using eq 4.8c, the equation we want to solve is

$$\hat{L}_z\Phi = L_z\Phi \qquad \text{eq 4.10}$$

Explicitly, it is

$$-i\hbar\frac{d\Phi}{d\phi} = L_z\Phi \qquad \text{eq 4.11}$$

We can guess that the eigenfunctions are

$$\Phi(\phi) = Ae^{im\phi} \qquad \text{eq 4.12a}$$

where A is a normalization constant, and m is another constant related to the eigenvalue[1]

$$L_z = \hbar m \qquad \text{eq 4.12b}$$

The question now is: what are the allowed values of the constant m? The answer to this question is provided by the general principle that all functions in quantum theory must be single-valued, as discussed previously. The range of the variable ϕ in eq 4.12a is from 0 to 2π such that ϕ=0 and ϕ=2π represent the same physical point. It is therefore necessary that the functions of eq 4.12a must satisfy: $\Phi(0)= \Phi(2\pi)$, or explicitly (since A can not be zero)

$$1 = e^{im2\pi} \qquad \text{eq 4.12c}$$

This equation is satisfied only when m is zero or an integer. Thus the allowed values of m, and therefore of L_z are

$$L_z = \hbar m, \qquad m = 0, \pm1, \pm2, \cdots \qquad \text{eq 4.12d}$$

You should show that the value of the normalization constant in eq 4.12a is: $A=1/(2\pi)^{1/2}$. Note that in contrast to the particle in a 1D box problem, here the value m=0 does not make Φ zero, and is therefore allowed. Also, the functions Φ with negative m values are different from those with positive values (i.e.

[1] Please do not confuse the quantum number m here with the mass of the particle.

the effect of replacing *m* with –*m* is not just a change in the sign of *A*, in this case). We will label these functions with the quantum number *m*: Φ_m (e.g. Φ_0, Φ_1, Φ_{-1}, etc.).

4.3 Rigid Rotor with one degree of freedom

Suppose that the motion of the rigid rotor is further constrained so that in addition to the restriction $r=R_0$, it is confined to move in the *x*-*y* plane of Figure 4.1 (i.e. θ is fixed at $\pi/2$). Now the particle has only one degree of freedom, namely ϕ (Figure 4.2). We will refer to such a particle as a "1 df rotor". It is also called "particle in a ring" because the path traversed by the classical particle is a circle with radius R_0.

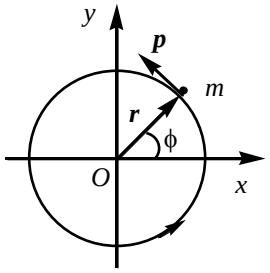

Figure 4.2 Rigid rotation in 2D physical space. The magnitude of the position vector ***r*** is constant, equal to R_0.

What are the allowed energies of the "1 df rotor"? In this problem, the only nonzero component of the angular momentum of the particle is $\hat{L}_z$, and therefore $\hat{H} = \hat{L}^2/2I = \hat{L}_z^2/2I$, now. The Schrödinger equation is $\left(\frac{\hat{L}_z^2}{2I}\right)\Psi = \mathrm{E}\Psi$. Since *I* is a constant, eigenfunctions of $\hat{H}$ are the same as those of $\hat{L}_z^2$, which in turn are the same as those of $\hat{L}_z$: i.e. Φ_m (note that $\hat{H}$, $\hat{L}_z^2$, and $\hat{L}_z$ are commuting operators). Thus, $\Psi_m=\Phi_m$, and the allowed energies, E_m, of the "1 df rotor" are

$E_m = B\,m^2, \qquad m = 0, \pm1, \pm2, \cdots$ eq 4.13

where

$B = \frac{\hbar^2}{2I}$ eq 4.14

is called the "rotational constant" of the rigid rotor. It has energy units. Energy levels of the "1 df rotor" are shown in Figure 4.3. All levels except the ground state are doubly degenerate. Note also the similarity in the spacing of the energy levels to those in the "particle in a 1D box" problem.

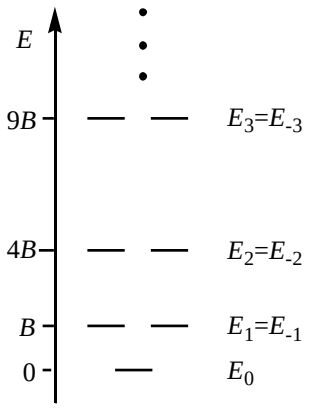

Figure 4.3 Allowed energy levels of a "1 df rotor".

We interpret the rotational state functions Φ_m of the "1 df rotor" as follows. When the rotor is in the rotational ground state, $\Phi_0=A$, its $L_z=0$, and hence it has no angular momentum. In states Φ_m with $|m|>0$, the particle does have angular momentum. From eq 4.12d, positive values of m give positive L_z values, and such states Φ_m describe counterclockwise (around the z-axis) rotation of the rotor as in Figure 4.2. Likewise, states with negative m describe clockwise rotation.

Exercise 4.1 What is the rotational ZPE of the rotor?

Exercise 4.2 What is the ground state energy of a system of 6 noninteracting (i.e. independent) electrons if it is assumed that each electron is rotating like a "1 df rotor"? Remember the Pauli principle. Give your answer in terms of B. Since the mass of the electron is known, what additional data do you need in order to calculate B?

Exercise 4.3 Show by explicit integration that the functions Φ_m with $A=1/(2\pi)^{1/2}$ are orthonormal. The volume element is $d\phi$.

4.4 Rigid Rotor with two degrees of freedom

We now return to the original problem in which the rotor has two degrees of freedom (Figure 4.1). We will refer to it as the "2 df rotor". Its Hamiltonian is given in eq 4.5 where $\hat{L}^2$ is the full expression in eq 4.9. The problem of solving the Schrödinger equation, $\hat{H}\Psi = \mathrm{E}\Psi$, for the "2 df rotor" is essentially that of finding eigenvalues and eigenfunctions of the $\hat{L}^2$ operator. The latter problem is well known in mathematics, and we will simply quote the results. Denoting the eigenfunctions and the eigenvalues by the symbols Y and L^2, respectively, the eigenvalue-eigenfunction equation for $\hat{L}^2$ is

$$\hat{L}^2 Y = L^2 Y \qquad \text{eq 4.15}$$

The solutions for *Y* are the standard functions $Y_{lm}(\theta,\phi)$ known in the literature as the "spherical harmonics", with associated eigenvalues

$$L^2 = \hbar^2 l(l+1), \qquad l = 0, 1, 2, \ldots \qquad \text{eq 4.16}$$

The functions Y_{lm} are labeled by two quantum numbers such that for a given l, allowed values of m are integers restricted to the range $-l \le m \le l$. Thus there are $(2l+1)$ different functions Y_{lm}, all with the same l, but differing in their m labels. These functions have a "product" form in the variables θ and ϕ:

$$Y_{lm}(\theta,\phi) = T_{l|m|}(\theta)\Phi_m(\phi) \qquad \text{eq 4.17}$$

where the θ-dependent factor is a real function, and the ϕ-dependent factor is the function in eq 4.12a. The latter function is complex-valued for $m \neq 0$. In other words, the functions Y_{lm} are real for m=0 (i.e. Y_{l0}), and complex for $m \neq 0$.

Using eq 4.17, you should verify that the spherical harmonics are also eigenfunctions of the $\hat{L}_z$ operator (eq 4.8c):

$$\hat{L}_z Y_{lm} = \hbar m\, Y_{lm} \qquad \text{eq 4.18}$$

This fact is expected because we know that the two operators $\hat{L}_z$ and $\hat{L}^2$ commute, and therefore they should have simultaneous eigenfunctions.

It was pointed out in Lecture Notes 2 that eigenfunctions of quantum mechanical operators have the orthogonality property (eq 2.20). Thus, the value of the integral

$$\int Y^*{}_{lm} Y_{l'm'}\, d\tau \qquad \text{eq 4.19}$$

is zero for all choices of *l, m, l'*, and *m'* except for the case where both *l=l'* and *m=m'*, in which case the integral becomes the normalization integral, and its value is 1.[2] The integral in eq 4.19 is a double integral because there are two independent variables (θ and ϕ) of integration. The volume element is, $d\tau = \sin(\theta)\, d\theta d\phi$, which is the angle-dependent part of the volume element in spherical polar variables (see Lecture Notes 2, section 2.2).

The Hamiltonian operator of the "2 df rotor" in eq 4.5 is $\hat{H}$=c $\hat{L}^2$, where the constant c=1/2*I*. The two operators $\hat{H}$ and $\hat{L}^2$ obviously commute, and therefore the functions Y_{lm} are the solutions of the Schrödinger equation, $\hat{H}\Psi = \mathrm{E}\Psi$, for the rigid rotor. Indeed,

$$\hat{H}Y_{lm} = \left(\frac{1}{2I}\right)\hat{L}^2 Y_{lm} = \frac{\hbar^2 l(l+1)}{2I} Y_{lm} = Bl(l+1)Y_{lm} \qquad \text{eq 4.20}$$

[2] All sources that tabulate explicit expressions for the spherical harmonics present them in normalized form.

The allowed energies of the "2 df rotor" are therefore

$E_l = B\, l(l+1), \qquad l = 0, 1, 2, \ldots$ eq 4.21

The energy levels are determined by the l quantum number only, whereas the rotational wavefunctions Y_{lm} depend on both the l and m quantum numbers. As pointed out above, for a given value of l there are $(2l+1)$ different functions Y_{lm}. Therefore, a given energy E_l is $(2l+1)$-fold degenerate.

4.5 Rotational energy levels of a diatomic molecule

The results obtained above for the properties of a "2 df rotor" are mainly applied to the rotational motion of a diatomic molecule about its center of mass (*c.m.*). Figure 4.4 shows a model of a diatomic molecule. The two masses rotate in concert about the *c.m.*, satisfying the condition

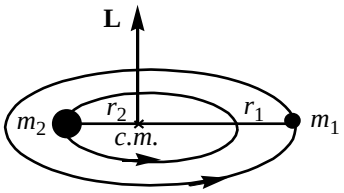

Figure 4.4 Rigid rotation of a diatomic molecule about its center of mass.

$m_1 r_1 = m_2 r_2$ eq 4.22

The distance between the masses is the bond length R_0, assumed to be "rigid" (i.e. unchanging) during the rotation. We have

$r_1 + r_2 = R_0$ eq 4.23

Using eqs 4.22-23, one finds that

$r_1 = (m_2/M)\, R_0$ and $r_2 = (m_1/M)\, R_0$ eq 4.24

where $M=m_1+m_2$. The moment of inertia of a diatomic molecule about the *c.m.* is defined as: $I = m_1 r_1^2 + m_2 r_2^2$. Using eq 4.24, one gets for I

$I = \mu R_0^2$ eq 4.25

where

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ eq 4.26

is called the "reduced mass".

The rotation of a diatomic molecule about its *c.m.* is entirely equivalent to the rotation of a "2 df rotor" shown in Figure 4.1. The fixed point *O* in that figure corresponds to the *c.m.* in the diatomic molecule. The only difference is that the reduced mass μ must be used for *m* in the calculation of *I* (eq 4.25), and therefore the rotational constant *B* (eq 4.14).

In applying the rigid rotor results to the rotational states of diatomic molecules, chemists use the capital letters J and M in place of *l* and *m*. Thus they write the allowed rotational energies of a diatomic molecule as (from eq 4.21)

$E_J = B\,J(J+1), \qquad J = 0, 1, 2, \ldots$ eq 4.27

and the rotational wavefunctions as Y_{JM}. The degeneracy, g_J, of a rotational level E_J is 2J+1. The spacing between neighboring energy levels is

$E_{J+1} - E_J = 2B\,(J+1)$ eq 4.28

The rotational levels of a diatomic molecule are shown in Figure 4.5.

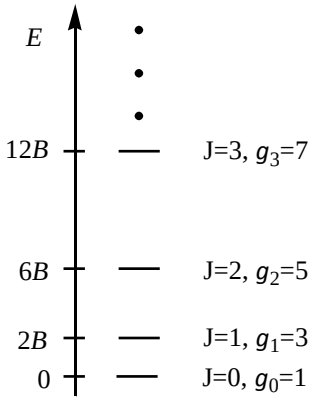

Figure 4.5 Allowed rotational energy levels, E_J, of a diatomic molecule in the rigid-rotor approximation. The degeneracies, g_J=2J+1, are also indicated.

Exercise 4.4 The bond length of the $^{12}C^{16}O$ molecule is 112.8 pm. Calculate (a) the reduced mass and (b) the rotational constant of $^{12}C^{16}O$. (c) Calculate the wavelength of the photon absorbed when a $^{12}C^{16}O$ molecule initially in the J=2 level, makes a transition to the J=3 level.

<u>*Note*</u>: In such calculations, you should use the appropriate "isotopic" masses, and not the average atomic masses given in the periodic table. The reason is: differences in the value of *B* due to different isotope masses are experimentally detectable. So, search for the masses of C-12 and O-16 isotopes.