

## 6.1 Coulomb interaction energy among charged particles in an atom or a molecule

The interaction energy between a pair of electric charges  $Q_1$  and  $Q_2$  separated by a distance  $\rho$  is given by the Coulomb law as

$$V = \frac{1}{4\pi\epsilon_0} \frac{Q_1 Q_2}{\rho} \quad \text{Coulomb interaction energy in SI units} \quad \text{eq 6.1}$$

where  $\epsilon_0 = 8.854\,188 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$  is the permittivity of vacuum. In atoms and molecules, the charged particles are electrons and nuclei whose charges are integral multiples of the elementary charge (magnitude of charge on an electron),  $e = 1.602\,177 \times 10^{-19} \text{ C}$ . For example, the charge of an electron is  $-1e$ , and the charge on the nucleus of an oxygen atom ( $Z=8$ ) is  $+8e$ . In atomic and molecular studies, it is convenient to take  $e$  as the unit of charge, and set

$$Q = q e \quad \text{eq 6.2}$$

The average distance between the electron and the nucleus in the H-atom is  $a_0 = 52.917\,725 \text{ pm}$ . We express distances between particles in an atom or molecule, taking  $a_0$  as the unit of distance (called the “*bohr*” unit), and set

$$\rho = r a_0 \quad \text{eq 6.3}$$

Note that  $r$  and  $q$  are dimensionless. With these units of charge and distance, we can write eq 6.1 in the form

$$V = \frac{q_1 q_2}{r} \text{ hartree} \quad \text{eq 6.4}$$

where

$$\text{hartree} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.35975 \times 10^{-18} \text{ J} = 27.21139 \text{ eV} \quad \text{eq 6.5a}$$

will be taken as the unit of energy.

When there are many charged particles, the total Coulomb interaction energy is obtained by adding contributions (of the form in eq 6.4) from all distinct pairs of charges.

**Atomic units.** The units  $e$ ,  $bohr$ , and  $hartree$  belong to a system of units called “atomic units” (a.u.).<sup>1</sup> Atomic units are used in theoretical calculations involving electrons, such as in the Schrödinger equation for the motion of electrons in atoms or molecules. Two other units in this system are mass of electron,  $m_e = 9.109\,382 \times 10^{-31} \text{ kg}$ , as the unit for mass, and  $\hbar = 1.054\,572 \times 10^{-34} \text{ J s}$  as the unit for angular momentum. In atomic units, eigenvalues of  $\hat{L}_z$  operator are written in dimensionless form as  $L_z = m$ , (i.e. without the  $\hbar$ ); similarly eigenvalues of  $\hat{L}^2$  operator are  $L^2 = l(l+1)$ , also dimensionless. Note here that there is an alternative expression for the *hartree* that gives the same numerical value as in eq 6.5a:

<sup>1</sup> Do not confuse “atomic units” of quantum chemistry with the “atomic mass unit”,  $u$ , which is defined as 1/12 of the mass of  $^{12}\text{C}$  isotope.

$$\text{hartree} = \frac{\hbar^2}{m_e a_0^2} \quad \text{eq 6.5b}$$

### 6.1.1 Coulomb interaction energy for an atom in atomic units

Consider an atom with atomic number  $Z$ , and having  $N$  electrons. For a neutral atom  $N=Z$ . We label the electrons by the integers  $1, 2, \dots, N$ . Let  $r_j$  be the distance of the  $j^{\text{th}}$  electron from the nucleus, and  $r_{ij}$  be the distance between the  $i^{\text{th}}$  and  $j^{\text{th}}$  electrons. Unit of distance is the *bohr*, unit of charge is  $e$ , and unit of energy is the *hartree* (i.e. atomic units). It is convenient to split the interactions into two types: i) electron-nucleus attractions, denoted by  $V_{en}$ , and ii) electron-electron repulsions,  $V_{ee}$ . We have

$$V_{en} = -\sum_{j=1}^N \frac{Z}{r_j} \quad \text{eq 6.6}$$

$$V_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}} \quad \text{eq 6.7}$$

and

$$V = V_{en} + V_{ee} \quad \text{eq 6.8}$$

The double sum in eq 6.7 is simply a sum over all different pairs of electrons; there are  $N(N-1)/2$  electron pairs.

As an example, let us write the expression in atomic units for the total Coulomb interaction energy in a neutral Li atom ( $Z=3$  and  $N=3$ ). The attractive electron-nucleus interaction energy is

$$V_{en} = -\frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} \quad \text{eq 6.9}$$

For the electron-electron repulsions, there are 3 electron pairs: 12, 13, and 23, and

$$V_{ee} = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \quad \text{eq 6.10}$$

so that

$$V = \left( -\frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} \right) + \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) \quad \text{eq 6.11}$$

### 6.1.2 Coulomb interaction energy for a molecule in atomic units

We consider a molecule with  $M$  nuclei and  $N$  electrons. The electrons are numbered as in atoms. We label the nuclei with the lowercase letters  $a, b, \dots$ , with  $Z_a$  denoting the atomic number of the  $a^{\text{th}}$  nucleus, and  $R_{ab}$  being the distance between nuclei  $a$  and  $b$ . The distance between the  $j^{\text{th}}$  electron and  $a^{\text{th}}$  nucleus is denoted by  $r_{ja}$ . We split the total interaction energy into 3 types:  $V_{en}$ ,  $V_{ee}$ , and the nucleus-nucleus repulsions,  $V_{nn}$ . One has

$$V_{en} = -\sum_a \sum_j \frac{Z_a}{r_{ja}} \quad \text{eq 6.12}$$

$$V_{ee} = \sum_i \sum_{j>i} \frac{1}{r_{ij}} \quad \text{eq 6.13}$$

$$V_{nn} = \sum_a \sum_{b>a} \frac{Z_a Z_b}{R_{ab}} \quad \text{eq 6.14}$$

and

$$V = V_{en} + V_{ee} + V_{nn} \quad \text{eq 6.15}$$

The double sum in eq 6.12 has  $M \times N$  terms to be added. The one in eq 6.13 is an equivalent notation to that in eq 6.7; i.e. a sum over all distinct electron pairs. Similarly, the double sum in eq 6.14 is a sum over all distinct nucleus pairs; there are  $M(M-1)/2$  pairs of nuclei.

Note that the zero point of the potential energy scale (where  $V=0$ ) corresponds to a spatial configuration of the charges such that all particles are separated from each other by an infinite distance. This is also the zero point of the total energy scale (where  $E=0$ ).<sup>2</sup>

**Exercise 6.1** Write explicit expressions in atomic units for  $V_{en}$ ,  $V_{ee}$ ,  $V_{nn}$ , and  $V$  for the  $H_2$  molecule.

### 6.1.3 Kinetic energy operator for an electron in atomic units

The operator for the kinetic energy in SI units for an electron moving in 3D is

$$\hat{T} = \frac{1}{2m_e} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) \quad \text{eq 6.16}$$

We denote the Cartesian variables with length units, of the electron, by  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$ , reserving the symbols  $x$ ,  $y$ , and  $z$  for dimensionless variables defined by  $\bar{x} = x a_0$ ,  $\bar{y} = y a_0$ , and  $\bar{z} = z a_0$ . We have  $\hat{p}_x^2/m_e = -\frac{\hbar^2}{m_e} \frac{\partial^2}{\partial \bar{x}^2} = -\frac{\hbar^2}{m_e a_0^2} \frac{\partial^2}{\partial x^2} = -\frac{\partial^2}{\partial x^2} \text{ hartree}$ , (see eq 6.5b), and similarly for the other terms in eq 6.16. Thus the expression for the kinetic energy operator of an electron in atomic units is

$$\hat{T} = -\frac{1}{2} \nabla^2 \quad \text{For one electron in a.u.} \quad \text{eq 6.17}$$

When there are  $N>1$  electrons, the operator for the total kinetic energy of the electrons is obtained by attaching integer labels to the expression above, and summing

$$\hat{T} = -\frac{1}{2} \sum_{j=1}^N \nabla_j^2 \quad \text{For } N>1 \text{ electrons in a.u.} \quad \text{eq 6.18}$$

This expression for the kinetic energy operator for electrons can be combined with the potential energy in eq 6.8 or eq 6.15 to write the explicit Hamiltonian operator in atomic units for  $N$  electrons in an atom or in a molecule, respectively. Note that this Hamiltonian does not include kinetic energy terms for the nuclei. It is called the “electronic Hamiltonian” of the atom or molecule under study.

<sup>2</sup> See beginning of Lecture Notes 3.

**Example 6.1** What is the explicit expression for the electronic Hamiltonian operator in Li atom?

*Answer:* There are  $N=3$  electrons in Li atom. The potential energy is given in eq 6.11. The electronic Hamiltonian operator is

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - 3\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right) + \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)$$

**Exercise 6.2** Write the explicit expression in atomic units for the electronic Hamiltonian operator of the single electron in the hydrogen molecule ion,  $H_2^+$ .

**Exercise 6.3** Write the explicit expression in atomic units for the electronic Hamiltonian operator of 2 electrons in the  $H_2$  molecule.

## 6.2 Allowed energy levels of the electron in H-atom

The electronic Hamiltonian in atomic units for the electron in H-atom ( $Z=1$ ) is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \quad \text{eq 6.19}$$

where  $r$  is the distance between the electron and the nucleus, in *bohrs*. The fact that the potential energy depends only on  $r$  suggests that it should be easier to solve the Schrödinger equation,

$$\hat{H}\psi = E\psi \quad \text{eq 6.20}$$

where  $E$  is in *hartrees*, using spherical polar variables ( $r, \theta, \phi$ ). The expression for the Laplacian operator in these variables is

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right) \quad \text{eq 6.21}$$

Comparison with eq 4.9 (in Lecture Notes 4) shows that the angle-dependent terms in the second parenthesis above is the  $\left(-\frac{1}{\hbar^2}\right)\hat{L}^2$  operator (dimensionless), so that

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2/\hbar^2}{r^2} \quad \text{eq 6.22}$$

Since the expression for  $\hat{L}^2$  contains only the  $\theta$  and  $\phi$  variables, it commutes with any expression involving only  $r$  (because the three variables are independent). Hence  $\hat{L}^2$  commutes with  $\hat{H}$  in eq 6.19. It follows that  $\hat{L}^2$  and  $\hat{H}$  have simultaneous eigenfunctions. Since we know that the eigenfunctions of  $\hat{L}^2$  are the spherical harmonics,  $Y_{lm}$ , the "orbitals"<sup>3</sup>  $\psi$  must have a product form

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) \quad \text{eq 6.23}$$

<sup>3</sup> See Sec. 3.3 in Lecture Notes 3.

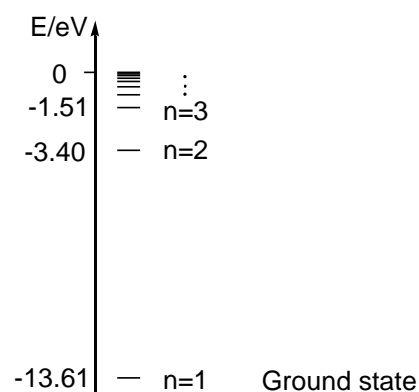
Thus the problem of solving eq 6.20 is reduced to that of determining the “radial” functions  $R(r)$ . In order to find them, one substitutes  $\psi$  of eq 6.23 into eq 6.20, and simplifies. You should verify that the resultant equation for  $R(r)$  is

$$-\frac{1}{2} \frac{d^2 R}{dr^2} - \frac{1}{r} \frac{dR}{dr} + \frac{l(l+1)}{2r^2} R - \frac{1}{r} R = ER \quad \text{eq 6.24}$$

The purpose up to this point has been to demonstrate how “commuting operators” simplify solution of the Schrödinger equation.<sup>4</sup> We will not go into the mathematical details of solving eq 6.24, and simply quote the results from the literature. It is found that “well-behaved”<sup>5</sup> solutions of eq 6.24 exist only for the following orbital energies (in *hartrees*)

$$E_n = -\frac{1}{2n^2}, \quad n = 1, 2, \dots \quad \text{eq 6.25}$$

The allowed energies (in eV) for a bound electron in the H-atom are depicted in Figure 6.1. The spacing between neighboring levels rapidly decreases as  $E$  increases, and approaches zero as  $n \rightarrow \infty$ . The zero point (where  $E=0$ ) of the energy scale corresponds to a situation where the electron is infinitely far away from the nucleus with zero kinetic energy; i.e. the “ionized” state in chemical terminology. According to eq 6.25, the ionization energy (IE) of H-atom in its ground state is 0.5 *hartree*=13.61 eV. This value is in excellent agreement with experimental observations.



**Figure 6.1** Allowed energy levels (orbital energies) of the electron in H-atom.

### 6.2.1 The radial functions $R(r)$

Eq 6.24 is an eigenvalue-eigenfunction equation for an operator that depends on the value of the angular momentum quantum number  $l$ . As seen in eq 6.25, the eigenvalues  $E_n$  are independent of  $l$ . Because the allowed energies are determined only by the  $n$  quantum number, the latter is called the “principal” quantum number. The eigenfunctions associated with a given energy level however, do depend on  $l$ , in addition to the  $n$  quantum number, so that they are labeled by both  $n$  and  $l$ :  $R_{nl}$ . It is found that  $l$  must be smaller than  $n$ ; i.e. for a given  $n$ , the functions  $R_{nl}$  exist only for  $l=0, 1, \dots, n-1$ .

<sup>4</sup> Eq 6.20 is a partial differential equation with 3 variables whereas eq 6.24 is an equation with only one independent variable.

<sup>5</sup> See Sec. 2.3 in Lecture Notes 2.

Since for a given  $l$ , there is a different spherical harmonic function  $Y_{lm}$  depending on the value of  $m$  in the range  $-l \leq m \leq l$ , the orbitals (eq 6.23) are labeled by 3 quantum numbers:  $n$ ,  $l$ , and  $m$

$$\psi_{nlm} = R(r)_{nl} Y_{lm}(\theta, \phi) \quad \text{Functional form of Atomic Orbitals} \quad \text{eq 6.26}$$

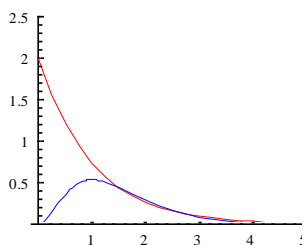
Atomic orbitals of this form also occur in approximate treatments of electronic states in many-electron atoms such as He, Li, etc, or their ions. The only difference in the latter is in the explicit expression for the radial function  $R$ ; its form depends on the atom or ion under study, especially on its atomic number  $Z$ . For the H-atom where  $Z=1$ , explicit expressions are given in Table 6.1 for the first few radial functions.

For a given  $n$  (which means a given orbital energy  $E_n$ ), let us count how many different orbitals are available according to eq 6.26. We have  $l=0,1,\dots,n-1$ , and for each  $l$ ,  $m=-l,-(l-1),\dots,0,1,2,\dots,l$ . One finds that the total number of functions is  $n^2$ . Thus the degeneracy of orbital energy  $E_n$  in the H-atom is  $g_n=n^2$ .

**Table 6.1** Radial functions in the orbitals (eq 6.26) of the electron in H-atom for  $n=1, 2$ , and 3.

$n$	$l$	$R_{nl}$	$N$
1	0	$N e^{-r}$	2
2	0	$N (2-r) e^{-r/2}$	$1/(2\sqrt{2})$
	1	$N r e^{-r/2}$	$1/(2\sqrt{6})$
3	0	$N (27-18r+2r^2) e^{-r/3}$	$2/(81\sqrt{3})$
	1	$N r(6-r) e^{-r/3}$	$4/(81\sqrt{6})$
	2	$N r^2 e^{-r/3}$	$4/(81\sqrt{30})$

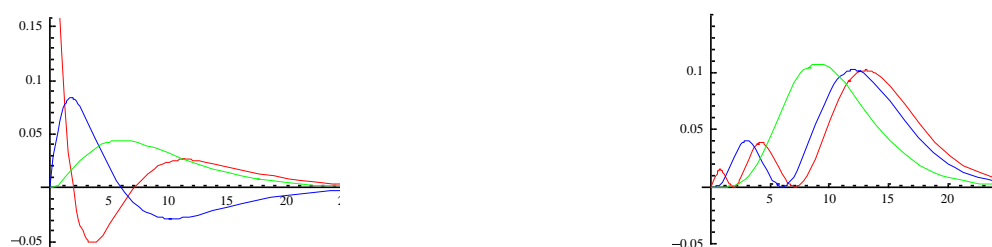
The general form of  $R_{nl}$  is:  $e^{-r/n}$  x polynomial of degree  $(n-1)$  in  $r$ . All are real functions. Because of the exponential factor, all become zero at  $r=\infty$ . The functions with  $l \neq 0$  are also zero at  $r=0$ . Aside from the origin and infinity, there are  $n-l-1$  zeroes (called "nodes") in  $R_{nl}(r)$ . These properties are useful in preparing graphs of these functions. Figures 6.2-4 show graphs of the radial functions given in Table 6.1.



**Figure 6.2** Graphs of  $R_{1s}$  (red) and  $r^2 R_{1s}^2$  (blue) in the 1s orbital.



**Figure 6.3** Left: Graphs of  $R_{2s}$  (red) and  $R_{2p}$  (blue). Right: Graphs of  $r^2 R_{2s}^2$  (red) and  $r^2 R_{2p}^2$  (blue).



**Figure 6.4** Left: Graphs of  $R_{3s}$  (red),  $R_{3p}$  (blue), and  $R_{3d}$  (green). Right: Graphs of  $r^2 R_{3s}^2$  (red),  $r^2 R_{3p}^2$  (blue), and  $r^2 R_{3d}^2$  (green).

The radial functions  $R_{nl}$  and the orbitals in eq 6.26 are labeled by integer subscripts. In an alternative notation of widespread usage, the value of  $l$  is indicated by a code letter:

letter	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>k</i>	...
<i>l</i>	0	1	2	3	4	5	6	7	...

Starting with *f*, the letters go in alphabetical order except that *j* is omitted. For example, the radial functions  $R_{10}$  and  $R_{21}$  are denoted by  $R_{1s}$  and  $R_{2p}$ , respectively. Similarly, the orbitals for  $l=0$  are shown by  $\psi_{1s}$ ,  $\psi_{2s}$ , etc., or more simply as  $1s$ ,  $2s$ , ... For orbitals with  $l > 0$ , there are several values  $m$ , and  $m$  is attached to the letter code as a subscript; e.g.  $\psi_{2p_{-1}}$ ,  $\psi_{2p_0}$ ,  $\psi_{2p_1}$  for the  $2p$  orbitals, or more simply as  $2p_{-1}$ ,  $2p_0$ , and  $2p_1$ .

**Normalization of the radial functions.** The normalization condition for the orbitals in eq 6.26 is (omitting the subscripts for simplicity)

$$I = \int \psi^* \psi d\tau = \int R^2 Y^* Y d\tau = 1 \quad \text{eq 6.27}$$

since  $R(r)$  is a real function whereas the spherical harmonics are complex except when  $m=0$ . The volume element is:

$$d\tau = r^2 \sin(\theta) dr d\theta d\phi = d\tau_1 d\tau_2 \quad \text{where } d\tau_1 = r^2 dr \text{ and } d\tau_2 = \sin(\theta) d\theta d\phi \quad \text{eq 6.28}$$

The triple integral in eq 6.27 is factorized:  $I = I_1 I_2$  where

$$I_1 = \int R^2 d\tau_1 = \int_0^\infty R(r)^2 r^2 dr \quad \text{and} \quad I_2 = \int Y^* Y d\tau_2 \quad \text{eq 6.29}$$

The double integral  $I_2$  has the value 1 because the spherical harmonics are normalized.<sup>6</sup> The orbitals will be normalized if  $I_1=1$ . Therefore, the normalization condition for the radial functions is

<sup>6</sup> See eq 4.19 in Lecture Notes 4.

$$\int_0^{\infty} R(r)^2 r^2 dr = 1 \quad \text{eq 6.30}$$

Values of N in Table 6.1 are obtained by this condition.

**The Radial Distribution Function.** The probability of finding the electron in a tiny volume  $d\tau$  in 3D is

$$\psi^* \psi d\tau = R^2 Y^* Y d\tau_1 d\tau_2 \quad \text{eq 6.31}$$

We now ask: What is the probability of finding the electron at a distance from the nucleus between  $r$  and  $r+dr$  (i.e. in  $d\tau_1$ ) with no restrictions on the angle variables  $\theta$  and  $\phi$ ? We must add up the probabilities in eq 6.31 for “all space” for  $\theta$  and  $\phi$ , keeping  $r$  and  $dr$  fixed. This amounts to integrating the expression in eq 6.31 over the angles

$$R^2 d\tau_1 \int Y^* Y d\tau_2 = R(r)^2 r^2 dr \quad \text{eq 6.32}$$

The function  $R(r)^2 r^2$ , which determines the probability of finding the electron at a distance  $r$  from the nucleus, is called the radial distribution function,  $P(r)$

$$P(r) = R(r)^2 r^2 \quad \text{The radial distribution function} \quad \text{eq 6.33}$$

Note that the probability of finding the electron in “all space for  $r$ ” is 1, due to the normalization condition eq 6.30. This is of course necessary, because the probability of finding the electron in the full 3D space must be 1.

Figures 6.2-4 include graphs of  $P(r)$  for the  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  orbitals. The “most probable distance”,  $r_{mp}$ , of the electron from the nucleus is the distance at which  $P(r)$  has the highest value. When there is more than one maximum, Figures 6.2-4 show that it occurs at the outermost maximum of  $P(r)$ . Note that for a given  $n$ ,  $r_{mp}$  decreases with increasing  $l$ . For example, a  $3d$  electron in the H-atom is most probably nearer to the nucleus than a  $3p$  electron, which in turn is nearer than a  $3s$  electron (Figure 6.4, right side).

The mathematical condition for finding a maximum (or a minimum) of  $P(r)$  is

$$\frac{dP}{dr} = 0 \quad \text{eq 6.34}$$

Using eq 6.33, this equation may be expressed in terms of  $R(r)$ . After simplifications, one has

$$R + rR' = 0 \quad \text{eq 6.35}$$

One picks  $r^*$  among the solutions of this equation that gives the largest value for  $P(r^*)$  as  $r_{mp}$ .

**Exercise 6.4** Find the most probable distance of the electron from the nucleus for an electron in a)  $3p$  and b)  $3d$  orbital. Compare your results with Figure 6.4.

**Exercise 6.5** Find the average distance of the electron from the nucleus for an electron in a)  $3p$  and b)  $3d$  orbital. *Answer:  $25/2$ ,  $21/2$  (in bohrs).*



## 6.2.2 Dependence of Atomic Orbitals on the angular variables

As pointed out in the “2 df rotor” problem in Lecture Notes 4, the spherical harmonics in eq 6.26 are complex functions for  $m \neq 0$ . They have the form (eq 4.17)

$$Y_{lm}(\theta, \phi) = T_{l|m|}(\theta)\Phi_m(\phi) \quad \text{eq 6.36}$$

The  $\theta$ -dependent factors are real functions. Table 6.2 presents first few of them for  $l=0, 1$ , and 2. The  $\phi$ -dependent factor is

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad \text{eq 6.37a}$$

normalized such that

$$\int_0^{2\pi} \Phi_m^* \Phi_m d\phi = 1 \quad \text{eq 6.37b}$$

**Table 6.2**

$l$	$m$	$T_{lm}(\theta)$
0	0	$\frac{1}{\sqrt{2}}$
1	0	$\frac{1}{2}\sqrt{6} \cos \theta$
	1	$\frac{1}{2}\sqrt{3} \sin \theta$
2	0	$\frac{1}{4}\sqrt{10} (3 \cos^2 \theta - 1)$
	1	$\frac{1}{2}\sqrt{15} \sin \theta \cos \theta$
	2	$\frac{1}{4}\sqrt{15} \sin^2 \theta$

For a given  $l$ , there are  $2l+1$  values of  $m$  in the range  $-l \leq m \leq l$ . For the purposes of this section we list the  $m$  values in the form: 0, (1,-1), (2,-2),..., ( $l,-l$ ). The  $\theta$ -dependent factor in eq 6.36 is the same expression for both  $m$  and  $-m$ , when  $m \neq 0$ , the only difference being in the  $\phi$ -dependent factor,  $\Phi_m$ . For  $m=0$ ,  $\Phi_0(\phi) = \frac{1}{\sqrt{2\pi}}$  is a real constant, and hence  $Y_{l0} = \frac{1}{\sqrt{2\pi}} T_{l0}(\theta)$  is a real function for all  $l=0, 1, 2, \dots$ . These real functions with  $m=0$ , for  $l=0, 1$ , and 2 are commonly designated by the symbols  $s$ ,  $p_z$ , and  $d_{z^2}$ , respectively, in chemical applications. For  $m \neq 0$ , the pair of complex functions  $e^{im\phi}$  and  $e^{-im\phi}$  are related to two real functions by

$$e^{im\phi} = \cos(m\phi) + i \sin(m\phi) \quad \text{eq 6.38a}$$

$$e^{-im\phi} = \cos(m\phi) - i \sin(m\phi) \quad \text{eq 6.38b}$$

Here we have 4 functions, but there are also 2 relations connecting them (note that the argument  $m\phi$  is the same in all 4 functions). Therefore, the number of independent functions is  $4-2=2$ . Any 2 out of 4 may be chosen as the independent functions. The spherical harmonics of eq 6.36 employ the complex exponentials, but we can also take the two real functions  $\cos(m\phi)$  and  $\sin(m\phi)$  as the independent functions. These two functions when normalized as in eq 6.37b are

$$C_m(\phi) = \frac{1}{\sqrt{\pi}} \cos(m\phi) \quad \text{eq 6.39a}$$

$$S_m(\phi) = \frac{1}{\sqrt{\pi}} \sin(m\phi) \quad \text{eq 6.39b}$$

For  $m>0$ , in place of the pair of complex functions  $(Y_{lm}, Y_{l,-m})$  we may use the pair of real functions:

$$T_{lm}(\theta)C_m(\phi), \quad \text{and} \quad \text{eq 6.40a}$$

$$T_{lm}(\theta)S_m(\phi), \quad m=1,2,\dots, l \quad \text{eq 6.40b}$$

Note that for a given  $l$ , the total number of real functions is  $2l + 1$ :  $2l$  functions in eqs 6.40a,b plus  $Y_{l0}$ . For  $l=1$ , the complex spherical harmonics are designated by  $p_1, p_0$ , and  $p_{-1}$  while the corresponding real functions are denoted by  $p_x, p_y$ , and  $p_z = p_0$ . Similarly the five  $l=2$  functions are designated by the letter  $d$  with the  $m$  value attached as a subscript in the case of complex functions, and Cartesian symbols for the real functions. The real spherical harmonics are given in Table 6.3 for  $l=0, 1$ , and  $2$ .

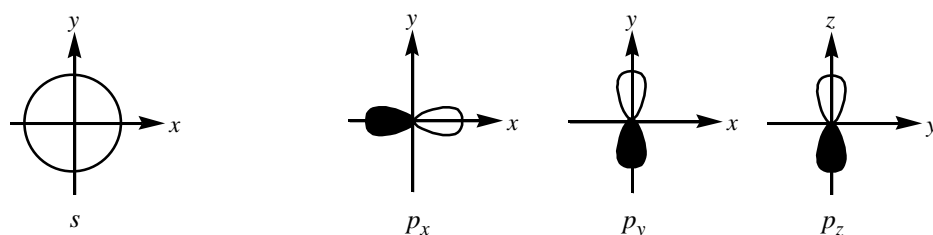
**Table 6.3** The normalized real spherical harmonics

$l$	$m$	Symbol	
0	$m=0$	$s$	$\frac{1}{\sqrt{4\pi}}$
1	$m=0$	$p_z$	$\sqrt{\frac{3}{4\pi}} \cos \theta$
	$m=1$	$p_x$	$\sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi$
	$m=1$	$p_y$	$\sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$
2	$m=0$	$d_{z^2}$	$\sqrt{\frac{10}{32\pi}} (3 \cos^2 \theta - 1)$
	$m=1$	$d_{xz}$	$\sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi$
	$m=1$	$d_{yz}$	$\sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi$
	$m=2$	$d_{x^2-y^2}$	$\sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$
	$m=2$	$d_{xy}$	$\sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi$

Real atomic orbitals (AO) are obtained by multiplying the angular functions in eq 6.40a,b with the radial function  $R_{nl}$ .<sup>7, 8</sup> The directional properties of AOs in 3D are contained in the angular parts. Magnitude of electric “charge density” in units of  $e$  (i.e. a.u. of charge) contributed by an electron in a normalized orbital  $\psi$  is  $\psi^2$  for a real orbital. The dependence of the electronic charge density on the angles is determined by the squares of the angular parts in the real AOs. Figures 6.5 and 6.6 depict 2D polar graphs that display how the charge density changes with direction for an electron in  $s$ ,  $p$ , and  $d$  AOs.

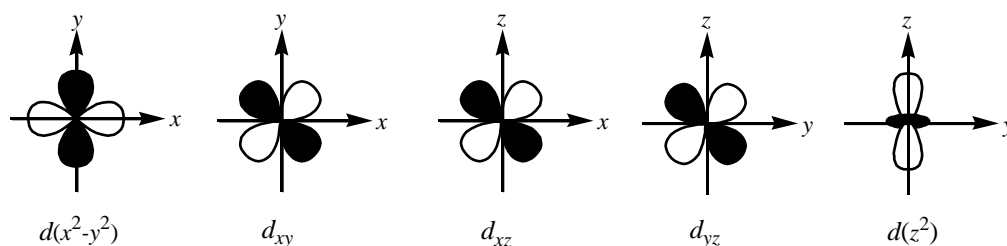
<sup>7</sup> Note that a radial function with a given  $l$  must be combined with angular functions of the same  $l$ .

<sup>8</sup> The real AOs are not eigenfunctions of the  $\hat{L}_z$  operator except for  $m=0$ . This fact does not present any problems in physical interpretations since the orbital energies are independent of  $m$ .



**Figure 6.5** Polar graphs of squares of  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  functions. Signs of the angular functions are indicated by shading.

The charge density of an  $s$  orbital is the same along all lines originating from the nucleus; i.e. it is independent of direction. The charge densities of the  $p$  orbitals are concentrated along the Cartesian directions  $x$ ,  $y$ , and  $z$ . The densities of four of the  $d$  orbitals are equally prominent along two orthogonal directions while that of  $d_{z^2}$  is mainly concentrated along the  $z$  direction, similar to the  $p_z$  orbital. Note that the number of nodal surfaces of the angular functions is equal to  $l$ . These nodal surfaces pass through the origin.<sup>9</sup> Thus the angular part of  $s$  orbitals ( $l=0$ ) has no nodal plane of this type, that of  $p$  orbitals ( $l=1$ ) has one, and  $d$  orbitals ( $l=2$ ) have two nodal surfaces.



**Figure 6.6** Polar graphs of squares of  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ , and  $d_{z^2}$  functions. Signs of the angular functions are indicated by shading.

**Exercise 6.6** A polar graph uses plane polar coordinates in plotting a function  $f(\phi)$ . The variable  $\phi$  is the angle from the positive  $x$ -axis, and  $|f(\phi)|$  is the distance from the origin to the point on the graph.

Consider the angular function  $p_x = N \sin \theta \cos \phi$ . On the  $xy$ -plane,  $\theta = \pi/2$ . Since we are interested in directional properties only, the factor  $N$  can be dropped and we may simply take  $p_x = \cos \phi$ . a) Sketch the polar graph of  $p_x$ . Indicate the signs of  $p_x$  in your graph. b) Sketch the polar graph of  $p_x^2$  and compare it with the one in Figure 6.5.

### 6.3 Energy levels and radial functions in hydrogenlike atoms

An atom of atomic number  $Z$  with only one electron such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ , etc. is called a hydrogenlike atom. The potential energy is  $V=-Z/r$ , and the Hamiltonian is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad \text{eq 6.41}$$

<sup>9</sup> The full orbitals also have another type of nodal surfaces due to the zeroes of  $R_{nl}$ , which do not pass through the origin. E.g. the  $2s$  orbital have a spherical nodal surface.

This Hamiltonian is related to that of the hydrogen atom with  $Z=1$  by a simple change of variable. Setting  $r=r'/Z$ , eq 6.41 may be written as

$$\hat{H} = Z^2 \left( -\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right) \quad \text{eq 6.42}$$

where the Laplacian operator with a prime is in terms of  $r'$ . It follows immediately that the eigenvalues of  $\hat{H}$  are

$$E_n = -\frac{Z^2}{2n^2}, \quad n = 1, 2, \dots \quad \text{eq 6.43}$$

The orbitals in the hydrogenlike atom has the same form as in eq 6.26. The radial functions  $R_{nl}$  are obtained from the expressions for the H-atom (Table 6.1) by replacing  $r$  with  $Zr$ , and multiplying the functions by the factor  $Z^{3/2}$  (needed for the correct normalization of hydrogenlike orbitals).

**Exercise 6.7** Consider a system of two electrons with the Hamiltonian

$$\hat{H} = \hat{h}(1) + \hat{h}(2)$$

where

$$\hat{h}(j) = -\frac{1}{2} \nabla_j^2 - \frac{2}{r_j}, \quad j = 1, 2.$$

- What are the allowed energy levels of electron 1? What are those of electron 2?
- Does  $\hat{h}(1)$  commute with  $\hat{h}(2)$ ? According to the expression for  $\hat{H}$  above, are the two electrons interacting with each other? Are they independent electrons or not?
- Write a formula that gives the allowed values for the total energies in this system.
- What is the energy of the ground state of this system? What is the energy of the first excited state of the system?
- What is the expression for the wavefunction for the ground state of the system?