

## Lecture notes 5

# 5. Spherically symmetric potentials

Chapter 5 of FY1006/TFY4215 — **Spherically symmetric potentials** — is covered by sections 5.1 and 5.4–5.7 in Hemmer's bok, together with the present Lecture notes 5. References will be given also to the relevant sections in B&J. In the courses FY2045/TFY4250, this chapter is part of the background, that you should study on your own.

## 5.1 Isotropic harmonic oscillator

(Hemmer 5.1, B&J 7.1)

The three-dimensional harmonic oscillator is discussed in section 5.1 in Hemmer and in 7.1 in B&J. Here we want to stress some important points.

**Point no 1: The energy eigenfunctions can be written on product form**

Even for an **anisotropic** oscillator, with *different* spring constants for the three Cartesian directions,

$$V = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2 \equiv \frac{1}{2}m\omega_x^2 x^2 + \frac{1}{2}m\omega_y^2 y^2 + \frac{1}{2}m\omega_z^2 z^2, \quad (\text{T5.1})$$

the Hamiltonian can be written as a sum of three independent (commuting) terms:

$$\widehat{H} = \widehat{H}^{(x)} + \widehat{H}^{(y)} + \widehat{H}^{(z)}, \quad \text{with} \quad \widehat{H}^{(x)} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_x^2 x^2, \quad \text{etc} \quad (\text{T5.2})$$

If we denote the well-know eigenfunctions of  $\widehat{H}^{(x)}$  by  $\psi_{n_x}(x)$ :

$$\widehat{H}^{(x)} \psi_{n_x}(x) = \hbar\omega_x \left(n_x + \frac{1}{2}\right) \psi_{n_x}(x) \equiv E^{(x)} \psi_{n_x}(x), \quad n_x = 0, 1, 2, \dots,$$

it is easily seen that the product states

$$\psi_{n_x n_y n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z) \quad (\text{T5.3})$$

are energy eigenstates (of  $\widehat{H}$ ) with the energy eigenvalues

$$E_{n_x n_y n_z} = E^{(x)} + E^{(y)} + E^{(z)} = \hbar\omega_x \left(n_x + \frac{1}{2}\right) + \hbar\omega_y \left(n_y + \frac{1}{2}\right) + \hbar\omega_z \left(n_z + \frac{1}{2}\right). \quad (\text{T5.4})$$

These are at the same time eigenfunctions of  $\widehat{H}^{(x)}$  etc, that is, **simultaneous eigenfunctions** of the operator set  $\widehat{H}, \widehat{H}^{(x)}, \widehat{H}^{(y)}, \widehat{H}^{(z)}$ , which all commute.

**Exercise:** Another example of such product states is encountered for the three-dimensional box, for which  $\widehat{H}^{(x)} = -(\hbar^2/2m)\partial^2/\partial x^2$ ,  $\widehat{H}^{(y)}$ ,  $\widehat{H}^{(z)}$  and  $\widehat{H} = \widehat{H}^{(x)} + \widehat{H}^{(y)} + \widehat{H}^{(z)}$  all commute. Here too we can construct eigenstates in the form of product states:

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{2^3}{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}.$$

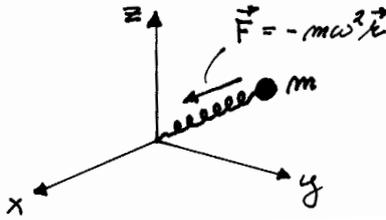
Find the energy eigenvalues expressed in terms of the independent quantum numbers  $n_x$ ,  $n_y$  and  $n_z$ .

In the example with the three-dimensional oscillator, we can call the  $x$ -,  $y$ - and  $z$ -directions the “quantization directions”. Since the three quantum numbers  $n_x$ ,  $n_y$  and  $n_z$  are independent, we also say that the motions in the  $x$ -  $y$  and  $z$ -directions represent three independent degrees of freedom.

If we now consider the special case where the three spring constants are equal,  $k_x = k_y = k_z = k$ , there emerges a *symmetry* in this system; the potential becomes **spherically symmetric** and the force becomes a **central force**:

$$V = \frac{1}{2}kx^2 + \frac{1}{2}ky^2 + \frac{1}{2}kz^2 = \frac{1}{2}kr^2 \equiv \frac{1}{2}m\omega^2 r^2, \quad \implies \quad (\text{T5.5})$$

$$\mathbf{F}(\mathbf{r}) = -\nabla V(r) = -m\omega^2 \mathbf{r}. \quad (\text{T5.6})$$



**Point no 2: The spherical symmetry leads to degenerate energy levels**

The energy now depends only on the sum of the three quantum numbers:

$$E = \hbar\omega(n_x + n_y + n_z + 3/2) \equiv \hbar\omega(N + \frac{3}{2}) \equiv E_N; \quad (N = 0, 1, 2, \dots).$$

As shown in the book, the number of states for level number  $N$  [the (degree of) **degeneracy**] is

$$g_N = \frac{1}{2}(N+1)(N+2).$$

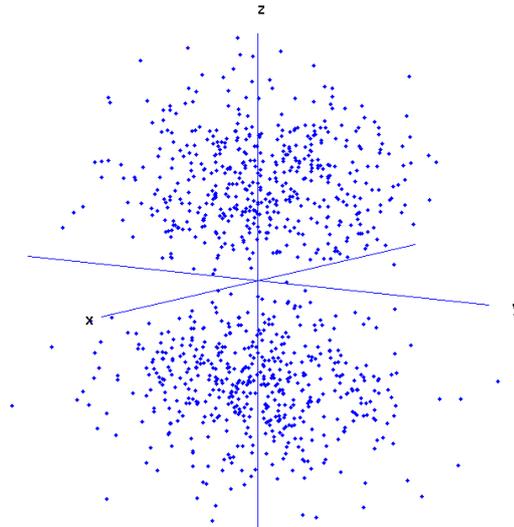
The ground state is (as always) non-degenerate; for the lowest energy ( $N = 0$ ,  $E = \frac{3}{2}\hbar\omega$ ) we have only one state,

$$\psi_{000}(x, y, z) \equiv (000) = \psi_0(x)\psi_0(y)\psi_0(z) = C_0^3 e^{-m\omega r^2/2\hbar}. \quad (\text{T5.7})$$

For the first excited level ( $N = 1$ ,  $E = \frac{5}{2}\hbar\omega$ ) we have three states,

$$\begin{aligned} \psi_{100} &\equiv (100) = \psi_1(x)\psi_0(y)\psi_0(z) = C_0^2 C_1 x e^{-m\omega r^2/2\hbar}, \\ \psi_{010} &\equiv (010) = \psi_0(x)\psi_1(y)\psi_0(z) = C_0^2 C_1 y e^{-m\omega r^2/2\hbar}, \\ \psi_{001} &\equiv (001) = \psi_0(x)\psi_0(y)\psi_1(z) = C_0^2 C_1 z e^{-m\omega r^2/2\hbar}. \end{aligned} \quad (\text{T5.8})$$

While the ground state  $\psi_{000}$  is spherically symmetric, we see that these three excited states are *not*. As an example, the state  $\psi_{001} \equiv (001)$  is rotationally symmetric with respect to the  $z$ -axis and antisymmetric with respect to the  $xy$ -plane. The figure below illustrates the simulated result of a series of 1000 measurements of the position of the particle when it is in this state. Here, you will notice that the factor  $z$  makes the  $xy$ -plane a nodal plane (where the probability density is equal to zero).



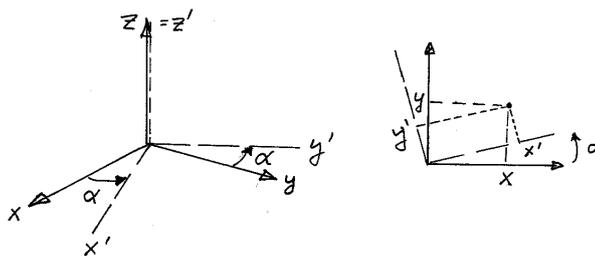
Similarly, the state (100) has rotational symmetry with respect to the  $x$ -axis and has the  $yz$ -plane as a nodal plane, and so on.

**A small exercise:** Suppose that the box mentioned above is cubical, with  $L_x = L_y = L_z = L$ . Find the degeneracy of the three lowest energy levels.

### Point no 3

is that when a degenerate level has several eigenfunctions with the same eigenvalue (here  $E = \frac{5}{2}\hbar\omega$ ), then these eigenfunctions are **not unique**. This is because we are free to use linear combinations of these eigenfunctions. Such linear combinations are also eigenfunctions with the same energy. They are therefore equally relevant. For the oscillator we can illustrate this point in several ways:

(i) Since the potential is spherically symmetric, we can just as well use another set of coordinate axes than the ones above, e.g.  $x', y', z' (= z)$ :



By repeating the above process, with  $x'$ ,  $y'$  and  $z'$  as quantization directions, we then find for  $N = 1$  the following three simultaneous eigenstates of the operators  $\widehat{H}$ ,  $\widehat{H}^{(x')}$ ,  $\widehat{H}^{(y')}$ ,  $\widehat{H}^{(z')}$ :

$$\begin{aligned} (100)' &\equiv \psi_1(x')\psi_0(y')\psi_0(z') = C_0^2 C_1 x' e^{-m\omega r^2/2\hbar}, \\ (010)' &\equiv \psi_0(x')\psi_1(y')\psi_0(z') = C_0^2 C_1 y' e^{-m\omega r^2/2\hbar}, \\ (001)' &\equiv \psi_0(x')\psi_0(y')\psi_1(z') = C_0^2 C_1 z' e^{-m\omega r^2/2\hbar}. \end{aligned}$$

Here there is a lot of “moral” to be gained:

- With  $V = V(r)$  there is nothing particular about the original axis system  $x, y, z$ . The new choice, and the resulting eigenfunctions are just as relevant.
- The new eigenfunctions are linear combinations of the old ones. Thus with the concrete choice of  $x', y', z'$  above, which corresponds to

$$\begin{aligned} x' &= x \cos \alpha + y \sin \alpha, \\ y' &= x(-\sin \alpha) + y \cos \alpha, \\ z' &= z, \end{aligned}$$

we have for example

$$\begin{aligned} (100)' &= (100) \cos \alpha + (010) \sin \alpha, \\ (010)' &= (100)(-\sin \alpha) + (010) \cos \alpha \\ (001)' &= (001). \end{aligned}$$

Here, the state  $(100)'$  has the same form seen from the  $x'$ -axis as  $(100)$  seen from the  $x$ -axis.

- The “change of basis” does not alter the degeneracy (which here is equal to 3).
- The eigenfunctions above are automatically orthogonal [cf (T2.34)]. (The orthogonality is in general important; cf the discussion of orbitals below.)

(ii) Another way to obtain a set of orthogonal eigenfunctions for a symmetric potential is to look for simultaneous eigenfunctions of  $\widehat{H}$ ,  $\widehat{\mathbf{L}}^2$  and one of the components of  $\widehat{\mathbf{L}}$ , e.g.  $\widehat{L}_z$ . Such eigenfunctions exist because the three operators mutually commute, as we shall see. Cf section 2.3.c, where we found that  $\widehat{\mathbf{L}}^2$  and  $\widehat{L}_z$  commute. Since these two operators contain derivatives only with respect to the angles  $\theta$  and  $\phi$ , it follows that they also commute with the Hamiltonian, when the potential is spherically symmetric.

The three-dimensional isotropic oscillator is very special in that the potential is both spherically symmetric and can be separated in terms of the independent (Cartesian) contributions  $\frac{1}{2}m\omega^2 x^2$  etc. In a short while we shall attack the hydrogen atom (the Coulomb

problem). Then again we have a spherically symmetric potential. However, this potential *can not* be separated into “Cartesian” terms. So in that case we are forced to look for simultaneous eigenfunctions of the operators  $\widehat{H}$ ,  $\widehat{\mathbf{L}}^2$  and one of the components of  $\widehat{\mathbf{L}}$ , e.g.  $\widehat{L}_z$ .

This must be **point no 4**: The angular momentum is an important physical observable for particles moving in a spherically symmetric potential, like that of the hydrogen atom. We shall therefore proceed to study angular momentum in the next section.

## 5.2 Angular momentum and spherically symmetric potentials

(Hemmer 5.4, B&J 6.1 and 6.3)

### 5.2.a Angular-momentum operators

All information about a state sits in the wave function, combined with the operators for energy, momentum etc. The momentum operator  $\widehat{\mathbf{p}} = (\hbar/i)\nabla$  essentially asks for the gradient of  $\psi$ , that is, how fast and in which direction  $\psi$  changes, the operator  $\widehat{K} = -(\hbar^2/2m)\nabla^2$  for the kinetic energy checks  $\text{div grad } \psi = \nabla^2\psi$ , etc.

Similarly, the orbital angular-momentum operator  $\widehat{\mathbf{L}} = \mathbf{r} \times \widehat{\mathbf{p}} = \mathbf{r} \times (\hbar/i)\nabla$  asks about the variation of  $\psi$  perpendicularly to  $\mathbf{r}$ . Thus it is the *variation in the angular direction* which determines the angular momentum. Then we understand immediately that the ground state of the hydrogen atom,  $\psi = (\pi a_0^3)^{-1/2} e^{-r/a_0}$ , is a state with zero angular momentum. This is because here the gradient points in the radial direction, so that

$$\widehat{\mathbf{L}}\psi = \mathbf{r} \times \frac{\hbar}{i}\nabla\psi = 0.$$

The “moral” is that

A spherically symmetric wave function  $\psi(r)$  corresponds to a state with zero angular momentum.

(T5.9)

Another example is the ground state (T5.7) of the isotropic oscillator,  $\psi_{000} \equiv (000) = C_0^3 e^{-m\omega r^2/2\hbar}$ .

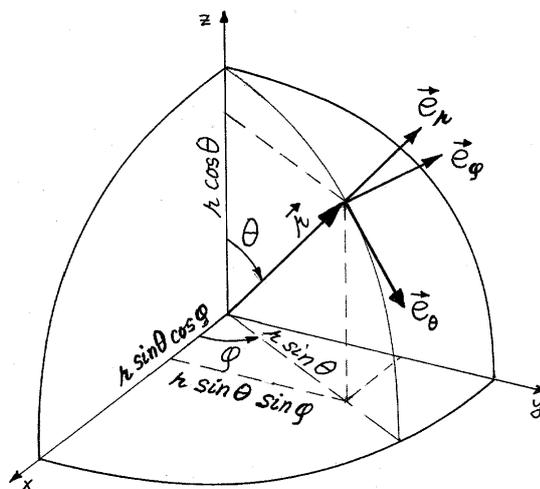
This conclusion ( $\widehat{\mathbf{L}}\psi(r) = 0$ ) also follows if we express the operators in spherical coordinates. As shown in section 5.2.g below, the gradient operator in spherical coordinates is

$$\nabla = \hat{\mathbf{e}}_r \frac{\partial}{\partial r} + \hat{\mathbf{e}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}. \quad (\text{T5.10})$$

It then follows that  $\widehat{\mathbf{L}}$  contains derivatives with respect to the angles:

$$\begin{aligned} \widehat{\mathbf{L}} &= \mathbf{r} \times \frac{\hbar}{i}\nabla \\ &= \frac{\hbar}{i} \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right), \end{aligned} \quad (\text{T5.11})$$

since  $\hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_r = 0$ ,  $\hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_\theta = \hat{\mathbf{e}}_\phi$ ,  $\hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_\phi = -\hat{\mathbf{e}}_\theta$ .



The same holds for the Cartesian components, even if it isn't obvious in the expressions

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x, \quad \text{etc.}$$

Thus, expressed in spherical coordinates the Cartesian components are

$$\begin{aligned} \hat{L}_x &= \frac{\hbar}{i} \left( -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right), \\ \hat{L}_y &= \frac{\hbar}{i} \left( \cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right), \\ \hat{L}_z &= \frac{\hbar}{i} \frac{\partial}{\partial\phi}. \end{aligned} \tag{T5.12}$$

And then it is perhaps not surprising that the same holds also for the square of the angular-momentum operator,

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right). \tag{T5.13}$$

Here we note that the spherical coordinates result in a particularly simple *form* for  $\hat{L}_z$ .<sup>1</sup>

## 5.2.b Compatible observables in spherically symmetric potentials

Spherically symmetric potentials  $V(r)$  play a central role in atomic physics, and for a particle moving in such a central potential the angular momentum is an important observable,

<sup>1</sup>In the figure above, the angle  $\theta$  between  $\mathbf{r}$  and the  $z$ -axis is the so-called **polar angle**. The angle  $\phi$  between the  $\mathbf{r}\hat{z}$ -plane and the  $xz$ -plane is the so-called **azimuthal angle**. In mathematics, you have possibly used a different notation.

together with the energy. For such systems the angular momentum and the energy are compatible observables — they can have sharp values simultaneously, because the angular-momentum operators commute with the Hamiltonian for a spherically symmetric potential,

$$\widehat{H} = \widehat{K} + V(r) = -\frac{\hbar^2}{2m} \nabla^2 + V(r).$$

By comparing the last part of the Laplace operator in spherical coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \quad (\text{T5.14})$$

with the above expression for  $\widehat{\mathbf{L}}^2$  we see that the Laplace operator can be written as

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\widehat{\mathbf{L}}^2}{\hbar^2 r^2}. \quad (\text{T5.15})$$

Using this expression we find a practical expression for the Hamiltonian for a particle moving in a spherically symmetric potential:

$$\widehat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} + V(r) \equiv \widehat{K}_r + \widehat{K}_L + V(r). \quad (\text{T5.16})$$

Here we note that the angular part of  $\widehat{K}$  is  $\widehat{K}_L = \widehat{\mathbf{L}}^2/(2mr^2)$ . Since  $\widehat{\mathbf{L}}^2$  contains only derivatives with respect to angles, we realize that the above Hamiltonian commutes with  $\widehat{\mathbf{L}}^2$ :

$$[\widehat{H}, \widehat{\mathbf{L}}^2] = 0 \quad (V = V(r)).$$

The “moral” is that the *size*  $|\mathbf{L}| = \sqrt{L_x^2 + L_y^2 + L_z^2}$  of the angular momentum can have a sharp value together with the energy.

But what about the *direction* of  $\mathbf{L}$ ? Well, here we must remember (cf 2.3.c in Lecture notes 2) that the operator components  $\widehat{L}_x$ ,  $\widehat{L}_y$  and  $\widehat{L}_z$  *do not commute*, but satisfy the so-called **angular-momentum algebra**

$$\begin{aligned} [\widehat{L}_x, \widehat{L}_y] &= i\hbar \widehat{L}_z, \\ [\widehat{L}_y, \widehat{L}_z] &= i\hbar \widehat{L}_x, \\ [\widehat{L}_z, \widehat{L}_x] &= i\hbar \widehat{L}_y. \end{aligned} \quad (\text{T5.17})$$

Then, according to the rules in section 4.1, there does not exist simultaneous eigenfunctions of  $\widehat{L}_x$ ,  $\widehat{L}_y$  and  $\widehat{L}_z$ , and hence of  $\widehat{\mathbf{L}}$ . Thus the observables  $L_x$ ,  $L_y$  and  $L_z$  can not be sharp simultaneously; they are **not compatible**. The only exception to this rule is when the angular momentum is zero, as we saw above. Apart from this exception, we can state that the angular-momentum operator  $\widehat{\mathbf{L}} = \mathbf{r} \times \widehat{\mathbf{p}}$  (contrary to the momentum operator  $\widehat{\mathbf{p}}$ ) has no eigenfunctions. Thus it is impossible for the particle to have a well-defined angular-momentum vector  $\mathbf{L}$ , with a sharply defined direction. On the other hand, we have seen in

Lecture notes 2 that  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  all commute with the *square* of the angular-momentum operator,  $\hat{\mathbf{L}}^2 = (\mathbf{r} \times \hat{\mathbf{p}}) \cdot (\mathbf{r} \times \hat{\mathbf{p}}) = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ :

$$\boxed{[\hat{\mathbf{L}}^2, \hat{L}_i] = 0,} \quad i = x, y, z. \quad (\text{T5.18})$$

Therefore it is possible to find simultaneous eigenfunctions of  $\hat{\mathbf{L}}^2$  and one of the components of  $\hat{\mathbf{L}}$  (e.g.  $\hat{L}_x$ , or  $\hat{L}_y$ , or  $\hat{L}_z$ , or for that matter any component  $\hat{\mathbf{n}} \cdot \hat{\mathbf{L}}$ ). It is customary to choose to work with simultaneous eigenfunctions of  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$ , because  $\hat{L}_z$  as stated has a particularly simple form in spherical coordinates.

Then it only remains to note that  $\hat{L}_z$  (as well as  $\hat{\mathbf{L}}^2$ ) only contains an angular derivative and therefore commutes with  $\hat{H} = \hat{K} + V(r)$ . Thus, for spherically symmetric potentials the energy  $E$ , the size  $|\mathbf{L}|$  of the angular momentum and its  $z$ -component  $L_z$  are compatible observables.

This means for example that it is possible to find energy eigenfunctions for the isotropic oscillator which are simultaneously eigenfunctions of  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$ . Since these operators depend only on the angles, such eigenfunctions can be written as products of a radial function  $R(r)$  and an angular function  $Y(\theta, \phi)$ :

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi).$$

As an example, let us consider one of the three states (T5.8) for the first excited level of the isotropic oscillator. With  $z = r \cos \theta$  we can write  $\psi_{001}$  as

$$\psi_{001} = RY, \quad \text{with} \quad R = C_0^2 C_1 r e^{-m\omega r^2/2\hbar} \quad \text{and} \quad Y = \cos \theta.$$

In this angular function there is no variation in the  $\phi$ -direction (cf the figure on page 3), so that the partial derivative of  $Y = \cos \theta$  with respect to  $\phi$  is equal to zero. Thus,  $\hat{L}_z Y = 0$ , that is,  $Y$  and hence  $\psi_{001}$  are eigenfunctions of  $\hat{L}_z$  with eigenvalue zero. It is also easy to show that the variation in the  $\theta$ -direction is such that  $Y$  is an eigenfunction of  $\hat{\mathbf{L}}^2$  with eigenvalue  $2\hbar^2$ .

**A small exercise:** Show this using (T5.13).

We can conclude that in the oscillator state  $\psi_{001}$  the energy is  $5\hbar\omega/2$ , while  $|\mathbf{L}|$  is  $\hbar\sqrt{2}$  and  $L_z$  is equal to zero. Note that all these quantities have sharp values (zero uncertainty).

**Another exercise:** Since  $x = r \sin \theta \cos \phi$  and  $y = r \sin \theta \sin \phi$ , the two other states in (T5.8) can be written as

$$\psi_{100} = R \cdot \sin \theta \cos \phi \quad \text{and} \quad \psi_{010} = R \cdot \sin \theta \sin \phi,$$

with the same radial function  $R$  as above. Show that also these two functions are eigenfunctions of  $\hat{\mathbf{L}}^2$  with the eigenvalue  $2\hbar^2$ . None of them are eigenstates of  $\hat{L}_z$ . Show that linear combinations  $(\psi_{100} \pm i\psi_{010})/\sqrt{2} = R/\sqrt{2} \cdot \sin \theta e^{\pm i\phi}$  are eigenfunctions of  $\hat{L}_z$ , with the eigenvalues  $\pm\hbar$ .

This is an example of the general fact that it is possible to find simultaneous eigenstates of  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$  for a spherically symmetric potential. (Cf rule **B** in section 4.1 of Lecture notes 4.)

### 5.2.c Quantization of angular momentum. The spherical harmonics

The example above also illustrates that the angular momentum is *quantized*. It turns out that the simultaneous eigenfunctions and the corresponding eigenvalues of the angular-momentum operators  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$  are given by:

$$\begin{aligned} \hat{\mathbf{L}}^2 Y_{lm}(\theta, \phi) &= \hbar^2 l(l+1) Y_{lm}(\theta, \phi), & l = 0, 1, 2, \dots \\ \hat{L}_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi), & m = 0, \pm 1, \pm 2, \dots, \pm l. \end{aligned} \quad (\text{T5.19})$$

Such an eigenfunction  $Y_{lm}$  corresponds to a state where both the *size*  $|\mathbf{L}| = \sqrt{\mathbf{L}^2}$  and the  $z$ -component of the angular momentum have sharp values, while  $L_x$  and  $L_y$  have to be uncertain, because they are not compatible with  $L_z$ . (Then also the direction of  $\mathbf{L}$  is uncertain.) We note that the possible eigenvalues are quantized. The size is given in terms of the so-called **orbital angular-momentum quantum number**  $l$ , which must be a non-negative integer. The  $z$ -component  $L_z$  is proportional to the so-called **azimuthal quantum number**  $m$ , also called the “**magnetic**” quantum number, which is an integer. Note that for a given quantum number  $l$ , the maximal  $|m|$  is  $l$ . This limitation is obviously connected with the fact that  $|L_z|$  can not be larger than  $|\mathbf{L}|$ .

The eigenfunctions  $Y_{lm}$  are known as the **spherical harmonics**. We shall soon discover that they can be written on the form

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta) e^{im\phi},$$

where the dependence on  $\theta$  and  $\phi$  is separated.

The quantization of angular momentum, as expressed by the quantum numbers  $l$  and  $m$  being integers, simply stated is a consequence of the fact that the angular space is “compact”, so that the angular functions must “bite themselves in the tail”, so to speak. This is seen most clearly when one tries to solve

### 5.2.d the eigenvalue equation $\hat{L}_z Y = \frac{\hbar}{i} \frac{\partial}{\partial \phi} Y = \hbar m Y$

The partial differentiation with respect to  $\phi$  means that  $\theta$  is to be kept fixed. This eigenvalue equation therefore takes the form  $dY/d\phi = imY$ , or

$$\frac{dY}{Y} = im d\phi,$$

which can be integrated to

$$\ln Y = im\phi + \ln \Theta(\theta), \quad \implies \quad Y(\theta, \phi) = \Theta(\theta) e^{im\phi},$$

where the integration constant  $\ln \Theta(\theta)$  is independent of  $\phi$ , but other than that can be an arbitrary function of  $\theta$ . The requirement that  $Y(\theta, \phi)$  be continuous then implies that the quantum number  $m$  must be an integer;

$$Y(\theta, 2\pi) = Y(\theta, 0) \quad \implies \quad e^{im \cdot 2\pi} = 1; \quad \implies \quad m = 0, \pm 1, \pm 2, \dots$$

Thus  $L_z$  is quantized;  $L_z = 0, \pm\hbar, \pm 2\hbar, \dots$ . Note that a non-integer  $m$  would imply a wave function  $\psi(r, \theta, \phi) = R(r)\Theta(\theta) e^{im\phi}$  with a discontinuity in a half-plane corresponding to  $\phi = 0$  ( $y = 0, x > 0$ ).

### 5.2.e The eigenvalue equation $\hat{L}^2 Y = \hbar^2 l(l+1) Y$

is more of a mathematical challenge. It is this equation that determines the quantized values of  $l$ , and the corresponding functions  $\Theta_{lm}(\theta)$ . This is explained in detail in Hemmer's book and also in B&J. The main points of the derivation are repeated here. Inserting  $Y = \Theta(\theta) \exp(im\phi)$  we note that  $\partial^2/\partial\phi^2$  gives a factor  $(im)^2 = -m^2$ . As in Hemmer, we introduce the abbreviation  $\cos\theta \equiv x$  (NB!  $x$  is *not the coordinate*  $x$ ), so that

$$\sin\theta = \sqrt{1-x^2} \quad \text{and} \quad dx = -\sin\theta d\theta.$$

Re-writing slightly,

$$\begin{aligned} \frac{d^2 f}{d\theta^2} + \cot\theta \frac{df}{d\theta} &= \frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{df}{d\theta} \right) = \frac{1}{\sin\theta} \frac{d}{d\theta} \left( \frac{\sin^2\theta}{\sin\theta} \frac{df}{d\theta} \right) \\ &= \frac{d}{dx} \left[ (1-x^2) \frac{df}{dx} \right] = (1-x^2) \frac{d^2 f}{dx^2} - 2x \frac{df}{dx}, \end{aligned}$$

we then find that the eigenvalue equation  $\hat{L}^2 Y = \hbar^2 l(l+1) Y$  can be written as

$$\left[ (1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + l(l+1) - \frac{m^2}{1-x^2} \right] \Theta(x) = 0. \quad (\text{T5.20})$$

Here we know that  $m$  is an integer, while the quantum number  $l$  is now regarded to be unknown, together with the possible solutions  $\Theta_{lm}(\theta)$  of this eigenvalue equation.

**For the case  $m=0$**  this is a standard equation in applied mathematics. It is called the **Legendre equation**:

$$\boxed{\left[ (1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + l(l+1) \right] P_l(x) = 0.} \quad (\text{T5.21})$$

As explained in the book, this equation can be solved using the power series expansion method.

With

$$\begin{aligned} \Theta &= \sum_{n=0}^{\infty} a_n x^n, & 2x\Theta' &= 2x \sum_{n=0}^{\infty} a_n n x^{n-1} \quad \text{and} \\ \Theta'' &= \sum_{n=2}^{\infty} a_n n(n-1) x^{n-2} = \sum_{n=0}^{\infty} a_{n+2} (n+2)(n+1) x^n \end{aligned}$$

inserted into equation (T5.21), we find that

$$\sum_{n=0}^{\infty} \{ a_{n+2} (n+2)(n+1) - a_n [n(n-1) + 2n - l(l+1)] \} x^n = 0.$$

This equation is satisfied for all  $x$  only if the coefficient of each power of  $x$  vanishes, that is, if all the expressions  $\{\dots\}$  are equal to zero. This gives the recursion relation

$$\frac{a_{n+2}}{a_n} = \frac{n(n+1) - l(l+1)}{(n+1)(n+2)} = \frac{(n-l)(n+l+1)}{(n+1)(n+2)}, \quad n = 0, 1, 2, \dots$$

Using this relation, we can express  $a_2, a_4$  etc in terms of  $a_0$  and, in the same manner,  $a_3, a_5$  etc in terms of  $a_1$ . The solution thus is the sum of two infinite power series, with respectively even and odd powers of  $x$ :

$$\Theta = a_0 \left[ 1 + \frac{-l \cdot (l+1)}{2!} x^2 + \frac{-l(-l+2) \cdot (l+1)(l+3)}{4!} x^4 + \dots \right] \\ + a_1 \left[ x + \frac{(-l+1) \cdot (l+2)}{3!} x^3 + \frac{(-l+1)(-l+3) \cdot (l+2)(l+4)}{5!} x^5 + \dots \right].$$

Here,  $a_0$  and  $a_1$  are two arbitrary constants.

From the recursion formula we note that

$$\frac{a_{n+2}}{a_n} = \frac{n}{n+2} \left( 1 + \mathcal{O}(n^{-2}) \right).$$

This means that both series will for large  $n$  behave as

$$\sum_n \frac{1}{n} x^n \quad (\text{where } n \text{ is even or odd}).$$

Both series will therefore diverge for  $x = \pm 1$ , corresponding to  $\theta = 0$  and  $\pi$ . In order to obtain a finite and acceptable solution (eigenfunctions) we must therefore demand that both series *terminate*, giving a polynomial solution. From the formula above (and from the recursion relation) we see that the series with *even* powers becomes a polynomial of degree  $l$  if  $l$  is a non-negative even number,

$$l = 0, 2, 4, \dots$$

In these cases, the series with odd powers does not terminate. We must therefore set the coefficient  $a_1$  equal to zero for even  $l$ . For *odd*  $l$  we must similarly set  $a_0$  equal to zero, and the solution becomes a polynomial of degree  $l$  with only odd powers of  $x$ . This is how the quantization of  $|\mathbf{L}|$  enters the picture, with integer **orbital angular-momentum quantum numbers**  $l = 0, 1, 2, \dots$ .

These polynomial solutions are uniquely determined by the recursion relation, apart from an arbitrary multiplicative constant ( $a_0$  or  $a_1$ ). When the solutions are normalized so that their value for  $x = 1$  ( $\theta = 0$ ) becomes 1, they are called the **Legendre polynomials**, and they are denoted by  $P_l(x) = P_l(\cos \theta)$ . Thus

$$P_l(1) = 1 \quad \text{and} \quad P_l(-x) = (-1)^l P_l(x), \quad (\text{T5.22})$$

where the last relation states that the parity is  $(-1)^l$  (because the powers of  $x$  are either even or odd). Explicitly the first few of these polynomials are

$$P_0(x) = 1, \quad (\text{med } x = \cos \theta :)$$

$$P_1(x) = x = \cos \theta,$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(3 \cos^2 \theta - 1),$$

$$P_3(x) = \frac{1}{2}(5x^3 - 3x) = \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta), \quad \text{etc.}$$

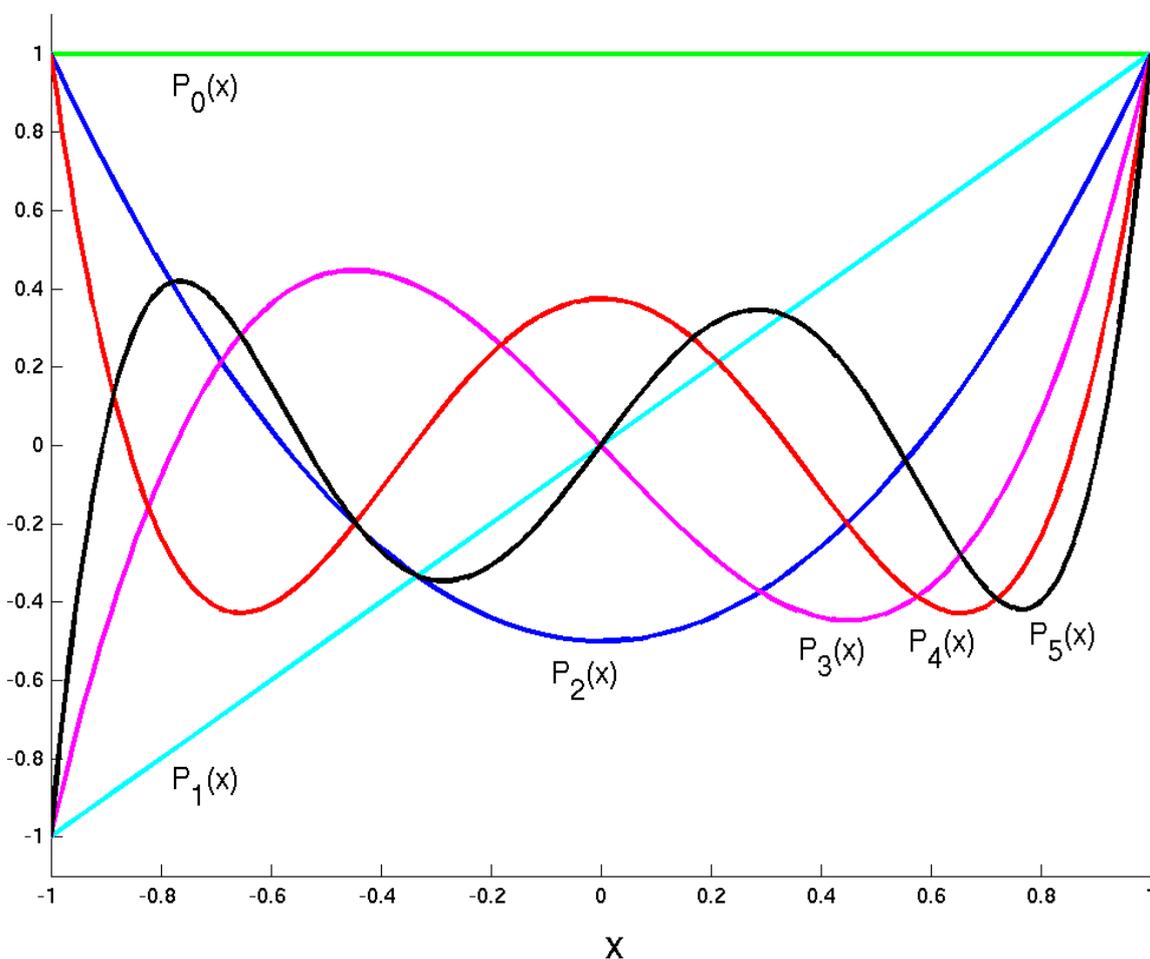
A useful formula for the Legendre polynomials is

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l. \quad (\text{Rodrigues' formula}) \quad (\text{T5.23})$$

So, for  $m = 0$  we have

$$\Theta_{l0}(\theta) \propto P_l(\cos \theta). \quad (\text{T5.24})$$

The diagram shows the six first polynomials  $P_0(x), \dots, P_6(x)$  as functions of  $x$ . Here we see that they are all equal to 1 for  $x = 1$ , which corresponds to  $\theta = 0$ , while the value for  $x = -1$  ( $\theta = \pi$ ) is  $(-1)^l$ .



Since all the polynomials are either symmetric or antisymmetric, we could of course have confined ourselves to show the curves only for the interval  $0 < x < 1$ . On page 95 in Hemmer's book, you can see how these polynomials behave as functions of  $\theta$  (for  $0 < \theta < \pi/2$ ).

**A small exercise: a.** In section 5.2.b we found that  $Y = \cos \theta$  is an eigenfunction of  $\widehat{L}^2$  and  $\widehat{L}_z$  with the eigenvalues  $\hbar^2 l(l+1) = 2\hbar^2$  and  $\hbar m = 0$ , that

is, a solution with the quantum numbers  $l = 1$  and  $m = 0$ . Check that Rodrigues' formula for  $\Theta_{10}(\theta) \propto P_1(\cos \theta)$  gives the same result. **b.** Use (T5.24) and (T5.23) to find the spherical harmonic  $Y_{20}$ , apart from the normalization.

**One more:** Check that Rodrigues' formula gives the above result for the Legendre polynomial  $P_3(x)$ . Use the above recursion relation, together with the normalization convention (T5.22), to show that

$$P_4(x) = \frac{1}{8} (35x^4 - 30x^2 + 3).$$

**For the case  $m \neq 0$**  we see that the differential equation (T5.20) depends only on  $m^2$ , that is on  $|m|$ . This means that we can set  $\Theta_l^{-m} = \Theta_l^m$ , and consider only the case  $m > 0$ . As explained in the book, one then finds that the acceptable solutions of this differential equation are the so-called **associated Legendre functions**;

$$\Theta_{lm}(\theta) = P_l^m(x) \equiv (1 - x^2)^{m/2} \left( \frac{d}{dx} \right)^m P_l(x), \quad (\text{T5.25})$$

where  $x = \cos \theta$  and  $(1 - x^2)^{m/2} = \sin^m \theta$ . You can find the proof in the book, or in the attachment at the end of this Lecture notes.

Since the highest power in  $P_l$  is  $x^l$ , the differentiation here gives a polynomial of degree  $l - m$ , and zero for  $m > l$ .<sup>2</sup> Thus we can conclude that the differential equation gives solutions for integer  $l$  which are  $\geq |m|$ , and the other way around: For a given orbital angular-momentum quantum number  $l$  the magnetic quantum number  $m$  is limited to

$$m = 0, \pm 1, \dots, \pm l.$$

The results for the normalized spherical harmonics can be written as

$$Y_{lm}(\theta, \phi) = \delta_m \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos \theta) e^{im\phi}, \quad (\text{T5.26})$$

where

$$\delta_m = \begin{cases} 1 & \text{for } m \leq 0, \\ (-1)^m & \text{for } m > 0 \end{cases}$$

is the most commonly used sign convention. In the table below you will find the explicit results for  $l \leq 3$ .

As you probably have observed, it takes quite a lot of work to obtain these results for the angular functions. If one finds it difficult to grasp all the details of the derivation, some consolation may be found by checking explicitly the eigenvalues of the functions given in the table. The normalization can be checked by integrating  $|Y_{lm}(\theta, \phi)|^2$  over all angles.

<sup>2</sup>Note also that the powers of  $x$  in this polynomial are even/odd when  $l - m$  is even/odd. This means that  $P_l^m(-x) = (-1)^{l-m} P_l^m(x)$ .

## Spherical harmonics

	$l$	$m$	$Y_{lm}(\theta, \phi)$
$s$	0	0	$Y_{00} = \sqrt{\frac{1}{4\pi}}$
$p$	1	0	$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$
		$\pm 1$	$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$
$d$	2	0	$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
		$\pm 1$	$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
		$\pm 2$	$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$
$f$	3	0	$Y_{30} = \sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
		$\pm 1$	$Y_{3,\pm 1} = \mp \sqrt{\frac{21}{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
		$\pm 2$	$Y_{3,\pm 2} = \sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
		$\pm 3$	$Y_{3,\pm 3} = \mp \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3i\phi}$

## 5.2.f Some points worth noticing

(i) All the functions  $Y_{lm}$  contain the factors  $\exp(im\phi)$  and  $\sin^{|m|}\theta$  together with the polynomial of degree  $l - |m|$  in  $x \equiv \cos \theta$ .

(ii) The spherical harmonics are parity eigenstates. The parity operation  $\hat{\mathcal{P}}$  means **space inversion**, that is, reflection with respect to the origin (see the figure p 6):

$$\begin{aligned} \hat{\mathcal{P}} : \quad \mathbf{r} &\rightarrow -\mathbf{r}, \quad \text{i.e.} \quad r \rightarrow r, \\ &\theta \rightarrow \pi - \theta, \\ &\phi \rightarrow \phi + \pi. \end{aligned} \tag{T5.27}$$

This corresponds to

$$\begin{aligned} x = \cos \theta &\rightarrow -\cos \theta = -x, \\ P_l(\cos \theta) &\rightarrow P_l(-\cos \theta) = (-1)^l P_l(\cos \theta), \\ P_l^{|m|}(\cos \theta) &\rightarrow (-1)^{l-|m|} P_l^{|m|}(\cos \theta), \\ e^{im\phi} &\rightarrow (-1)^m e^{im\phi}. \end{aligned}$$

Thus, the parity of  $Y_{lm}$  simply is  $(-1)^l$ :

$$\hat{\mathcal{P}} Y_{lm}(\theta, \phi) = Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \tag{T5.28}$$

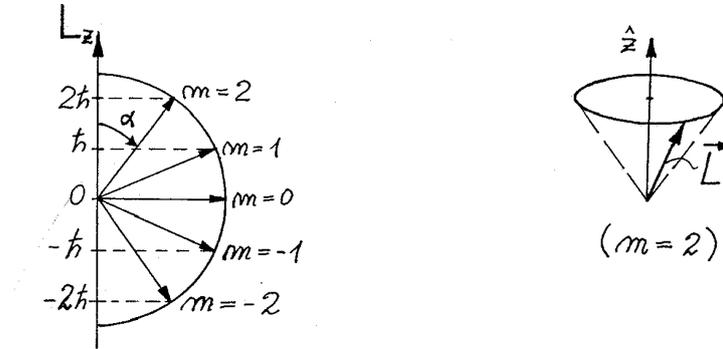
These symmetry properties are important e.g. when we want to study **hybrid orbitals**.

(iii) The functions  $Y_{lm}$  are not only normalized, but also orthogonal, because they are eigenfunctions with different eigenvalues [remember the rule (T2.34) in Lecture notes 2]:

$$\int Y_{l'm'}^* Y_{lm} d\Omega = \delta_{l'l} \delta_{m'm} \quad (\text{orthonormality}). \quad (\text{T5.29})$$

(iv) The fact that  $l$  can not be smaller than  $|m|$  is of course connected with the obvious fact that  $|\mathbf{L}| = \hbar\sqrt{l(l+1)}$  can not be smaller than  $|L_z| = \hbar|m|$ . As an example, let us consider  $l = 2$ , which corresponds to  $|\mathbf{L}| = \hbar\sqrt{6} \approx 2.45\hbar$ . As illustrated in the figure, the allowed values of  $L_z$  then are  $0, \pm\hbar$  and  $\pm 2\hbar$ . Each of these values corresponds to a well-defined angle  $\alpha$  between  $\mathbf{L}$  and the  $z$ -axis, given by

$$\cos \alpha = \frac{L_z}{|\mathbf{L}|} = \frac{m}{\sqrt{l(l+1)}} = \frac{m}{\sqrt{6}}, \quad (m = 2, 1, 0, -1, -2).$$



In this case we find the smallest angle for  $m = 2$ ,  $\alpha = \arccos(2/\sqrt{6}) = 35.6^\circ$ .<sup>3</sup> In this state  $Y_{22}$ , also

$$L_x^2 + L_y^2 = \mathbf{L}^2 - L_z^2 = 6\hbar^2 - (2\hbar)^2 = 2\hbar^2$$

is sharply defined. The observables  $L_x$  and  $L_y$ , on the other hand, are not compatible with  $L_z$ , and must therefore be uncertain. It is easy to show that the expectation values of both these observables are equal to zero:

$$\langle L_x \rangle_{Y_{22}} = \langle L_y \rangle_{Y_{22}} = 0.$$

From the symmetry we can also understand that the expectation values of  $L_x^2$  and  $L_y^2$  must be equal, and since the sum of them is  $2\hbar^2$ , we thus have that

$$\langle L_x^2 \rangle_{Y_{22}} = \langle L_y^2 \rangle_{Y_{22}} = \hbar^2.$$

It follows that the uncertainties in the state  $Y_{22}$  are

$$\Delta L_x = \Delta L_y = \hbar.$$

This situation can be illustrated (to a certain extent) by the sketch on the right in the figure above:  $|\mathbf{L}|$  and  $L_z$  are sharp. So is  $\sqrt{L_x^2 + L_y^2}$  (the radius of the circle).  $L_x$  and  $L_y$  are

<sup>3</sup>Note that the angle  $\alpha$  is not allowed to be zero, because that would correspond to a vector  $\mathbf{L}$  with a well-defined direction, and *that* as we know is impossible, because  $L_x, L_y$  and  $L_z$  are not compatible, that is, they can not have sharp values simultaneously.

uncertain (with zero averages), and then also the direction of  $\mathbf{L}$  is uncertain. In a way this means that  $\mathbf{L}$  is confined to the surface of a cone.<sup>4</sup>

(v) The spherical harmonics  $Y_{lm}(\theta, \phi)$  constitute a **complete set**; an arbitrary function of  $\theta$  and  $\phi$  can be expanded as:

$$g(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l c_{lm} Y_{lm}(\theta, \phi). \quad (\text{T5.30})$$

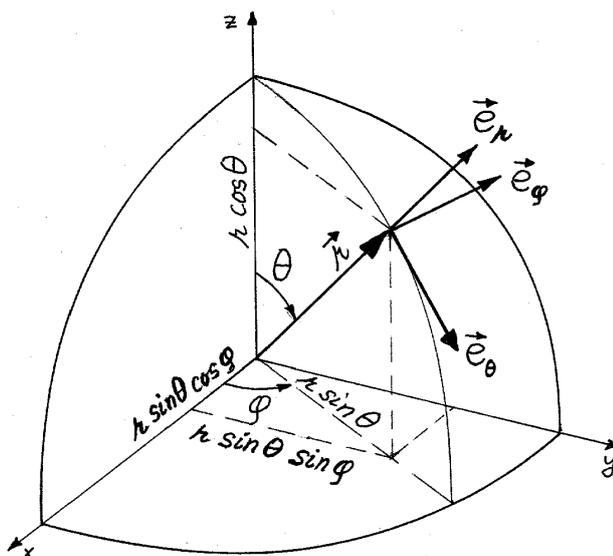
If the function depends only on  $\theta$ , one gets contributions only for  $m = 0$ , that is from  $Y_{l0} \propto P_l(\cos \theta)$ :

$$g(\theta) = \sum_{l=0}^{\infty} c_l P_l(\cos \theta). \quad (\text{T5.31})$$

Because of this completeness, the spherical harmonics are relevant under many circumstances, not only in quantum mechanics.

**A small exercise:** Write  $g(x) = x^3$  as a linear combination of Legendre polynomials  $P_l(x)$ . Answer:  $x^3 = \frac{3}{5}P_1(x) + \frac{2}{5}P_3(x)$ . Why does a corresponding expansion of  $x^7$  only contain  $P_l(x)$  with uneven  $l$ ?

## 5.2.g Attachment on spherical coordinates etc



From this figure we can read out the connections between the spherical coordinates  $r, \theta, \phi$  and the Cartesian coordinates  $x, y, z$ :<sup>5</sup>

$$\begin{aligned} x &= r \sin \theta \cos \phi & r &= \sqrt{x^2 + y^2 + z^2} \\ y &= r \sin \theta \sin \phi & \cos \theta &= z / \sqrt{x^2 + y^2 + z^2} \\ z &= r \cos \theta & \tan \phi &= y/x \end{aligned}$$

<sup>4</sup>However, here we must be careful. This illustration may lead us to believe that the *direction* of  $\mathbf{L}$  is an observable. *That* is not the case, because  $L_x, L_y$  and  $L_z$  are not compatible.

<sup>5</sup>In the figure above, the angle  $\theta$  between  $\mathbf{r}$  and the  $z$ -axis is the so-called **polar angle**. The angle  $\phi$  between the  $\mathbf{r}\hat{z}$ -plane and the  $xz$ -plane is the so-called **azimuthal angle**. From mathematics you are probably used to a different notation.

$$(0 \leq r < \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi < 2\pi).$$

From the figure it is also easy to see that infinitesimal increments  $dr$ ,  $d\theta$ ,  $d\phi$  of  $r, \theta, \phi$  correspond to an infinitesimal change of  $\mathbf{r}$  given by

$$d\mathbf{r} = \hat{\mathbf{e}}_r dr + \hat{\mathbf{e}}_\theta r d\theta + \hat{\mathbf{e}}_\phi r \sin \theta d\phi.$$

### Integration in spherical coordinates

Because the three unit vectors  $\hat{\mathbf{e}}_r, \hat{\mathbf{e}}_\theta$  and  $\hat{\mathbf{e}}_\phi$  are orthonormal, we can figure out that the volume element can be written as

$$d^3r \equiv dV = dr \cdot r d\theta \cdot r \sin \theta d\phi = r^2 dr \sin \theta d\theta d\phi.$$

Integration over the entire space is accomplished by integrating  $r$  from 0 to  $\infty$ ,  $\theta$  from 0 to  $\pi$ , and  $\phi$  from 0 to  $2\pi$ . For a spherically symmetric integrand this simplifies to

$$\begin{aligned} \int f(r) d^3r &= \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty f(r) \cdot r^2 dr && [\sin \theta d\theta = -d(\cos \theta)] \\ &= 2\pi \int_{\cos \theta = -1}^{\cos \theta = 1} d(\cos \theta) \int_0^\infty f(r) r^2 dr \\ &= \int_0^\infty f(r) \cdot 4\pi r^2 dr. \end{aligned}$$

Note that  $4\pi r^2 dr$  is the volume of a spherical shell with radius  $r$  and thickness  $dr$ .

**A tiny exercise:** Calculate the volume of an eighth of a sphere by a similar integration. (Assume that it is in the first octant, where  $x, y$  and  $z$  are all positive, and use the relevant integration limits for the angles.)

### The gradient operator in spherical coordinates

For a function  $f(\mathbf{r})$ , the infinitesimal change  $d\mathbf{r}$  (given above) corresponds to an infinitesimal change of the function, given by the scalar product of  $d\mathbf{r}$  and the gradient of the function:

$$\begin{aligned} df &= f(\mathbf{r} + d\mathbf{r}) - f(\mathbf{r}) = \nabla f \cdot d\mathbf{r} \\ &= \{\hat{\mathbf{e}}_r (\nabla f)_r + \hat{\mathbf{e}}_\theta (\nabla f)_\theta + \hat{\mathbf{e}}_\phi (\nabla f)_\phi\} \cdot \{\hat{\mathbf{e}}_r dr + \hat{\mathbf{e}}_\theta r d\theta + \hat{\mathbf{e}}_\phi r \sin \theta d\phi\} \\ &= (\nabla f)_r dr + (\nabla f)_\theta r d\theta + (\nabla f)_\phi r \sin \theta d\phi. \end{aligned}$$

Comparing with

$$df = \frac{\partial f}{\partial r} dr + \frac{\partial f}{\partial \theta} d\theta + \frac{\partial f}{\partial \phi} d\phi$$

we then find that the components of the gradient of  $f$  in spherical coordinates are given by

$$(\nabla f)_r = \frac{\partial f}{\partial r}, \quad (\nabla f)_\theta = \frac{1}{r} \frac{\partial f}{\partial \theta}, \quad (\nabla f)_\phi = \frac{1}{r \sin \theta} \frac{\partial f}{\partial \phi}.$$

Thus the gradient operator is (see also Rottmann)

$$\nabla = \hat{\mathbf{e}}_r \frac{\partial}{\partial r} + \hat{\mathbf{e}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}.$$

The orbital angular-momentum operator in spherical coordinates then is

$$\begin{aligned}\hat{\mathbf{L}} &= \mathbf{r} \times \hat{\mathbf{p}} = \mathbf{r} \times \frac{\hbar}{i} \nabla \\ &= \frac{\hbar}{i} \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right),\end{aligned}$$

$$\text{since } \hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_r = 0, \quad \hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_\theta = \hat{\mathbf{e}}_\phi, \quad \hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_\phi = -\hat{\mathbf{e}}_\theta.$$

Here it is important to notice that the orbital angular-momentum operator  $\hat{\mathbf{L}}$  contains derivatives only with respect to the angles  $\theta$  and  $\phi$ . This implies among other things that a spherically symmetric function  $f(r)$  is an eigenfunction of the angular-momentum operator with eigenvalue zero. Then the function  $f(r)$  is also an eigenfunction of  $\hat{\mathbf{L}}^2 \equiv \hat{\mathbf{L}} \cdot \hat{\mathbf{L}}$  with zero eigenvalue. Thus a wave function that depends only on  $r$  (and not on the angles) describes a state with zero angular momentum.

### $\hat{L}_x$ , $\hat{L}_y$ and $\hat{L}_z$ in spherical coordinates

By careful consideration of the figure one finds that

$$\begin{aligned}\hat{\mathbf{e}}_r &= \hat{\mathbf{e}}_x \sin \theta \cos \phi + \hat{\mathbf{e}}_y \sin \theta \sin \phi + \hat{\mathbf{e}}_z \cos \theta, \\ \hat{\mathbf{e}}_\theta &= (\hat{\mathbf{e}}_x \cos \phi + \hat{\mathbf{e}}_y \sin \phi) \cos \theta - \hat{\mathbf{e}}_z \sin \theta, \\ \hat{\mathbf{e}}_\phi &= -\hat{\mathbf{e}}_x \sin \phi + \hat{\mathbf{e}}_y \cos \phi.\end{aligned}$$

Using these formulae and the above expression for  $\hat{\mathbf{L}}$  it is easy to see that the Cartesian components of the orbital angular-momentum operator can be expressed in spherical coordinates as

$$\begin{aligned}\hat{L}_x &= \frac{\hbar}{i} \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \\ \hat{L}_y &= \frac{\hbar}{i} \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right), \\ \hat{L}_z &= \frac{\hbar}{i} \frac{\partial}{\partial \phi}.\end{aligned}$$

You should pay attention particularly to the last one.

### $\hat{\mathbf{L}}^2$ in spherical coordinates. The Laplace operator

By squaring the expression for  $\hat{\mathbf{L}}$  in spherical coordinates we have

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \frac{\hbar}{i} \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right) \cdot \frac{\hbar}{i} \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right).$$

Here it is important to understand that  $\hat{\mathbf{e}}_\theta$  depends both on  $\theta$  and  $\phi$ ; it can be shown that

$$\frac{\partial \hat{\mathbf{e}}_\theta}{\partial \theta} = -\hat{\mathbf{e}}_r, \quad \frac{\partial \hat{\mathbf{e}}_\theta}{\partial \phi} = \hat{\mathbf{e}}_\phi \cos \theta,$$

while  $\hat{\mathbf{e}}_\phi$  is independent of  $\theta$ :

$$\frac{\partial \hat{\mathbf{e}}_\phi}{\partial \theta} = 0, \quad \frac{\partial \hat{\mathbf{e}}_\phi}{\partial \phi} = -\hat{\mathbf{e}}_r \sin \theta - \hat{\mathbf{e}}_\theta \cos \theta.$$

Inserting into the expression above, one then arrives at the expression for  $\hat{\mathbf{L}}^2$  in spherical coordinates,

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).$$

By comparing with the Laplacean in spherical coordinates,

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

we see that the angular part of  $\nabla^2$  can be expressed in terms of  $\hat{\mathbf{L}}^2$ :

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2}.$$

Using this expression we finally arrive at a practical expression for the Hamiltonian for a spherically symmetric potential:

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r).$$

## 5.3 Rigid rotator

(Hemmer 5.5, B&J 6.4)

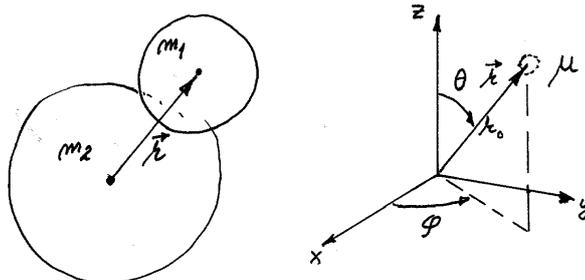
### 5.3.a What is a rigid rotator

Let us consider a particle of mass  $\mu$  which is forced to move on the (two-dimensional) surface of a sphere with radius  $r_0$ . We can imagine that the particle is attached to one end of a weightless rod (the other end being attached to the origin). This is called a **rigid rotator**. It is also frequently called a *free* rotator, because the motion on the spherical surface is free; there is no force acting parallel to the surface.

Such a rotator can be used to model the rotational motion of a two-atomic molecule. Then  $\mu$  stands for the **reduced mass** of the two atoms,<sup>6</sup>

$$\mu = \frac{m_1 m_2}{m_1 + m_2},$$

The radius  $|\mathbf{r}| = r_0$  is the (equilibrium) distance between the two nuclei, and the angles  $\theta$  and  $\phi$  specify the orientation of the vector from  $m_2$  to  $m_1$ .



### 5.3.b Energy eigenvalues and eigenfunctions

For the rigid rotator there is no radial motion, only rotation. The particle with mass  $\mu$  is moving perpendicularly to  $\mathbf{r}$ ; so that  $\mathbf{p} = \mathbf{p}_\perp$  ( $\perp \mathbf{r}$ ). With  $\mathbf{L} = |\mathbf{r} \times \mathbf{p}_\perp| = r_0 p_\perp$ , the (kinetic) energy then is given classically by the expression

$$E = K = \frac{p_\perp^2}{2\mu} = \frac{\mathbf{L}^2}{2\mu r_0^2} \equiv \frac{\mathbf{L}^2}{2I} \quad (I = \mu r_0^2 = \text{moment of inertia}).$$

The corresponding Hamiltonian is

$$\widehat{H} = \widehat{K} = \frac{\widehat{\mathbf{L}}^2}{2\mu r_0^2} = \frac{\widehat{\mathbf{L}}^2}{2I}. \quad (\text{T5.32})$$

Here we note that there is no potential energy since, as mentioned, there is no force acting parallel to the surface. Thus the Hamiltonian in this case simply reduces to the angular part ( $\widehat{K}_L$ ) of the kinetic energy operator in (T5.16).

<sup>6</sup>By considering the two-atomic molecule as a rigid rotator we are neglecting among other things the vibrational motion (Cf the discussion in Lecture notes 3.)

A particle moving on a bounded surface will in general have quantized energy. And with the present spherical surface, we see that the energies simply are determined by the eigenvalues of  $\hat{\mathbf{L}}^2$ :

$$E_l = l(l+1) \frac{\hbar^2}{2I}. \quad (\text{T5.33})$$

Each of these levels is degenerate, with  $g_l = 2l + 1$  independent states. As energy eigenfunctions we can then use the spherical harmonics

$$\psi_{lm} = Y_{lm}(\theta, \phi), \quad m = 0, \pm 1, \pm 2, \dots, \pm l, \quad (\text{T5.34})$$

but linear combinations of these can also be used.

Note that the position  $(r_0, \theta, \phi)$  of the particle on the surface (alternatively the direction vector

$$\hat{\mathbf{r}} \equiv \frac{\mathbf{r}}{r} = \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \hat{\mathbf{e}}_x \sin \theta \cos \phi + \hat{\mathbf{e}}_y \sin \theta \sin \phi + \hat{\mathbf{e}}_z \cos \theta$$

from nucleus 2 to nucleus 1) is uniquely determined by the angles  $\theta$  and  $\phi$ . Note also that  $|Y(\theta, \phi)|^2$  now gives the probability density per unit solid angle, such that  $|Y(\theta, \phi)|^2 d\Omega$  is the probability of finding the particle within the solid angle  $d\Omega$ . The normalization condition

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta |Y(\theta, \phi)|^2 \equiv \int |Y(\theta, \phi)|^2 d\Omega = 1$$

states that the probability of finding the particle *somewhere* on the surface is equal to 1 (or, alternatively, that the direction vector from nucleus 2 to nucleus 1 must point somewhere).<sup>7</sup>

**A small exercise:** What is the probability per unit *area* on the surface (which has the radius  $r_0$ )?

### 5.3.c Radiative transitions. Rotational spectra

When such a molecule exchanges energy with its surroundings, it can take place e.g. via absorption or emission of photons. It can be shown that transitions between states of the type (T5.34) almost always respect the **selection rule**

$$\Delta l = \pm 1, \quad (\text{T5.35})$$

meaning that  $l$  very rarely changes by more than one unit ( $\pm 1$ ). This implies that the exchanged photons have energies given by

$$\Delta E_l \equiv E_l - E_{l-1} = \frac{\hbar^2}{I} l, \quad l = 1, 2, \dots \quad (\text{T5.36})$$

These energies typically are of the order of  $10^{-4} - 10^{-3} eV$ , and correspond to photons in the infrared frequency range. We note that the emitted photons give a frequency spectrum with equidistant lines, a so-called **rotational spectrum**.

Experiments agree well with this simple theory, when one measures the emission spectra from hot two-atomic gases at moderate temperatures. (See Hemmer p 99.) This agreement

<sup>7</sup>From (T5.28) we see that the probability density  $|Y_{lm}(\theta, \phi)|^2$  is always *symmetric* with respect to inversion about the origin. This means among other things that the probability of finding the particle on e.g. the upper half-sphere is 50 percent when the rotator is in a state described by one of the functions  $Y_{lm}$ .

may be somewhat surprising because, when treating the two atoms as point particles with a constant distance  $r_0$ , we have in fact simplified in a seemingly rather brutal way. Among other things, we have neglected the following effects:

(1) **Vibration.** The distance between the two nuclei actually is not constant, but may vary slightly about the (classical) equilibrium distance  $r_0$ . For small deviations this corresponds to a one-dimensional *harmonic* oscillation, as discussed in Lecture notes 3. The distance  $\hbar\omega$  between the energy levels of such an oscillator typically is of the order of  $0.1\text{ eV}$ , which is significantly larger than the energy amounts ( $10^{-4} - 10^{-3}\text{ eV}$ ) which are needed to excite the rotational degrees of freedom. In statistical mechanics one learns that the probability of finding a molecule in an excited vibrational state is negligible when the temperature is so low that  $k_B T \ll \hbar\omega$ , that is, when

$$T \ll \frac{\hbar\omega}{k_B} \sim \frac{0.1\text{ eV}}{8.6 \cdot 10^{-5}\text{ eV/K}} \sim 10^3\text{ K}.$$

( $k_B = 8.6 \cdot 10^{-5}\text{ eV/K}$  is Boltzmann's constant). Thus at low temperatures there are practically no excitations of the vibrational degree of freedom. This way the system becomes effectively two-dimensional, as a rotator, with  $r_0$  equal to the equilibrium distance between the two nuclei.<sup>8</sup>

(2) **Rotation about the axis through the two nuclei.** A rigid body actually has *three* rotational degrees of freedom. Two of these were taken into account in the “point-like” rigid rotator treated above. The third degree of freedom lies in the possibility of a rotation about the axis through the two nuclei. However, this degree of freedom is not excited at low temperatures. The reason is that the moments of inertia of the electrons with respect to this axis are very small (a factor  $\sim 10^{-4}$  smaller than for the rigid rotator above). The moments of inertia of the nuclei with respect to this axis are even smaller. Based on this we can state that the excitation energy for the “electronic” degree of freedom will be of the order of electronvolts. (Cf the hydrogen atom, for which it takes  $10.2\text{ eV}$  to excite the electron from the ground state to the “rotational”  $2p$ -state.)

This is the reason why the simple rigid-rotator model above works so well at low temperatures. At higher temperatures, one finds spectra corresponding to excitation of both rotational and vibrational degrees of freedom.

### 5.3.d Comments

(i) *Physically*, we can prepare states with well-defined  $|\mathbf{L}|^2$  and  $L_z$  for the rotator by *measuring* these observables. According to the measurement postulate, we must then necessarily get a pair of eigenvalues  $\hbar^2 l(l+1)$  and  $\hbar m$ , and after the measurement the rotator will be left in the corresponding state  $Y_{lm}$ .

(ii) We should keep in mind that the rotator (as well as the hydrogen atom or any other system described by a spherically symmetric potential  $V(r)$ ) has an underlying spherical symmetry: There is no preferred direction. Thus, physically there is nothing particular about the  $z$ -axis. Instead of  $L_z$  we can therefore just as well measure any other component

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<sup>8</sup>Note that at room temperature,  $T \sim 300\text{ K}$ , we have  $k_B T (= 0.025\text{ eV})$ , which is much larger than the amount needed to excite the rotational degree of freedom ( $10^{-4} - 10^{-3}\text{ eV}$ ). In statistical mechanics one learns that the average rotational energy under such circumstances is equal to  $k_B T$ . This implies, e.g., that air molecules at room temperature will have average orbital angular-momentum quantum numbers of the order of  $l \sim 10$ .

of  $\mathbf{L}$  together with  $|\mathbf{L}|$ , e.g.  $L_x$ , or for that matter an arbitrary component  $\mathbf{L} \cdot \hat{\mathbf{n}}$ . From the symmetry we realize that the simultaneous eigenstates in which the system is left after such a measurement will “look the same” seen from the  $\hat{\mathbf{n}}$ -axis as  $Y_{lm}$  seen from the  $\hat{\mathbf{z}}$ -axis. Examples are the angular functions

$$p_x \equiv \sqrt{\frac{3}{4\pi}} \frac{x}{r} \quad \text{and} \quad p_y \equiv \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \quad (\text{T5.37})$$

which have the same “appearance” seen from respectively the  $\hat{\mathbf{x}}$ -axis and the  $\hat{\mathbf{y}}$ -axis as

$$p_z \equiv \sqrt{\frac{3}{4\pi}} \frac{z}{r} = \sqrt{\frac{3}{4\pi}} \cos \theta = Y_{10}(\theta, \phi)$$

has seen from the  $\hat{\mathbf{z}}$ -axis. More generally,

$$p_{\hat{\mathbf{n}}} \equiv \sqrt{\frac{3}{4\pi}} \frac{\hat{\mathbf{n}} \cdot \mathbf{r}}{r} = \sqrt{\frac{3}{4\pi}} \cos \theta_{nr} \quad (\text{T5.38})$$

has the same appearance seen from the  $\hat{\mathbf{n}}$ -axis.

(iii) All these states are  $p$ -states ( $l = 1$ ), and from (T5.30) it then follows that they must be linear combinations of the set  $Y_{lm}$ ,  $m = 0, \pm 1$ . This holds both for

$$p_x = -\frac{1}{\sqrt{2}}(Y_{11} - Y_{1,-1}) = -\text{sqr}t2 \Re(Y_{11}) \quad \text{and} \quad p_y = \frac{i}{\sqrt{2}}(Y_{11} + Y_{1,-1}) = -\text{sqr}t2 \Im(Y_{11}),$$

and it also holds for

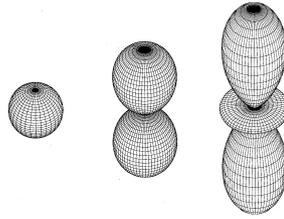
$$p_{\hat{\mathbf{n}}} \equiv \sqrt{\frac{3}{4\pi}} \frac{\hat{\mathbf{n}} \cdot \mathbf{r}}{r} = n_x p_x + n_y p_y + n_z p_z = \dots$$

“Moral”: The choice of the  $\hat{\mathbf{z}}$ -axis as “quantization axis” and the resulting set of states  $Y_{lm}$  are not unique. However, this is no problem; all possible angular functions that might be of interest can be expanded in terms of the set  $Y_{lm}$ , due to the completeness of this set.<sup>9</sup>

(iv) In chemistry one learns that directed “bonds” and **hybridized orbitals** are important for the **structure** of molecules. Angular functions are an important part of the discussion of such orbitals.

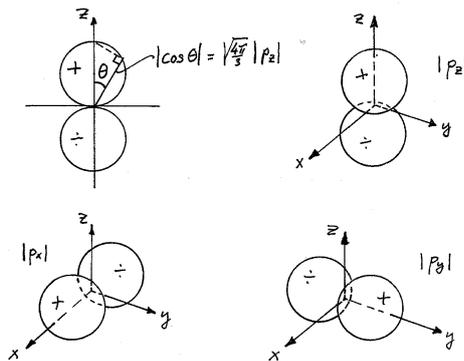
(v) Because the probability distributions  $|Y_{lm}(\theta, \phi)|^2$  are independent of the azimuthal angle  $\phi$ , that is, are rotationally symmetric with respect to the  $\hat{\mathbf{z}}$ -axis, they can be illustrated by **polar diagrams**, where the size of  $|Y_{lm}|^2$  as a function of  $\theta$  is marked along a line in the direction  $\theta$ . See p 286 in B&J, which shows such polar diagrams for  $l = 0, 1, 2$ . To visualize the rotational symmetry we can imagine that these polar diagrams are rotated around the  $z$ -axis. We then obtain three-dimensional polar “diagrams”, where each of the curves in the book creates a two-dimensional surface. For  $|Y_{00}|^2$ , e.g., this surface is a sphere with radius  $1/4\pi$ . The figure below shows sketches of such surfaces for  $|Y_{00}|^2$ ,  $|p_z|^2 = |Y_{10}|^2 = \cos^2 \theta \cdot 3/4\pi$ , together with  $|Y_{20}|^2 = (3 \cos^2 \theta - 1)^2 \cdot 5/16\pi$ .

<sup>9</sup>By superposing many such angular functions with sufficiently large quantum numbers, it is possible to describe a “wave packet” with small extension in angular space. This is relevant if we want to describe a rotator with a reasonably well-defined “direction”  $\theta, \phi$  at a given point in time.



By rotating the sketch for  $|p_z|^2$  by 90 degrees with respect to the  $y$ -axis (or the  $x$ -axis) you can obtain the corresponding surfac for  $|p_x|^2$  (or  $|p_y|^2$ ).

For the real functions  $p_x$ ,  $p_y$  and  $p_z$  it can even be interesting to make polar diagrams for the functions themselves (not only for the absolute squares as above). Since these functions take both positive and negative values, we choose to show their absolute values  $|p_x|$ ,  $|p_y|$  and  $|p_z|$ . The figure below shows the polar diagram for  $\sqrt{4\pi/3} |p_z| = |\cos \theta|$  (which simply consists of two circles touching each other), together with the corresponding two-dimensional surfaces, which are rotationally symmetric with respect to respectively the  $x$ -,  $y$ - and  $z$  axes. The signs indicate where the functions  $p_x$  etc are positive or negative. These signs at the same time tells us that these functions have parity  $-1$ ; they are antisymmetric with respect to the origin.



The  $p$ -state  $p_{\hat{n}}$  mentioned above is of the same type, with the unit vector  $\hat{n}$  as symmetry axis. Angular functions of this type are relevant in the discussion of hybridized orbitals.

(vi) The degeneracy in this problem, the fact that we have  $g_l = 2l + 1$  states with the same energy, is caused by the spherical symmetry. We have a *free* rotator, where no forces act along the spherical surface. Thus no particular direction is favoured. This degeneracy, where the energy levels are independent of the quantum number  $m$ , is common for all spherically symmetric potentials.

**A small exercise:** Suppose that the rigid rotator is prepared in the state

$$p_x = \sqrt{\frac{3}{4\pi}} \frac{x}{r} = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi = -\frac{1}{\sqrt{2}} (Y_{11} - Y_{1,-1}),$$

and that the energy  $E$  and the  $z$ -component  $L_z$  of the angular momentum are measured. Find the possible results of the measurements and the probabilities for these results. What can you say about the state of the rotator after such a measurement?

Answer:  $E = E_1 = \hbar^2 / (\mu r_0^2)$  with probability 1.  $L_z = \pm \hbar$  with 50 % probability for each of these results. After the measurement of  $L_z = \pm \hbar$  the state is  $Y_{1,\pm 1}$ . (Cf the measurement postulate in Lecture notes 2.)

**A small challenge:** Suppose that the rotator is prepared in the state  $Y = C \sin \theta$ .

1. Show that  $C = \sqrt{3/8\pi}$  gives a normalized state.
2. Show that this state is an eigenfunction of  $\hat{L}_z$ .
3. Suppose that we measure  $L_z$  and the energy when the rotator is in the state  $Y$ . What result do we then measure for  $L_z$ ? According to section 2.5 in Lecture notes 2 the probability amplitude that these measurements leave the rotator in a given state  $Y_{\text{after}}$  is given as the projection of the state *before* the measurement onto the state *afterwards*,  $\langle Y_{\text{after}}, Y \rangle$ . Why can the energy measurement not give the energy  $E_1$  (1. excited level)? [Hint: Consider the parities of  $Y$  and the relevant final states.]
4. Find the probability of measuring the ground-state energy  $E_0$  (and leaving the rotator in the ground state.) [Answer: 0.9253.]

Let us finish this section by simulating a large number  $N$  of position measurements for the particle on the spherical surface. For the ground state  $Y_{00}$ , with the probability density  $|Y_{00}|^2 = 1/4\pi$  in the angular space, these positions will be distributed (fairly) evenly over the whole surface. This is illustrated for  $N = 500$  in the figure on the left below. The figure on the right shows a corresponding distribution for the  $p_z$  state  $Y_{10}$ . Here you can see that the density is largest in the “polar areas” and small near the “equator”. The Matlab program “rotator.m” which was used to produce these distributions is available on the homepage. Try to run it, and observe that you can rotate the figures.



## 5.4 Motion in spherically symmetric potential. Radial equation

(Hemmer 5.6, B&J 7.2, Griffiths 4.1.)

When we allow also for motion in the radial direction, in a spherically symmetric potential  $V(r)$ , we can return to the Hamiltonian (T5.16), on the form <sup>10</sup>

$$\widehat{H} = \widehat{K} + V(r) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} + V(r). \quad (\text{T5.39})$$

Here, we note that the first term on the right is the radial part  $\widehat{K}_r$  of the operator  $\widehat{K}$  for the kinetic energy. Note that the angular part,  $\widehat{K}_L = \widehat{\mathbf{L}}^2/(2mr^2)$ , has the same form as for the

<sup>10</sup>Here, we take the risk of using the old symbol  $m$  for the mass, even if the same  $m$  is also used for the magnetic quantum number.

rotator.

Since the angular differentiations in  $\widehat{\mathbf{L}}^2$  and  $\widehat{L}_z$  commute both with  $\partial/\partial r$  and with the  $r$ -dependent factors, we note that  $\widehat{H}$ ,  $\widehat{\mathbf{L}}^2$  and  $\widehat{L}_z$  are a set of commuting operators. The simultaneous eigenfunctions of these operators must be proportional to both  $e^{im\phi}$  and  $\Theta_{lm}(\theta)$ , that is, to  $Y_{lm} = \Theta_{lm}(\theta)e^{im\phi}$ :

$$\boxed{\psi_{Elm}(r, \theta, \phi) = R_{El}(r)Y_{lm}(\theta, \phi)} = R_{El}(r)\Theta_{lm}(\theta)e^{im\phi}. \quad (\text{T5.40})$$

Here we have succeeded in factorizing the dependence on the three variables  $r$ ,  $\theta$  and  $\phi$ . You should also notice that the angular functions are the same, no matter which potential  $V(r)$  we are considering.

The **radial function**  $R(r)$ , on the other hand, depends on the potential. Inserting into the time-independent Schrödinger equation  $\widehat{H}\psi = E\psi$ , we note that  $\widehat{\mathbf{L}}^2$  applied to the angular function  $Y_{lm}$  gives the factor  $\hbar^2 l(l+1)$ . Thus all the terms in the equation become proportional to  $Y_{lm}$ , and we are left with a second-order differential equation for the radial function, **the radial equation**

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left\{ \frac{2m}{\hbar^2} [E - V(r)] - \frac{l(l+1)}{r^2} \right\} R = 0. \quad (\text{T5.41})$$

As we shall see, this equation determines the allowed energy eigenvalues  $E$  and the corresponding radial functions  $R_{El}(r)$ . Note that the quantum number  $m$  does not occur in this equation. Therefore the energy levels will be independent of this quantum number; we have the so-called  *$m$ -degeneracy* for spherically symmetric potentials.

You should now have a look at section 7.2 in B&J. There you will see that it is an advantage to introduce the function  $u(r) = rR(r)$  instead of the radial function  $R(r)$ . The substitution

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) = \frac{u(r)}{r}Y_{lm}, \quad \frac{dR}{dr} = \frac{u'}{r} - \frac{u}{r^2}, \quad \frac{d^2 R}{dr^2} = \frac{u''}{r} - \frac{2u'}{r^2} + \frac{2u}{r^3}$$

gives a radial equation for the function  $u(r)$  with the same form as the one-dimensional time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x).$$

This “one-dimensional” radial equation for the function  $u(r)$  is:

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} + V_{\text{eff}}^l(r) u(r) = E u(r)}. \quad (\text{T5.42})$$

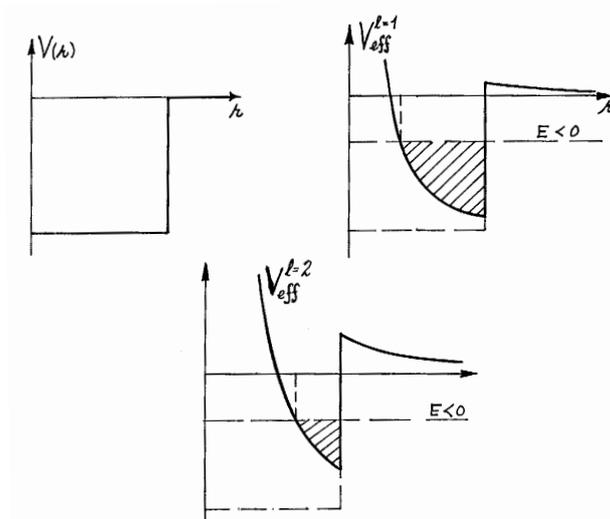
Here,

$$V_{\text{eff}}^l(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$$

is the sum of the real potential  $V(r)$  and the  $l$ -dependent **centrifugal term**  $l(l+1)\hbar^2/2mr^2$ . For a particle with angular momentum  $|\mathbf{L}| = \hbar\sqrt{l(l+1)}$ , we see that this term, seen from

a “one-dimensional” viewpoint, acts as a (fictitious) repulsive potential proportional to  $1/r^2$  and to  $l(l+1)\hbar^2$ . This term will therefore make the region close to the origin less accessible the larger  $l$  is.

The big advantage of this radial equation for  $u(r) = rR(r)$  on one-dimensional form is that we can reason in just the same way that we are used to for one-dimensional problems, as regards curvature, classical turning points (actually turning radii in this case), classically allowed and forbidden regions, zeros, etc.



The figure shows the effective potentials for  $l = 1$  and  $l = 2$ , for the case that the potential itself is a spherical well. In general we must have some kind of “well” in order for bound states to exist. As illustrated in the figure, the “effective” well becomes smaller the larger the angular momentum ( $l$ ) is. From these sketches, it should be obvious that the ground state for a potential  $V(r)$  will in general be a so-called  $s$ -state, that is, a state with  $l = 0$ , because the “effective” well for  $l = 0$  is deepest. Examples are the ground states of the hydrogen atom and of the three-dimensional harmonic oscillator.

For a given value of  $l$ , that is, for a given effective potential  $V_{\text{eff}}^l(r)$ , we can expect to find several radial functions  $u(r)$  corresponding to bound states, provided that the effective well is sufficiently big. Of these states, the one with the lowest energy will have zero nodes (no zero), that is, it will have minimal curvature and minimal radial kinetic energy. For the other states, the energy will increase with the number of nodes, which is called the **radial quantum number** ( $n_r$ ). For a given  $l$ , we thus find a set of states with energies  $E_{n_r l}$  such that

$$E_{0l} < E_{1l} < E_{2l} < E_{3l} < E_{4l} \dots$$

The “moral” is that the energy eigenvalues for a spherically symmetric potential normally depends both on  $l$  and the radial quantum number  $n_r$ , which gives the number of zeros in the radial function, but not on the magnetic quantum number  $m$ , which does not enter the radial equation. This means that the degeneracy of such an energy level is equal to the number of  $m$ -values,  $g_l = 2l + 1$ . This degeneracy is characteristic for the spherical symmetry. For the Coulomb potential ( $\propto 1/r$ ), something special happens. For this potential, the energies turn out to depend only on the sum of the quantum numbers  $l$  and  $n_r$ . This means that several  $l$ -values give the same energy, so that the degree of degeneracy becomes larger. More about that later.

If  $V(r)$  approaches zero for large  $r$  (as the centrifugal term does), the bound states must have negative energies,  $E < 0$ . Then  $u'' \approx -(2mE/\hbar^2)u \equiv \kappa^2 u$  for large  $r$ , and it follows that the asymptotic behaviour for large  $r$  is given by  $u \propto e^{\pm\kappa r}$ . Here only the exponentially decreasing solution is acceptable as an eigenfunction. Thus we have <sup>11</sup>

$$u(r) \propto e^{-\kappa r}, \quad \kappa \equiv \sqrt{-2mE/\hbar^2} \quad (r \rightarrow \infty). \quad (\text{T5.43})$$

For *positive* energies,  $E > 0$ , one finds a continuous spectrum of *unbound* states. For large  $r$  we then have  $u'' \approx -(2mE/\hbar^2)u \equiv -k^2 u$ , and it follows that the asymptotic behaviour for large  $r$  is given by  $u(r) \sim \sin(kr + \alpha_l)$ . Such solutions are relevant when one considers *scattering* on a potential  $V(r)$ .

It is also possible to find the general behaviour of the radial functions  $u_l(r)$  for *small*  $r$ , without specifying the potential. Provided that the potential  $V(r)$  is less singular than  $1/r^2$  (that is, approaches infinity slower than  $1/r^2$ ), we note that (for  $l > 0$ ) the centrifugal term will dominate over the other terms in the differential equation for small  $r$ , so that

$$\frac{d^2 u}{dr^2} \simeq \frac{l(l+1)}{r^2} u \quad (r \rightarrow 0).$$

By setting  $u(r) = c_0 r^s + c_1 r^{s+1} + \dots$ , we can then determine the exponent  $s$  in the dominant power for small  $r$ . We find the two solutions  $s = l + 1$  and  $s = -l$ . The last one gives a non-normalizable wave function, which is not acceptable. (The integral  $\int_0^\infty |u(r)|^2 dr$  does not exist.) Thus the dominant power in  $u(r)$  for small  $r$  is given by

$$u_l(r) \simeq c_0 r^{l+1} \quad \text{dvs} \quad R_l(r) \simeq c_0 r^l \quad (r \rightarrow 0). \quad (\text{T5.44})$$

This argument, which holds for bound as well as unbound states, is valid for  $l \geq 1$ . However, it can be shown that the result holds also for  $l = 0$ : <sup>12</sup>

$$u_{l=0}(r) \simeq c_0 r^1 = c_0 r, \quad \text{that is,} \quad R_{l=0} \simeq c_0 \quad (r \rightarrow 0).$$

The factor  $r^{l+1}$  implies that the wave function for small  $r$  becomes more suppressed the larger  $l$  is. This can also be understood qualitatively from the diagram above: We see that the effective potentials make the region for small  $r$  more and more “forbidden” the larger  $l$  is.

**A small exercise:** For a sufficiently large  $l$ , the effective potential  $V_{\text{eff}}^{(l)}(r)$  for the spherical well discussed above will be positive for all  $0 \leq r < \infty$ . Why can there not be any bound states for such a value of  $l$ ? [Hint: Can an energy eigenvalue be lower than the “bottom” of the effective potential?]

<sup>11</sup>For the ground state of the Coulomb potential,  $\psi = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$ , the exact result is  $u \propto r \exp(-\kappa r)$ . It turns out that the solutions  $u_l$  for the Coulomb potential in general are given by the exponential function multiplied by a polynomial in which the dominant power for large  $r$  is  $r^n$ , where  $n$  is the principal quantum number. Thus, asymptotically we have

$$u_l(r) \simeq C r^n e^{-\kappa r} \quad (r \rightarrow \infty).$$

<sup>12</sup>The ground state  $\psi = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$  of the hydrogen atom provides an example of this behaviour.

## 5.5 The Coulomb potential

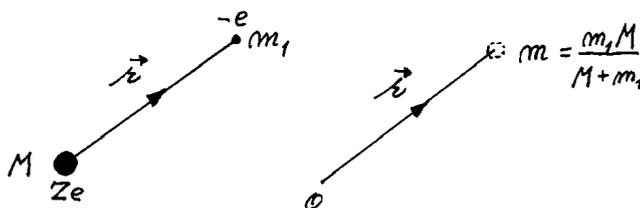
(Hemmer 5.7, B&J 7.5, Griffiths 4.2.)

### 5.5.a Hydrogenlike system reduced to one-particle problem

The Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$$

describes the interaction between two particles forming a **hydrogenlike system**. One of these particles usually is a nucleus with charge  $Ze$ , while the other one often (but not always) is an electron with charge  $-e$ .



Here the masses of the two particles are denoted respectively by  $M$  (the “nuclar” mass) and  $m_1$  (the “electron” mass). As shown in an exercise, the relative motion of the two particles is described by the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(r) \psi(\mathbf{r}) = E \psi(\mathbf{r}),$$

where  $\mathbf{r}$  is the **relative coordinate** (the distance vector from  $M$  to  $m_1$ ) and

$$m = \frac{m_1 M}{M + m_1} = \frac{m_1}{1 + m_1/M}$$

is the **reduced mass** of this two-particle system.

Formally, this Schrödinger equation describes a one-particle system, where a (fictitious) particle with the reduced mass  $m$  is moving in a static Coulomb potential. Thus, as far as the *relative* motion of the two particles is concerned, the system is *effectively reduced* to a one-particle system. (In the exercise it is shown that the motion of the center of gravity of the system is described by the Schrödinger equation for a free particle.)

The central example is the hydrogen atom, which corresponds to  $Z = 1$ ,  $m_1 = m_e$ ,  $M = m_p$  and hence a reduced mass <sup>13</sup>

$$m = \frac{m_e}{1 + m_e/m_p} \approx 0.9995 m_e.$$

The fact that  $m$  lies so close to  $m_e$  simply means that no big mistake is made by neglecting the motion of the proton from the beginning, calculating as if the proton were at rest (cf an earlier exercise). However, as we have just seen, it is very easy to improve on this approximation, calculating with the reduced mass. This means e.g. that the binding energies are reduced by  $\sim 0.05\%$ .

In an introductory course in chemical physics, the hydrogen atom is a very important topic for several reasons:

<sup>13</sup>Other examples are the ions  $\text{He}^+$  ( $Z = 2$ ),  $\text{Li}^{++}$  ( $Z = 3$ ) etc, which all are one-electron systems.

- This system is the first testing ground for any theory which aims to explain the structure of atoms and molecules
- In a certain sense, the hydrogen atom is the only atom which is “exactly solvable”
- For heavier atoms, the mathematics is much more complicated, and accurate solutions for wave functions and energies can only be obtained by the application of advanced numerical methods. These methods are far beyond the scope of the present course, where we have to confine ourselves to qualitative considerations. In such considerations, the explicit solutions for the hydrogen orbitals serve as an important background for the discussion.

### 5.5.b Energy quantization

In section 5.4 above, we found that the simultaneous eigenfunctions of  $\widehat{H}$ ,  $\widehat{L}^2$  and  $\widehat{L}_z$  can be written as

$$\psi(r, \theta, \phi) = R_l(r) Y_{lm}(\theta, \phi) = \frac{u_l(r)}{r} Y_{lm}(\theta, \phi). \quad (\text{T5.45})$$

The spherical harmonics  $Y_{lm}(\theta, \phi)$ , which describe the angular dependence of the energy eigenfunctions, were studied in great detail in sections 5.2 and 5.3. We have also seen that the radial function  $u_l(r)$  for a given value of  $l$  satisfies the “one-dimensional” radial equation

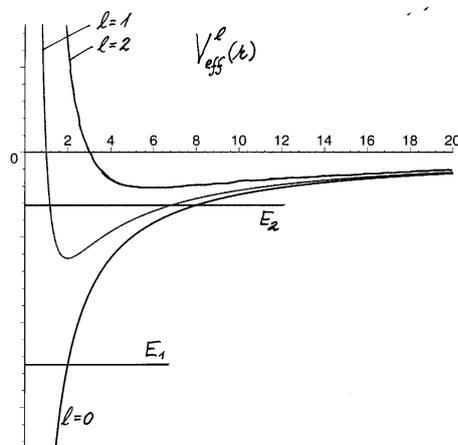
$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{\text{eff}}^l(r) \right] u_l(r) = E u_l(r), \quad u_l(0) = 0, \quad (\text{T5.46})$$

where  $V_{\text{eff}}^l(r)$  is the sum of the real potential and the centrifugal term  $\hbar^2 l(l+1)/(2mr^2)$ . This is the equation that determines the energies of the ground state and the excited levels of the hydrogenlike atom, and the corresponding radial functions  $u(r) = rR(r)$ .

The figure shows the effective potentials,

$$V_{\text{eff}}^l(r) = -\frac{Z e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2 l(l+1)}{2mr^2}, \quad (\text{T5.47})$$

for  $l = 0, 1$  and  $2$ .



### Qualitative discussion

Taking this diagram and the radial equation above as our starting point, we can understand a lot without much calculation:

- For each value of the orbital angular-momentum quantum number  $l$ , we have a one-dimensional problem; cf equation (T5.46), with an “effective potential well”  $V_{\text{eff}}^l(r)$  which approaches zero as  $r \rightarrow \infty$ . Bound states in such a well must then have negative, quantized energies, and for each of these energies there will be one solution  $u(r)$ , as we are used to for one-dimensional potentials.
- For a given (given  $l$ ) the solution with the lowest energy will have zero nodes (when we do not count the zero at the origin). The solution with the second lowest energy will have one zero, etc. The number of nodes is called the **radial quantum number**,  $n_r$ . The energy increases with  $n_r$ , because more nodes means faster curvature (cf the experience with the one-dimensional box or oscillator).
- As shown in the figure, the depth of the “effective” well decreases for increasing  $l$ . The well for  $l = 0$  is deepest. We must therefore expect to find the lowest energy (the ground-state energy) for  $l = 0$  and  $n_r = 0$ .
- The ground state is essentially already known, from an exercise. There we used a slightly different potential,  $V = -e^2/(4\pi\epsilon_0 r)$ , and the mass  $m_e$  (instead of the reduced mass  $m$ , as here), and we found that

$$\psi = (\pi a_0^3)^{-1/2} e^{-r/a_0}$$

is an energy eigenfunction with “extension”

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad (\text{the Bohr radius}),$$

and with the energy

$$E = -\frac{1}{2}\alpha^2 m_e c^2 = -\frac{\hbar^2}{2m_e a_0^2} \quad (\approx -13.6 \text{ eV}).$$

With the potential  $V = -Ze^2/(4\pi\epsilon_0 r)$  and the mass  $m$  it should then be rather obvious that we can replace  $e^2$  with  $Ze^2$  and  $m_e$  with  $m$  in the formulae above, so that the corresponding energy eigenfunction becomes

$$\psi = (\pi a^3)^{-1/2} e^{-r/a},$$

with the “extension”

$$a = \frac{4\pi\epsilon_0\hbar^2}{(Ze^2)m} = a_0 \cdot \frac{m_e}{m} \cdot \frac{1}{Z} \quad (\text{T5.48})$$

and the energy

$$E_1 = -\frac{\hbar^2}{2ma^2} = -\frac{\hbar^2}{2m_e a_0^2} \cdot \frac{m}{m_e} \cdot Z^2. \quad (\text{T5.49})$$

**Exercise:** Show this using the Hamiltonian

$$\widehat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{L}^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}.$$

The “moral” is that the “extension” of the ground-state orbital for this hydrogenlike atom **scales** as  $m_e/m$  and as  $1/Z$ , while the energy scales as  $m/m_e$  and as  $Z^2$ . We shall soon see that the excited states “scale” in exactly the same manner.

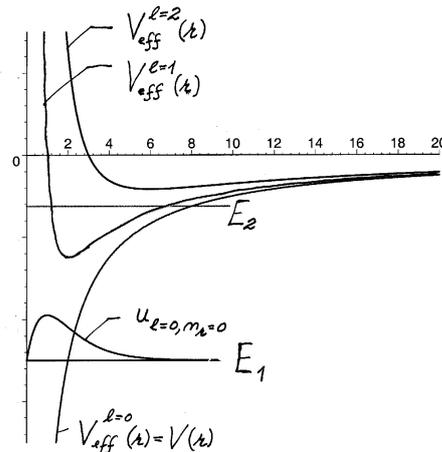
- Why is the state  $\psi$  above the ground state? Answer: Firstly, it is spherically symmetric and therefore has zero angular momentum. Therefore,

$$u = rR \propto r\psi \propto r e^{-r/a}$$

must be a solution for the  $l=0$ -well.

**Exercise:** Check this using (T5.46) and (T5.47).

Secondly, this solution has no node, and then it must be the “ground state”  $u_{(l=0, n_r=0)}$  of this well. Since this well for  $l=0$  is the deepest one, we then understand that  $\psi = u_{l=0, n_r=0}/r \propto e^{-r/a}$  is the true ground state of the hydrogenlike atom. In the figure below, we have drawn the “energy line”  $E_1$  and, with this line as abscissa, the “ground state”  $u_{n=0, n_r=0} \propto r e^{-r/a}$  of the well with  $l=0$  as a function of  $r/a$ .



- As you can see, the energy  $E_1$  lies lower than the bottom of the “next” well,  $V_{\text{eff}}^{l=1}(r)$ . In the diagram we have also drawn the energy line ( $E_2$ ) for the state with the lowest energy in the well with  $l=1$  (that is, the “ground state” of *this* well, which is the state  $u_{l=1, n_r=0}$ ). This energy of course must lie above the bottom of this well. Then what about the next-lowest energy for the *deepest* well (corresponding to the “first excited” state of the  $l=0$  well,  $u_{(l=0, n_r=1)}$ , with one zero)? Strangely enough, the energy of this state turns out to be the same ( $E_2$ ) as for the state  $u_{l=1, n_r=0}$ . So the energy  $E_2$  is the first excited level of the hydrogenlike atom, and this level is degenerate; the energy  $E_2$  is shared by the four states

$$\begin{aligned} \psi &= \frac{u_{(l=0, n_r=1)}}{r} Y_{00} \quad \text{and} \\ \psi &= \frac{u_{(l=1, n_r=0)}}{r} Y_{1m}(\theta, \phi), \quad m = 0, \pm 1. \end{aligned} \quad (\text{T5.50})$$

(See below, about the “l-degeneracy”.)

- The classical turning radii for a solution  $u_l(r)$  with energy  $E$  are the points where the energy line crosses the effective potential  $V_{\text{eff}}^l(r)$ . The inner turning radius is equal to zero for  $l = 0$ . For  $l > 0$ , this radius  $r_{\text{inner}}$  is larger than zero, so that the region near the origin is classically forbidden. This is reflected by the general behaviour which was studied above, in section 5.4; cf equation (T5.44):

$$u_l(r) \sim r^{l+1} \quad \text{for small } r. \quad (\text{T5.51})$$

- For bound states ( $E < 0$ ), which is our main concern presently, we have an outer turning radius (in addition to the inner one), and also the region outside  $r_{\text{outer}}$  is classically forbidden. This is reflected by the fact that  $u_l(r)$  decreases essentially exponentially for large  $r$ . Asymptotically, it was found in (T5.43) that

$$u_l(r) \propto e^{-\kappa r} \quad \text{for large } r \quad (\kappa = \sqrt{-2mE/\hbar^2}). \quad (\text{T5.52})$$

- Since  $u_l(r)$  curves *outwards* from the axis in the forbidden regions, we note that the  $n_r$  nodes must lie in the classically allowed regions, between the inner and the outer turning radius. [As mentioned before, the zero at the origin is not counted.]

**Exercise:** What we know about the “ground state” of the well  $V_{\text{eff}}^1(r)$  for  $l = 1$ ,  $u_{(l=1, n_r=0)}$ , is that it goes as  $r^{l+1} = r^2$  for small  $r$  and as  $e^{-\kappa r}$  for large  $r$ . Since it does not have any nodes ( $n_r = 0$ ), it is tempting to insert a trial solution  $u = r^2 e^{-\kappa r}$  in (T5.46). Show that this function in fact is a solution, with the energy  $E = E_1/4$ , when  $\kappa$  is set equal to  $1/2a$ . (You can find  $a$  and  $E_1$  in (T5.48) and (T5.49).)

### General method of solution for the radial equation (T5.46)

All the properties mentioned above are verified by the explicit solutions for the radial functions. How these solutions can be derived is beautifully described in section 5.7 in Hemmer and in section 7.5 in B&J, which you are now advised to study. Note that the dimensionless variable which is introduced instead of  $r$  can be written as

$$\rho = r\sqrt{-8mE/\hbar^2} \equiv 2\kappa r, \quad (\text{T5.53})$$

so that the acceptable asymptotic behaviour that was found above for large  $r$  (or  $\rho$ ) becomes

$$u_l(\rho) \propto e^{-\kappa r} = e^{-\rho/2}.$$

Note also that the other dimensionless variable,  $\lambda$ , is an indirect measure of the energy:

$$\lambda \equiv \frac{Ze^2}{4\pi\epsilon_0\hbar} \sqrt{\frac{m}{-2E}} = Z\alpha \sqrt{\frac{mc^2}{-2E}} \quad \Longleftrightarrow \quad E = -\frac{1}{2}(Z\alpha)^2 \frac{mc^2}{\lambda^2}. \quad (\text{T5.54})$$

Otherwise, the procedure is the same as the one used for the harmonic oscillator, where we successfully “factored out” the asymptotic factor  $\exp(-m\omega q^2/2\hbar) = \exp(-x^2/2)$ , which appeared in all the eigenfunctions. We can hope for a similar success here, by writing

$$u(\rho) = e^{-\rho/2}v(\rho).$$

By calculating

$$\frac{du}{d\rho} = e^{-\rho/2}(v' - \frac{1}{2}v) \quad \text{and} \quad \frac{d^2u}{d\rho^2} = e^{-\rho/2}(v'' - v' + v/4)$$

and inserting in (T5.46), you will find that the function  $v(\rho)$  must satisfy the differential equation

$$v'' - v' + \frac{\lambda}{\rho}v - \frac{l(l+1)}{\rho^2}v = 0. \quad (\text{T5.55})$$

We attempt to solve this equation by an infinite power series in  $\rho$ . According to (T5.51) this series must start with the power  $\rho^{l+1}$ . With

$$v = \sum_{k=0}^{\infty} a_k \rho^{l+1+k}, \quad v' = \sum_{k=0}^{\infty} a_k (l+1+k) \rho^{l+k} \quad \text{and} \quad v'' = \sum_{k=0}^{\infty} a_k (l+1+k)(l+k) \rho^{l+k-1}$$

you can notice that

$$\begin{aligned} v'' - \frac{l(l+1)}{\rho^2}v &= \sum_{k=0}^{\infty} a_k [(l+1+k)(l+k) - l(l+1)] \rho^{l+k-1} \\ &= \sum_{k=0}^{\infty} a_k [k(2l+1+k)] \rho^{l+k-1} = \sum_{k=1}^{\infty} a_k [k(2l+1+k)] \rho^{l+k-1}, \end{aligned}$$

since  $k=0$  does not contribute. Also the contributions from the remaining terms in (T5.55) can be written as sums starting with  $k=1$ , with powers  $\rho^{l+k-1}$ :

$$\begin{aligned} -v' + \frac{\lambda v}{\rho} &= -\sum_{k=0}^{\infty} a_k [l+1+k-\lambda] \rho^{l+k} \\ &= -\sum_{k=1}^{\infty} a_{k-1} [l+k-\lambda] \rho^{l+k-1}. \end{aligned}$$

Inserting into (T5.55) we then find that the coefficient multiplying the power  $\rho^{l+k-1}$  adds up to

$$a_k k(2l+1+k) - a_{k-1}(l+k-\lambda).$$

The equation requires that all these coefficients are equal to zero. This gives the recursion relation

$$a_k = a_{k-1} \frac{l+k-\lambda}{k(2l+1+k)}, \quad k = 1, 2, \dots$$

Using this, we find that

$$\begin{aligned} a_1 &= a_0 \frac{l+1-\lambda}{2l+2}, \quad a_2 = a_1 \frac{l+2-\lambda}{2(2l+3)} = a_0 \frac{(l+1-\lambda)(l+2-\lambda)}{(2l+2)(4l+6)}, \\ a_3 &= a_0 \frac{(l+1-\lambda)(l+2-\lambda)(l+3-\lambda)}{(2l+2)(4l+6)(6l+12)}, \quad \text{etc.} \end{aligned}$$

Thus the solution for  $u_l(\rho)$  becomes

$$\begin{aligned} u_l(\rho) &= e^{-\rho/2} v_l(\rho) = \rho^{l+1} e^{-\rho/2} [a_0 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 + \dots] \\ &= \rho^{l+1} e^{-\rho/2} a_0 \left[ 1 + \frac{l+1-\lambda}{2l+2} \rho + \frac{(l+1-\lambda)(l+2-\lambda)}{(2l+2)(4l+6)} \rho^2 + \dots \right]. \quad (\text{T5.56}) \end{aligned}$$

As explained in the book, the infinite series inside the brackets behaves as  $\exp(+\rho)$  for large  $\rho$ , if the series does not terminate. This will give a “solution”  $u_l(\rho)$  which behaves asymptotically as a power of  $\rho$  multiplied by  $\exp(+\rho/2)$ . This solution diverges for large  $\rho$  and therefore is not an eigenfunction. Thus, in order to provide an eigenfunction, the series must *terminate*. The above expression shows that this happens only if  $\lambda$  is equal to  $l + 1$ , or to  $l + 2$ , or in general to  $l + 1 + n_r$ , where  $n_r$  is a non-negative integer:

$$\lambda = l + 1 + n_r, \quad (n_r = 0, 1, 2, \dots).$$

The above expression inside the brackets then becomes a polynomial of degree  $n_r$ ,

$$[ ] = 1 + \frac{-n_r}{2l+2}\rho + \frac{-n_r(-n_r+1)}{(2l+2)(4l+6)}\rho^2 + \frac{-n_r(-n_r+1)(-n_r+2)}{(2l+2)(4l+6)(6l+12)}\rho^3 + \dots$$

For  $n_r = 0$ , we see that  $[ ] = 1$ . For  $n_r = 1$ , we get a linear expression,  $[ ] = 1 - \rho/(2l+2)$ , with a zero at  $\rho = 2l+2$ , etc. In general, the polynomial ensures that the radial function gets  $n_r$  zeros, which all are found in the classically allowed region between the inner and outer turning radii (cf the discussion p 34). Thus we can identify the integer  $n_r$  as the **radial quantum number** discussed on p 32. Note that with this method we have in “one stroke” found all the radial functions, for  $l = 0, 1, 2, \dots$  and, for each of these, for  $n_r = 0, 1, 2, \dots$ . These radial functions will be studied more closely in what follows.

The above derivation shows that the energy quantization is due to the criterion that terminates the series, which leads to the integer values of  $\lambda = l + 1 + n_r$ ; inserting this in (T5.54) we have

$$E = -\frac{1}{2}(\alpha Z)^2 \frac{mc^2}{(l+1+n_r)^2} \equiv -\frac{1}{2}(\alpha Z)^2 \frac{mc^2}{n^2} \equiv E_n, \quad (\text{T5.57})$$

where the integer  $l + 1 + n_r \equiv n$  is called the **principal quantum number**;

$$n = l + 1 + n_r; \quad l = 0, 1, 2, \dots; \quad n_r = 0, 1, 2, \dots \quad (\text{T5.58})$$

For each value of  $l$ , that is, for each of the effective potentials  $V_{\text{eff}}^l = -Ze^2/(4\pi\epsilon_0 r) + \hbar^2 l(l+1)/(2mr^2)$ , we thus find an infinite number of radial functions, with a number of zeros ( $n_r$ ) which varies from zero to infinity.<sup>14</sup>

The formula

$$E = -\frac{\frac{1}{2}(\alpha Z)^2 mc^2}{(l+1+n_r)^2}$$

shows that the energy increases (towards zero from below) when the number  $n_r$  of zeros increases, as expected. More zeros means a more “rapid” curvature and increasing radial kinetic energy  $\langle K_r \rangle$ . It is also not very surprising that the energy also increases with  $l$  for fixed  $n_r$ ; cf the effective potentials in the diagram p 31. This can also be understood

<sup>14</sup>Usually a well of finite depth can only accommodate a finite number of bound states. The fact that the number of bound states here is infinite is connected with the (slow) way that the Coulomb potential approaches zero for large distances  $r$ .

from the fact that increasing  $l$  means an increasing rotational part of the kinetic energy,  $\langle K_L \rangle = \langle \mathbf{L}^2 / 2mr^2 \rangle = \hbar^2 l(l+1) \langle 1/r^2 \rangle / 2m$ .

Note also that the energy eigenvalues are proportional to  $Z^2$  and to  $m$ , as found for the ground state.

**Exercise:** Show that the energy  $E_n$  can be expressed in terms of the length  $a$  given in (T5.48):

$$E_n = -\frac{\hbar^2}{2ma^2} \frac{1}{n^2}.$$

### 5.5.c Degeneracy

The funny thing about these energy eigenvalues is that they depend only on  $n = l + 1 + n_r$ , that is, on the *sum* of the two quantum numbers  $l$  and  $n_r$ . This means that if we increase  $l$  or  $n_r$  with 1, then we get the same increase in the energy. The explanation lies in the special  $1/r$ -form of the Coulomb potential, which causes a much higher degree of degeneracy than we usually find for a spherically symmetric potential.

In order to find the degeneracy of the energy level  $E_n$  we only need to count the number of possible  $l$ -values for the principal quantum number  $n$ . Since  $n_r$  is a non-negative integer, we see that  $l$  for a given  $n$  can take the values <sup>15</sup>

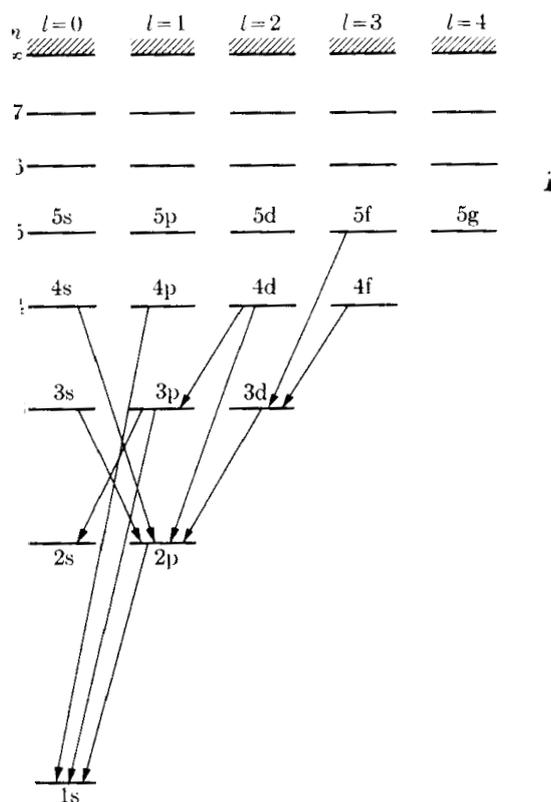
$$l = 0, 1, 2, \dots, n - 1. \quad (\text{T5.59})$$

For each of these  $l$ -values, the number of  $m$ -values is  $2l + 1$ . The (degree of) degeneracy then is given as the sum of an arithmetic series with  $n$  terms:

$$g_n = \sum_{l=0}^{n-1} (2l + 1) = (1) + (3) + (5) + \dots + (2n - 1) = \frac{1}{2} \cdot n \cdot [(1) + (2n - 1)] = n^2. \quad (\text{T5.60})$$

It is customary to draw an energy level diagram which shows the allowed  $l$ -values for each principal quantum number  $n$ . In the following diagram we illustrate in addition the allowed quantum jumps, which give rise to the spectral lines of hydrogen; cf the discussion in Lecture notes 1 of the Balmer series (caused by the transitions  $n \rightarrow 2$ ), the Lyman series (caused by the transitions  $n \rightarrow 1$ ), etc.

<sup>15</sup>That the energy  $E_n$  this way is independent of  $l$  is called  $l$ -degeneracy.



These transitions correspond to the selection rules

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1, \quad (\text{T5.61})$$

which in reality are due to the conservation of angular momentum; the emitted photon has an intrinsic angular momentum (the so-called spin) corresponding to an angular-momentum quantum number 1.

### 5.5.d Radial functions and complete wave functions

With  $\lambda = n$  we can write the radial functions (T5.56) as

$$u_{nl}(\rho) = \rho^{l+1} e^{-\rho/2} a_0 \left[ 1 + \frac{-n_r}{2l+2} \rho + \frac{-n_r(-n_r+1)}{(2l+2)(4l+6)} \rho^2 + \frac{-n_r(-n_r+1)(-n_r+2)}{(2l+2)(4l+6)(6l+12)} \rho^3 + \dots \right], \quad (\text{T5.62})$$

where  $n_r = n - l - 1$ . From this formula it is a simple matter to obtain formulae for  $R_{nl}(\rho) = u_{nl}/\rho$ . In order to translate from the dimensionless variable  $\rho$  to  $r$ , we insert the result for  $E_n$  in the definition (T5.53). The result can be written as

$$\rho = r \sqrt{-8mE_n/\hbar^2} = \frac{2r}{na}, \quad \text{with} \quad a \equiv \frac{1}{Z} \frac{m_e}{m} \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} \equiv \frac{1}{Z} \frac{m_e}{m} a_0, \quad (\text{T5.63})$$

where  $a_0 \approx 0.529 \cdot 10^{-10}$  m is the Bohr radius. This means that the factor  $\exp(-\kappa r) = \exp(-\rho/2)$ , which dominates the behaviour for large  $r$ , takes the form  $\exp(-r/na)$ . This factor decreases most slowly for large  $n$ . Cf the table below, which gives some of the radial functions  $R_{nl}(r)$ . See also the table p 363 in B&J, which gives some of the resulting energy eigenfunctions

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \phi).$$

The solutions  $u_{n0}(r)$  give a set of spherically symmetric  $s$ -waves  $\psi_{n00}$ , the solutions  $u_{n1}(r)$  give the  $p$ -waves  $\psi_{n1m}$ , the solutions  $u_{n2}(r)$  give  $d$ -waves  $\psi_{n2m}$ , etc.

These energy eigenfunctions satisfy the normalization condition

$$\int |\psi_{nlm}|^2 d^3r = \int_0^\infty [R_{nl}(r)]^2 r^2 dr \cdot \int |Y_{lm}(\theta, \phi)|^2 d\Omega = \int_0^\infty [u_{nl}(r)]^2 dr \cdot 1 = 1.$$

The table gives the normalized radial functions  $R_{nl}(r)$ .

### Radial functions for hydrogenlike atoms

$n$	$l$	$R_{nl}(r)$	
1	0	$R_{10}(r) = \frac{2}{a^{3/2}} e^{-r/a}$	1s
2	0	$R_{20}(r) = \frac{1}{\sqrt{2} a^{3/2}} (1 - \frac{r}{2a}) e^{-r/2a}$	2s
	1	$R_{21}(r) = \frac{1}{2\sqrt{6} a^{3/2}} \frac{r}{a} e^{-r/2a}$	2p
3	0	$R_{30}(r) = \frac{2}{3\sqrt{3} a^{3/2}} (1 - \frac{2r}{3a} + \frac{2r^2}{27a^2}) e^{-r/3a}$	3s
	1	$R_{31}(r) = \frac{8}{27\sqrt{6} a^{3/2}} \frac{r}{a} (1 - \frac{r}{6a}) e^{-r/3a}$	3p
	2	$R_{32}(r) = \frac{4}{81\sqrt{30} a^{3/2}} (\frac{r}{a})^2 e^{-r/3a}$	3d

Here we note the factors  $r^l$ , which make  $R_{nl}$  and  $\psi_{nlm}$  equal to zero at the origin, except for  $s$ -waves. (We remember that this is due to the centrifugal term.) We note also the polynomials of degree  $n_r$ , which take care of the zeros in the classically allowed regions.

The normalization formula above implies as you see that the probability of finding the particle at a distance in the interval between  $r$  and  $r + dr$  is  $[u_{nl}(r)]^2 dr$ . Thus the probability density per “unit radius”, the so-called **radial density**, is

$$P_{nl}(r) = [u_{nl}(r)]^2 = r^2 [R_{nl}(r)]^2. \quad (\text{T5.64})$$

On page 362 in B&J you will find diagrams showing  $P_{10}$ ,  $P_{20}$  and  $P_{21}$ . By the use of the radial density one can also in principle calculate the various expectation values which are

listed on page 372 in B&J. We note in particular that <sup>16</sup>

$$\langle 1/r \rangle_{nlm} = \int \frac{1}{r} |\psi_{nlm}|^2 d^3r = \int_0^\infty \frac{1}{r} P_{nl} dr = \frac{1}{n^2 a}. \quad (\text{T5.65})$$

The inverse of  $\langle 1/r \rangle_{nlm}$  can be used as a measure of the “radius” or the “extension” of a given orbital. We see that this rough measure goes as

$$n^2 a = n^2 \frac{1}{Z} \frac{m_e}{m} a_0.$$

The “moral” is that the excited states are strongly “inflated” compared to the ground state.

**Exercise:** Use (T5.65) to show that the *sum* of the expectation value  $\langle K_r \rangle$  of the radial part of the kinetic energy and the rotational part  $\langle K_L \rangle$  is independent of  $l$ , and is equal to the binding energy  $E_B = |E_n|$ , for the states  $\psi_{nlm}$ .

**Another one:** Show that the radial function  $R_{21}$  in the table above is normalized, and calculate  $\langle 1/r \rangle$  for the states  $\psi_{21m}$ .

The above results confirm that the wave function

$$\psi_{100} = R_{10} Y_{00} = \frac{u_{10}}{r} Y_{00} = (\pi a^3)^{-1/2} e^{-r/a} \quad \left( a = \frac{1}{Z} \frac{m_e}{m} a_0 \right)$$

describes the ground state, as discussed above. The fact that this is the state with the lowest possible energy is due to the independence of the angles ( $l = 0$ ) and the minimal radial variation ( $n_r = 0$ , no zeros).

As we have seen in an exercise, it is possible to find *other* functions (than  $\psi_{100}$ ) which give a smaller “quantum wildness”

$$\langle K \rangle = \frac{\hbar^2}{2m} \int |\nabla \psi|^2 d^3r.$$

This is achieved e.g. by using the formula above with a smaller  $a$ , but then  $\langle V \rangle$  increases. It is also possible to have a smaller  $\langle V \rangle$  than above (e.g. by using a *smaller*  $a$ ), but then  $\langle K \rangle$  becomes larger. However, the *sum*  $\langle K + V \rangle = \langle E \rangle$  is minimal (equal to  $E_1$ ) for the function  $\psi_{100}$  above. In general, it can be stated that:

The ground state (for any system) by definition is the energy eigenstate with the lowest possible energy, and this state minimizes the total energy  $\langle E \rangle = \langle K + V \rangle$ .

(T5.66)

This is the quantum-mechanical principle that determines the form and the size of e.g. a hydrogenlike atom, and also of more complicated systems like heavy atoms and more or less complicated molecules: The ground state is the “configuration” that minimizes the total

<sup>16</sup>The normalization integrals and these expectation value integrals can all be expressed in terms of sums of integrals of the type

$$\int_0^\infty r^n e^{-\beta r} dr = \frac{1}{\beta^{n+1}} \int_0^\infty x^n e^{-x} dx = \frac{n!}{\beta^{n+1}}.$$

energy, including the “quantum wildness”  $\langle K \rangle$  and all the contributions to the potential energy.

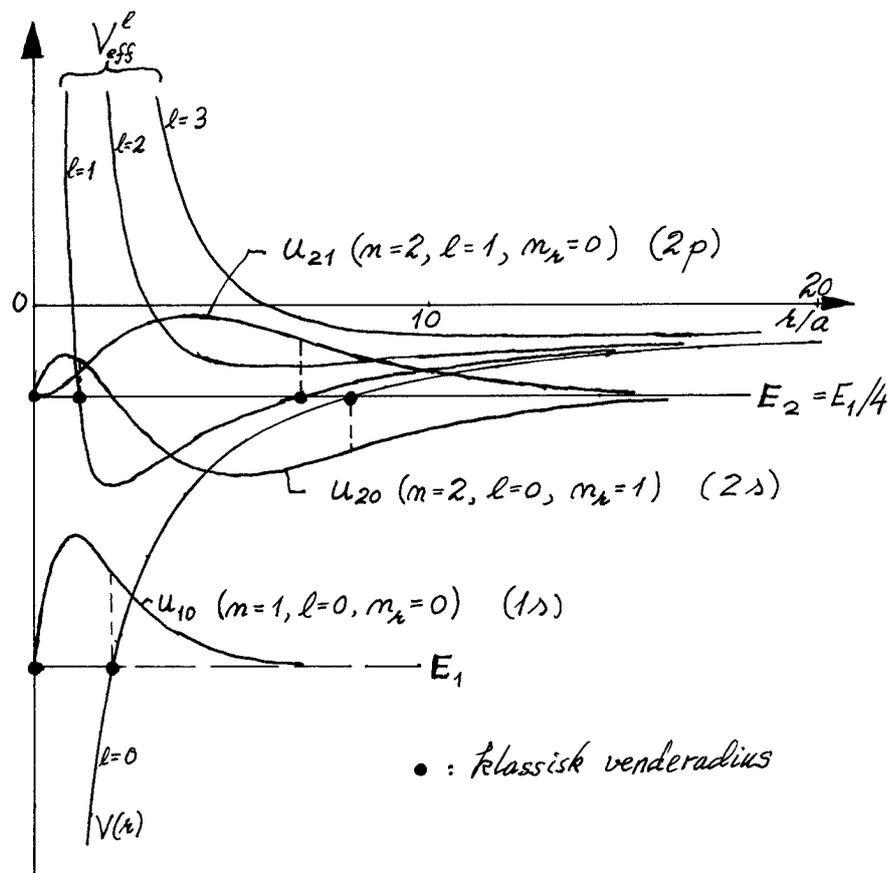
As we have seen, the size of the hydrogenlike atom in the ground state can be characterized by the “radius”

$$\langle 1/r \rangle^{-1} = a = a_0 \cdot 1/Z \cdot m_e/m,$$

where  $a_0$  is the Bohr radius and  $m$  is the reduced mass. The “moral” is that the radius of the ground state (and also of the excited states) “scales” with the factors  $m_e/m$  and  $1/Z$ . This is relevant for the hydrogenlike ions  $\text{He}^+$ ,  $\text{Li}^{++}$  etc.

From this scaling property it can also be inferred that the radius of the innermost orbit (the K-shell) in a many-electron atom will be *roughly*  $a_0/Z$ . Furthermore, the binding energy of a K-electron will be roughly a factor  $Z^2$  larger than in hydrogen ( $Z = 1$ ). This means that the K-electrons in the heaviest atoms have binding energies of the order of 100 keV, which is 20 % of the rest energy of the electron. Accurate calculations for such atoms therefore require relativistic theory.

The scaling with the factor  $m_e/m$  in the expression for the “radius” tells us that if e.g. a  $\pi^-$  meson (with mass  $m_{\pi^-} \approx 140 \text{ MeV}/c^2$ ) is captured by an atom, then it will eventually be found in orbitals lying much closer to the nucleus than the electronic orbitals.<sup>17</sup>



<sup>17</sup>The inner meson orbitals are so close to the nucleus that **strong interactions** (nuclear forces) between the  $\pi$  meson and the nucleons play a role, in addition to the Coulomb force, even if the nuclear force has a very short range, of the order of  $\sim 1 \text{ fm}$ . This is important for  $s$  orbitals, for which  $\psi$  is not equal to zero for  $r = 0$ .

In the figure we have again drawn the effective potentials, for  $l = 0, 1, 2, 3$ . As discussed above, the deepest well is the one for  $l = 0$ ,  $V_{\text{eff}}^0(r) = V(r)$ . One of the solutions for  $l = 0$  is  $u_{10} \propto r e^{-r/a}$ , which describes the ground state ( $1s$ ), with the energy  $E_1$ . In this state, we have seen that there is no angular dependence (zero angular momentum), while also the variation in the radial direction is minimal ( $n_r = 0$ , no zeros; cf the figure).

It is characteristic for all the *excited* states that the wave functions show *more variation*, in the radial and/or angular directions, so that the energy

$$E = \langle K_r + K_L + V \rangle = \langle K_r \rangle + \langle V_{\text{eff}}^l \rangle$$

becomes larger than  $E_1$ . If we choose e.g. to “excite the rotational degree of freedom”, corresponding to one of the angular functions  $Y_{1m}$  with  $l = 1$ , then the radial function must be one of the solutions for the effective well  $V_{\text{eff}}^1(r)$ . Among these the lowest energy is found for the  $2p$  solution  $u_{21}(r)$ , with  $n_r = 0$  (no zeros); see the figure. This solution has the energy  $E_2$ , and leads to the wave functions (orbitals)  $\psi_{21m} = r^{-1}u_{21}(r)Y_{1m}$  ( $m = 0, \pm 1$ ).

Alternatively, we can keep  $l = 0$  and instead “excite the radial degree of freedom”. We must then look for the  $s$ -state with the next-lowest energy, that is, the second solution for the “one-dimensional” potential  $V_{\text{eff}}^0 = V(r)$ . This is the  $2s$ -function  $u_{20}$ , with one zero. This increased variation in the radial direction implies a higher energy (than  $E_1$ ), corresponding to a larger outer turning radius. As we have seen this energy turns out to be exactly the same ( $E_2$ ) as for the solution  $u_{21}$ . As already mentioned, this so-called  $l$ -degeneracy is not accidental, but is due to a hidden symmetry property connected to the  $1/r$ -form of the Coulomb potential.

As illustrated in the diagram the classically allowed regions for the  $2s$  and  $2p$  states (limited by the classical turning radii) are much larger than for the ground state. This is reflected by the fact that  $\langle 1/r \rangle_{nlm}^{-1}$  increases as  $n^2 a$ .

For a potential  $V(r)$  which *deviates* from the  $1/r$  form, the “moral” of the discussion above is that the  $l$ -degeneracy goes away. This is the situation for the potential which is experienced by an electron in a many-electron atom. The force felt by a given electron at a distance  $r$  from the nucleus is the collective force from the nucleus and the part of the “electron cloud” which is inside a sphere of radius  $r$ . When this electron is far out (large  $r$ ), the resulting charge within the sphere is close to  $Ze - e(Z - 1) = e$  (because the other electrons are closer to the nucleus). When the electron is close to the nucleus, it feels only the unscreened force from the nuclear charge,  $-Ze^2/(4\pi\epsilon_0 r^2)$ . Clearly, this electron experiences a force which is not proportional to  $1/r$ .

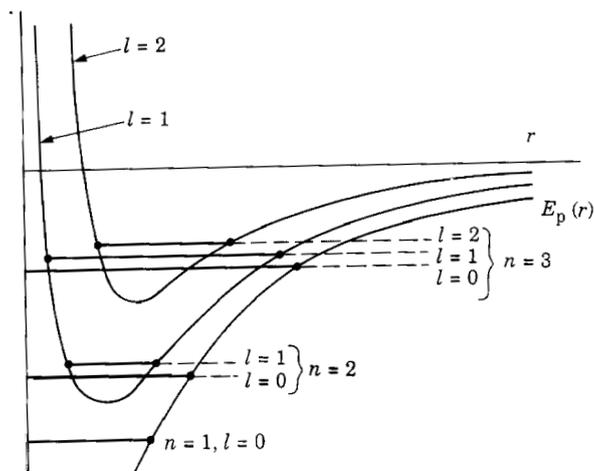
In such a potential, there is no  $l$ -degeneracy, so that the energy levels no longer depend solely on the *sum* of  $l$  and the radial quantum number  $n_r$ . It is customary to define a quantum number  $n$  also here, as

$$n = l + 1 + n_r,$$

as for the hydrogen atom. In this case, however, the energy is not specified by  $n$  alone; we need to specify both  $l$  and  $n_r$  or, equivalently,  $l$  and  $n$ :

$$E = E_{nl}.$$

It turns out that the energies  $E_{nl}$  for a given  $n$  in general increase with increasing  $l$ . As an example, the energy  $E_{20}$  is in general lower than the energy  $E_{21}$  of the  $2p$  states. Similarly, the  $n=3$  level is split into  $3s$ ,  $3p$  and  $3d$  levels, as illustrated in the diagram below.

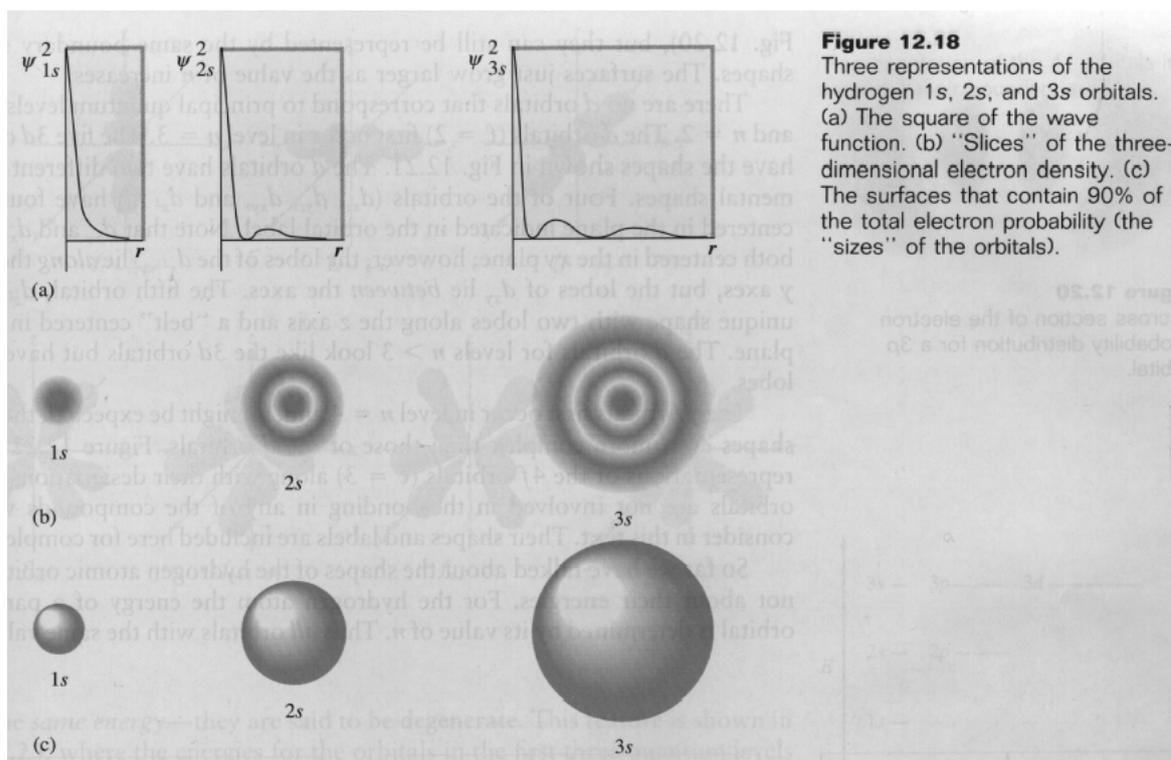


This splitting, and the order of the energy levels, is important when we later discuss the “filling sequence” of heavier atoms.

### 5.5.e Orbitals

It is customary to speak of the wave functions  $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi)$  as **orbitals**. This word is derived from “orbit” but, as we have seen, we are not speaking of orbits in the classical sense; the absolute square  $|\psi|^2$  of the orbital gives the probability density for the position.

The *forms* of the orbitals are important, particularly when one wants to study bindings. In order to read out the form of an orbital, we must try to combine the angular dependence in  $Y_{lm}$  with the  $r$ -dependence in the radial function  $R_{nl}(r) = u_{nl}(r)/r$ . This is very easy for  $s$  states; the angular function  $Y_{00} = 1/\sqrt{4\pi}$  gives a spherically symmetric wave function and a spherically symmetric probability density.



The figure above shows three ways of illustrating the probability densities of the 1s, 2s and 3s orbitals

$$\begin{aligned}\psi_{100} &= (\pi a^3)^{-1/2} e^{-r/a}, \\ \psi_{200} &= (32\pi a^3)^{-1/2} (2 - r/a) e^{-r/2a} \quad \text{and} \\ \psi_{300} &= (27\pi a^3)^{-1/2} \left(1 - \frac{2r}{3a} + \frac{2r^2}{27a^2}\right) e^{-r/3a} : \end{aligned} \quad (\text{T5.67})$$

(a) shows  $|\psi|^2$  as functions of  $r$ . (b) shows cross sections (through the origin), where the point densities illustrate the probability densities. For all three of these  $s$  orbitals the probability density is maximal at the origin (where the darkness in the figure is maximal). For the 1s orbital,  $|\psi|^2$  simply decreases exponentially. For the 2s orbital, on the other hand, we have a nodal surface (where  $\psi = 0$ ) for  $r = 2a$ , symbolized by the bright ring in the cross section. For the 3s orbital we have two such nodal surfaces.

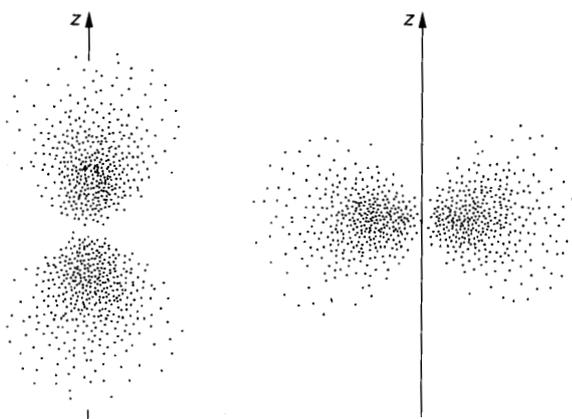
In analogy with the contour lines of a map, we can here imagine contour *surfaces* (surfaces with constant probability densities). For  $s$  states, these surfaces are spheres. In chemistry it is customary to visualize the "form" of an orbital by showing such a "constant-density surface", e.g. the surface which contains 90 percent of the probability. Such a surface defines (a somewhat arbitrary) "boundary surface" of the orbital. With this (arbitrary) definition, the boundary surface of the 1s orbital of hydrogen is a sphere with radius  $2.6a$ . (Cf exercise.) In this way we can obtain a definition of both the form and the size of an orbital. The boundary surfaces of the three orbitals are shown in (c).

The figure below show corresponding cross sections of the probability densities for the 2p orbitals

$$2p_z = \psi_{210} = (32\pi a^5)^{-1/2} r e^{-r/2a} \cos \theta \quad (\text{T5.68})$$

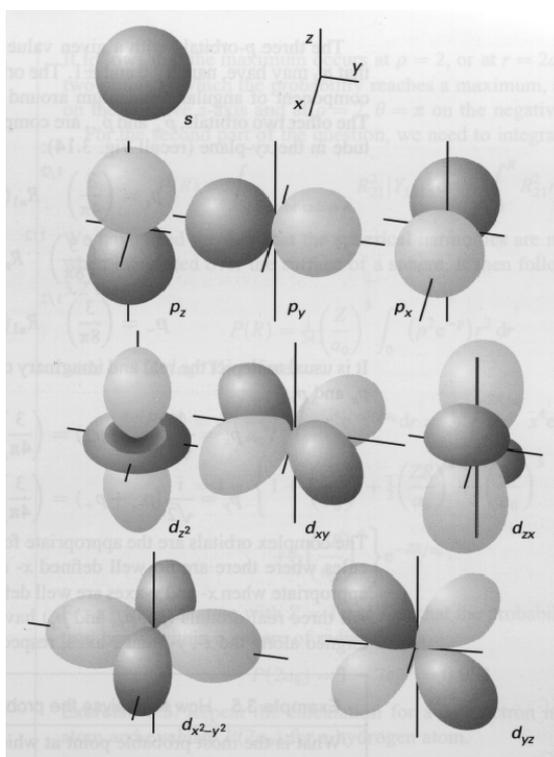
and

$$\psi_{21\pm 1} = (64\pi a^5)^{-1/2} r e^{-r/2a} \sin \theta e^{\pm i\phi}. \quad (\text{T5.69})$$



These orbitals contain the radial function  $R_{21}(r)$ , which is zero only at the origin. We note that  $\psi_{210}$  has a nodal surface in the  $xy$ -plane ( $\theta = \frac{1}{2}\pi$ ), while  $\psi_{21\pm 1}$  has a nodal *line* in the  $z$ -axis. Here too we can imagine contour surfaces of constant probability densities (contour lines in the cross sections in the figure), and we can define boundary surfaces containing e.g. 90 percent of the probability. One of these surfaces will resemble a doughnut.

By combining the radial function  $R_{21}(r)$  with the *real* angular functions  $p_x$  and  $p_y$  instead of  $Y_{1\pm 1}$  (cf section 5.3 above), we can construct the orbitals  $2p_x$  and  $2p_y$ , which are rotationally symmetric with respect to the  $x$ -axis and the  $y$ -axis, respectively. These two orbitals have the same *form* as the  $2p_z$  orbital. The boundary surfaces of all these three  $p$  orbitals are shown in the figure below.



This figure also shows the boundary surfaces of five  $d$  orbitals ( $l = 2$ ). While  $p$  orbitals exist for  $n \geq 2$ ,  $d$  orbitals exist only for  $n \geq 3$ . The five angular functions which give these orbitals (together with the radial function  $R_{n2}(r)$ ) are real linear combinations of the

set  $Y_{2m}$ , ( $m = 0, \pm 1, \pm 2$ ):

$$\begin{aligned}
 d_{z^2} &\equiv Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) = \sqrt{\frac{5}{16\pi}} \left(3 \frac{z^2}{r^2} - 1\right), \\
 d_{x^2-y^2} &\equiv \frac{1}{\sqrt{2}}(Y_{22} + Y_{2,-2}) = \sqrt{\frac{15}{16\pi}} \frac{x^2 - y^2}{r^2}, \\
 d_{xy} &\equiv \frac{1}{i\sqrt{2}}(Y_{22} - Y_{2,-2}) = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2}, \\
 d_{yz} &\equiv \frac{1}{i\sqrt{2}}(Y_{21} + Y_{2,-1}) = -\sqrt{\frac{15}{4\pi}} \frac{yz}{r^2}, \\
 d_{zx} &\equiv \frac{1}{\sqrt{2}}(Y_{21} - Y_{2,-1}) = -\sqrt{\frac{15}{4\pi}} \frac{zx}{r^2}.
 \end{aligned} \tag{T5.70}$$

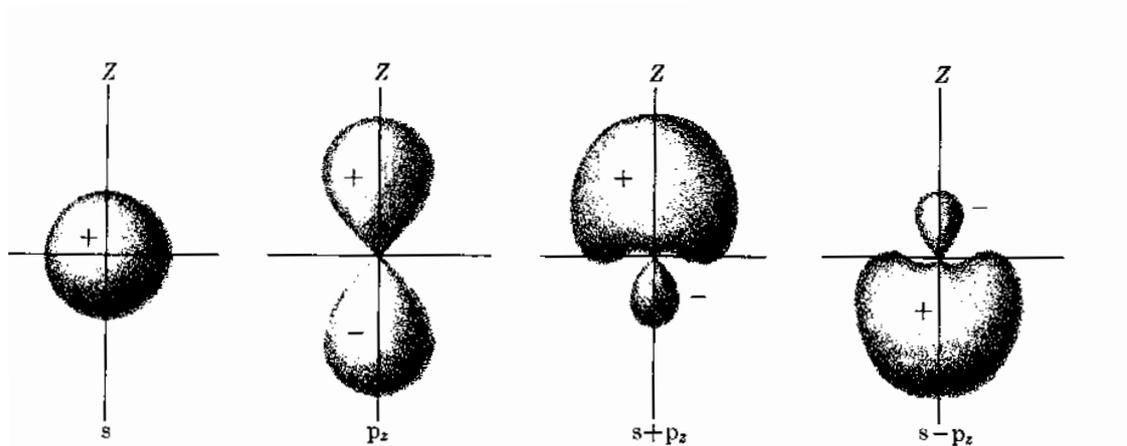
These orbitals are used frequently in chemistry.

**A small exercise:** Compare the number of nodal surfaces of the  $3d$ -orbitals in the figure with the number of nodal surfaces for the  $3s$  orbital. How many nodal surfaces does the  $3p_z$  orbital have?

### 5.5.f Hybridization

Each of the orbitals discussed and shown above has a well-defined orbital angular-momentum quantum number  $l$  and hence a well-defined parity  $(-1)^l$ . Each of them thus is either symmetric or antisymmetric with respect to space inversion. This means that the probability densities are symmetric. Then it is easy to understand that the expectation value of the electron position  $\mathbf{r}$  is equal to zero for all these orbitals; all the probability distributions have their “center of gravity” at the origin.

The question then is: Is there no hydrogenic orbital with the center of gravity displaced from the origin? The answer is: Yes, but from the argument above we understand that such an orbital can not be a parity eigenstate. Thus we have to “mix” energy eigenfunctions with different parities (that is with even and odd  $l$ ). For a hydrogenlike atom this is no problem. Because of the  $l$ -degeneracy, for example the  $ns$  orbital ( $l = 0$ ) and the  $np$  orbitals ( $l = 1$ ) have the same energy  $E_n$ . A linear combination of the  $ns$  orbital and one or more of the  $np$  orbitals will then be a perfectly acceptable energy eigenfunction (with the energy  $E_n$ ). This linear combination is asymmetric, and the center of gravity of its probability distribution lies a certain distance away from the origin.



The figure shows the result of such a **hybridization**, where the orbitals on the right are 50/50 mixtures of  $s$  and  $p$  orbitals. Here we see that a linear combination of a symmetric and an antisymmetric orbital gives an **asymmetric** orbital. Such “directed” orbitals are relevant in the discussion of molecular bindings. Cf the exercises.

**Attachment:** Proving that the angular function  $\Theta_{lm}(x)$  is proportional to the associated Legendre function  $P_l^m(x)$

The Legendre *polynomials* satisfy the Legendre equation (T5.21),

$$\left( (1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + l(l+1) \right) P_l(x) = 0.$$

We want to prove that the associated Legendre *functions*, defined as

$$P_l^m(x) = (1-x^2)^{m/2} \left( \frac{d}{dx} \right)^m P_l(x), \quad (m \geq 0)$$

satisfy (T5.20),

$$\left( (1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + l(l+1) - \frac{m^2}{1-x^2} \right) \Theta_{lm}(x) = 0.$$

Here comes the proof: We define the function

$$g_m(x) \equiv \left\{ (1-x^2) \left( \frac{d}{dx} \right)^2 - 2(m+1)x \frac{d}{dx} + l(l+1) - m(m+1) \right\} \left( \frac{d}{dx} \right)^m P_l(x).$$

By calculating the derivative of

$$g_{m-1}(x) \equiv \left\{ (1-x^2) \left( \frac{d}{dx} \right)^{m+1} - 2mx \left( \frac{d}{dx} \right)^m + [l(l+1) - (m-1)m] \left( \frac{d}{dx} \right)^{m-1} \right\} P_l(x)$$

with respect to  $x$  we then find that

$$\begin{aligned} \frac{d}{dx} g_{m-1}(x) &= \left\{ (1-x^2) \left( \frac{d}{dx} \right)^{m+2} - 2(m+1)x \left( \frac{d}{dx} \right)^{m+1} + [l(l+1) - m(m+1)] \left( \frac{d}{dx} \right)^m \right\} P_l(x) \\ &= g_m(x). \end{aligned}$$

This means that

$$\begin{aligned} g_m(x) &= \frac{d}{dx} g_{m-1}(x) = \frac{d}{dx} \frac{d}{dx} g_{m-2}(x) = \cdots = \left(\frac{d}{dx}\right)^m g_0(x) \\ &= \left(\frac{d}{dx}\right)^m \left\{ (1-x^2) \left(\frac{d}{dx}\right)^2 - 2x \frac{d}{dx} + l(l+1) \right\} P_l(x) = 0. \end{aligned}$$

In the last step we have used the Legendre equation. Thus the expression  $g_m(x)$  is identically equal to zero for all  $m$  ( $=0,1,2,\dots$ ). In this expression we now replace  $(d/dx)^m P_l(x)$  with  $(1-x^2)^{-m/2} P_l^m(x)$ ; cf the definition of  $P_l^m(x)$  above. The identity  $g_m(x) = 0$  can then be expressed in the following way:

$$g_m(x) \equiv \left\{ (1-x^2) \left(\frac{d}{dx}\right)^2 - 2(m+1)x \frac{d}{dx} + l(l+1) - m(m+1) \right\} (1-x^2)^{-m/2} P_l^m(x) = 0.$$

Here, we note that

$$\frac{d}{dx} (1-x^2)^{-m/2} P_l^m(x) = (1-x^2)^{-m/2} \frac{d}{dx} P_l^m(x) + mx(1-x^2)^{-m/2-1} P_l^m(x).$$

By calculating the second derivative in a similar manner, and then multiplying by  $(1-x^2)^{m/2}$ , we find after some manipulation that

$$\left( (1-x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + l(l+1) - \frac{m^2}{1-x^2} \right) P_l^m(x) = 0.$$

The conclusion is that the associated Legendre functions  $P_l^m(x)$ , defined above, satisfy the same differential equation as  $\Theta_{lm}(x)$ . This is what we wanted to prove.