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(Angular Momentum & Qualitative of H and H like atoms)

Angular Momentum in Quantum Mechanics

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This part of the course is based on Refs. [1] – [3].

1. Introduction

Angular momentum plays a central role in both classical and quantum mechanics. In classical mechanics, all isolated systems conserve angular momentum (as well as energy and linear momentum); this fact reduces considerably the amount of work required in calculating trajectories of planets, rotation of rigid bodies, and many more.

Similarly, in quantum mechanics, angular momentum plays a central role in understanding the structure of atoms, as well as other quantum problems that involve rotational symmetry.

Like other observable quantities, angular momentum is described in QM by an operator. This is in fact a vector operator, similar to momentum operator. However, as we will shortly see, contrary to the linear momentum operator, the three components of the angular momentum operator do not commute.

In QM, there are several angular momentum operators: the total angular momentum (usually denoted by $\vec{J}$), the orbital angular momentum (usually denoted by $\vec{L}$) and the intrinsic, or **spin** angular momentum (denoted by $\vec{S}$). This last one (spin) has no classical analogue. Confusingly, the term "angular momentum" can refer to either the total angular momentum, or to the orbital angular momentum.

The classical definition of the orbital angular momentum, $\vec{L} = \vec{r} \times \vec{p}$ can be carried directly to QM by reinterpreting $\vec{r}$ and $\vec{p}$ as the operators associated with the position and the linear momentum.

The spin operator, $\mathbf{S}$, represents another type of angular momentum, associated with "intrinsic rotation" of a particle around an axis; Spin is an intrinsic property of a particle

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(nearly all elementary particles have spin), that is unrelated to its spatial motion. The existence of spin angular momentum is inferred from experiments, such as the Stern-Gerlach experiment, in which particles are observed to possess angular momentum that cannot be accounted for by orbital angular momentum alone.

The total angular momentum, **J**, combines both the spin and orbital angular momentum of a particle (or a system), namely $\vec{J} = \vec{L} + \vec{S}$.

2. Orbital angular momentum

Consider a particle of mass m, momentum $\vec{p}$ and position vector $\vec{r}$ (with respect to a fixed origin, $\vec{r} = 0$). In classical mechanics, the particle's orbital angular momentum is given by a vector $\vec{L}$, defined by

$$\vec{L} = \vec{r} \times \vec{p}. \tag{1}$$

This vector points in a direction that is perpendicular to the plane containing $\vec{r}$ and $\vec{p}$, and has a magnitude $L = rp \sin \alpha$, where α is the angle between $\vec{r}$ and $\vec{p}$. In Cartesian coordinates, the components of $\vec{L}$ are

$$\begin{aligned} L_x &= yp_z - zp_y; \\ L_y &= zp_x - xp_z; \\ L_z &= xp_y - yp_x. \end{aligned} \tag{2}$$

The corresponding QM operators representing L_x, L_y and L_z are obtained by replacing x, y, z and p_x, p_y and p_z with the corresponding QM operators, giving

$$\begin{aligned} L_x &= -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right); \\ L_y &= -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right); \\ L_z &= -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \end{aligned} \tag{3}$$

In a more compact form, this can be written as a **vector operator**,

$$\vec{L} = -i\hbar(\vec{r} \times \vec{\nabla}). \tag{4}$$

It is easy to verify that $\vec{L}$ is Hermitian.

Using the commutation relations derived for $\vec{x}$ and $\vec{p}$, the commutation relations between the different components of $\vec{L}$ are readily derived. For example:

$$[L_x, L_y] = [(yp_z - zp_y), (zp_x - xp_z)] = [yp_z, zp_x] + [zp_y, xp_z] - [yp_z, xp_z] - [zp_y, zp_x] \tag{5}$$

Since y and p_x commute with each other and with z and p_z, the first term reads

$$[yp_z, zp_x] = yp_z zp_x - zp_x yp_z = yp_x[p_z, z] = -i\hbar yp_x \tag{6}$$

Similarly, the second commutator gives

$$[zp_y, xp_z] = zp_y xp_z - xp_z zp_y = xp_y[z, p_z] = i\hbar xp_y \tag{7}$$

The third and forth commutators vanish; we thus find that

$$[L_x, L_y] = i\hbar(xp_y - yp_x) = i\hbar L_z. \tag{8}$$

In a similar way, it is straightforward to show that

$$[L_y, L_z] = i\hbar L_x \tag{9}$$

and

$$[L_z, L_x] = i\hbar L_y \tag{10}$$

The three equations are equivalent to the vectorial commutation relation:

$$\vec{L} \times \vec{L} = i\hbar\vec{L}. \tag{11}$$

Note that this can only be true for operators; since, for regular vectors, clearly $\vec{L} \times \vec{L} = 0$.

The fact that the operators representing the different components of the angular momentum do not commute, implies that it is impossible to obtain definite values for all component of the angular momentum when measured simultaneously. This means that if the system is in eigenstate of one component of the angular momentum, it will in general not be an eigenstate of either of the other two components.

We define the operator representing the square of the magnitude of the orbital angular momentum by

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2. \tag{12}$$

It is easy to show that $\vec{L}^2$ does commute with each of the three components: L_x, L_y or L_z. For example (using $[L_x^2, L_x] = 0$):

$$\begin{aligned} [\vec{L}^2, L_x] &= [L_y^2 + L_z^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\ &= -i\hbar(L_yL_z + L_zL_y) + i\hbar(L_zL_y + L_yL_z) = 0. \end{aligned} \tag{13}$$

Similarly,

$$[\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0, \tag{14}$$

which can be summarized as

$$[\vec{L}^2, \vec{L}] = 0. \tag{15}$$

Physically, this means that one can find simultaneous eigenfunctions of $\vec{L}^2$ and one of the components of $\vec{L}$, implying that both the magnitude of the angular momentum and one of its components can be precisely determined. Once these are known, they fully specify the angular momentum.

In order to obtain the eigenvalues of $\vec{L}^2$ and one of the components of $\vec{L}$ (typically, L_z), it is convenient to express the angular momentum operators in spherical polar coordinates: r, θ, ϕ, rather than the Cartesian coordinates x, y, z. The spherical coordinates are related to the Cartesian ones via

$$\begin{aligned} x &= r \sin\theta \cos\phi; \\ y &= r \sin\theta \sin\phi; \\ z &= r \cos\theta. \end{aligned} \tag{16}$$

After some algebra, one gets:

$$\begin{aligned} L_x &= -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \\ L_y &= -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\ L_z &= -i\hbar \frac{\partial}{\partial\phi}; \\ \vec{L}^2 &= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \end{aligned} \tag{17}$$

We thus find that the operators L_x, L_y, L_z and $\vec{L}^2$ depend on θ and ϕ only, that is they are independent on the radial coordinate $\vec{r}$. All these operators therefore commute with any function of r,

$$[L_x, f(r)] = [L_y, f(r)] = [L_z, f(r)] = [\mathbf{L}^2, f(r)] = 0. \tag{18}$$

Also, obviously, if a wavefunction depends *only* on r (but not on θ, ϕ) it can be simultaneously an eigenfunction of L_x, L_y, L_z and $\mathbf{L}^2$. In all cases, the corresponding eigenvalue will be 0. (This is the only exception to the rule that that eigenvalues of one component (e.g., L_x) cannot be simultaneously eigenfunctions of the two other components of $\mathbf{L}$).

3. Eigenvalues and eigenfunctions of $\mathbf{L}^2$ and L_z

Let us find now the common eigenfunctions to $\mathbf{L}^2$ and L_z, for a single particle. The choice of L_z (rather than, e.g., L_x) is motivated by the simpler expression (see Equation 17).

3.1. Eigenvalues of L_z

Since, in spherical coordinates L_z depends only on ϕ, we can denote its eigenvalue by $m\hbar$ and the corresponding eigenfunctions by $\Phi_m(\phi)$. We thus have:

$$L_z \Phi_m(\phi) = m\hbar \Phi_m(\phi), \tag{19}$$

namely

$$-i \frac{\partial}{\partial \phi} \Phi_m(\phi) = m \Phi_m(\phi). \tag{20}$$

The solutions to this equation are

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \tag{21}$$

This is satisfied for any value of m; however, physically we require the wave function to be *single valued* (alternatively: *continuous*), namely $\Phi_m(2\pi) = \Phi_m(0)$, from which we find

$$e^{i2\pi m} = 1. \tag{22}$$

This equation is satisfied for $m = 0, \pm 1, \pm 2, \pm 3, ...$ The eigenvalues of the operator L_z are thus $m\hbar$, with m being integer (positive or negative) or zero. The number m is called the **magnetic quantum number**, due to the role it plays in the motion of charged particles in magnetic fields.

This means, that when measuring the z-component of an orbital angular momentum, one can only obtain $0, \pm\hbar, \pm 2\hbar, ...$ Since the choice of the z direction was arbitrary, we see that the component of the orbital angular momentum about **any** axis is quantized.

The wavefunctions $\Phi_m(\phi)$ are orthonormal, namely

$$\int_0^{2\pi} \Phi_n^\star(\phi) \Phi_m(\phi) d\phi = \delta_{nm}. \tag{23}$$

Furthermore, they form a complete set, namely every function $f(\phi)$ can be written as

$$f(\phi) = \sum_{m=-\infty}^{+\infty} a_m \Phi_m(\phi), \tag{24}$$

where the coefficients a_m are C-numbers.

3.2. Simultaneous eigenvalues of $\mathbf{L}^2$ and L_z

Let us denote simultaneous eigenfunctions of the operator $\mathbf{L}^2$ and L_z as $Y_{lm}(\theta,\phi)$. We will write the eigenvalues of $\mathbf{L}^2$ as $l(l+1)\hbar^2$ (from reason which will become clear shortly). We then have:

$$\mathbf{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi) \tag{25}$$

and

$$L_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi) \tag{26}$$

Comparing equation 26 and equation 19, we see that we can separate $Y_{lm}(\theta,\phi)$,

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi) \tag{27}$$

where the functions $\Phi_m(\phi)$ are given by Equation 21, $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$.

Using the expression for $\mathbf{L}^2$ in spherical coordinates (Equation 17), we write Equation 25 as

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y_{lm}(\theta,\phi) = -l(l+1)Y_{lm}(\theta,\phi). \tag{28}$$

Using the variable separation, as well as equation 21 for $\Phi_m(\phi)$, Equation 28 becomes

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) + \left\{l(l+1) - \frac{m^2}{\sin^2\theta}\right\}\right]\Theta_{lm}(\theta) = 0 \tag{29}$$

This equation is not easy to solve. In order to proceed, we change variable, writing $w = \cos\theta$ and $F_{lm}(w) = \Theta_{lm}(\theta)$. Equation 29 becomes

$$\left[\left(1-w^2\right)\frac{d^2}{dw^2} - 2w\frac{d}{dw} + l(l+1) - \frac{m^2}{1-w^2}\right]F_{lm}(w) = 0 \tag{30}$$

This equation is known in mathematics as the **Legendre's associated differential equation** (the $m = 0$ case is simply called **Legendre's differential equation**), honoring the French mathematician Adrien-Marie Legendre.

The solutions to this equation are given by the **associated Legendre's functions**, $P_l^m|(w)$, which are defined by

$$P_l^m(w) = (1-w^2)^{|m|/2}\left(\frac{d}{dw}\right)^{|m|} P_l(w), \tag{31}$$

where $P_l(w)$ is known as the l**th Legendre polynomial**, which is defined by the **Rodrigues formula**,

$$P_l(w) = \frac{1}{2^l l!}\left(\frac{d}{dw}\right)^l (w^2-1)^l \tag{32}$$

(Note that for $m = 0$, $P_l^0(w) = P_l(w)$).

In order for Rodrigues formula to make sense, l **must be non-negative integer.** Moreover, if $|m| > l$, then Equation 31 implies $P_l^m = 0$. Thus, the physically accepted values of l and m are

$$\begin{aligned} &l = 0, 1, 2, ... \\ &m = -l, -l+1, ..., -2, -1, 0, 1, 2, ..., l-1, l. \end{aligned} \tag{33}$$

This result can be understood physically as follows: Since $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$, the expectation value of $\mathbf{L}^2$ in a given state Ψ is $\langle \mathbf{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$. Since L_x and L_y are Hermitian, $\langle L_x^2 \rangle \geq 0$ and $\langle L_y^2 \rangle \geq 0$, and therefore

$$\langle \mathbf{L}^2 \rangle \geq \langle L_z^2 \rangle \tag{34}$$

For a state Ψ such that its angular part is an eigenfunction of both $\mathbf{L}^2$ and L_z, we thus have from Equations 25, 26 and 34

$$l(l+1) \geq m^2, \tag{35}$$

from which the result in Equation 33, namely that m is restricted to $|m| \leq l$ follows. The quantum number l, whose allowed values are given in Equation 33, is called the **orbital angular momentum quantum number**.

By using Rodrigues formula (Equation 32), one can immediately find the first few Legendre Polynomials:

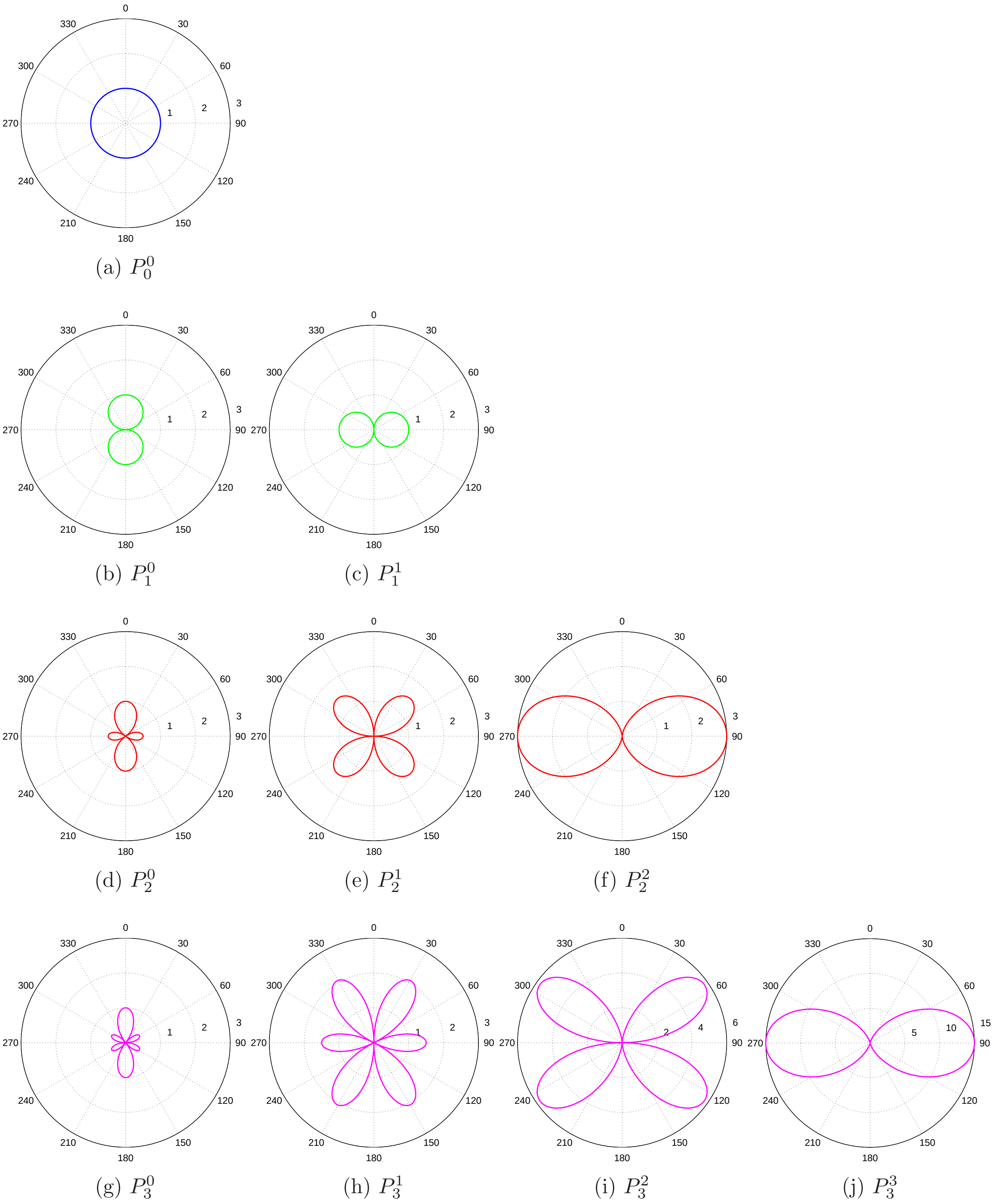
$$\begin{aligned} P_0(w) &= 1; \\ P_1(w) &= \tfrac{1}{2}\tfrac{d}{dw}(w^2 - 1) = w; \\ P_2(w) &= \tfrac{1}{2}\left(3w^2 - 1\right); \\ P_3(w) &= \tfrac{1}{2}\left(5w^3 - 3w\right); \\ P_4(w) &= \tfrac{1}{8}\left(35w^4 - 30w^2 + 3\right); \\ P_5(w) &= \tfrac{1}{8}\left(63w^5 - 70w^3 + 15w\right); \end{aligned} \tag{36}$$

and so on.

Using Equation 31, one can determine the associated Legendre's functions, P_l^m. The first few are (inserting again $w = \cos\theta$):

$$\begin{array}{llll} P_0^0 = 1; & & & \\ P_1^0 = \cos\theta; & P_1^1 = \sin(\theta); & & \\ P_2^0 = \frac{1}{2}\left(3\cos^2\theta - 1\right); & P_2^1 = 3\sin\theta\cos\theta; & P_2^2 = 3\sin^2\theta; & \\ P_3^0 = \frac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right); & P_3^1 = \frac{3}{2}\sin\theta\left(5\cos^2\theta - 1\right); & P_3^2 = 15\sin^2\theta\cos\theta; & P_3^3 = 15\sin^3\theta; \end{array} \tag{37}$$

etc.



(a) P_0^0

(b) P_1^0 (c) P_1^1

(d) P_2^0 (e) P_2^1 (f) P_2^2

(g) P_3^0 (h) P_3^1 (i) P_3^2 (j) P_3^3

Fig. 1.— Polar plots of $r = \mathrm{abs}[P_l^m(\theta)]$ as a function of θ.

Plots of the first few associated Legendre functions, $P_l^m(\theta)$ are shown in Figure 1.

Using Rodrigues formula and integrating by parts, one can show that the associated Legendre's functions, P_l^m are *orthogonal* to each other, but *are not normalized* to unity, namely:

$$\int_{-1}^{+1} dw P_l^{|m|}(w) P_{l'}^{|m|}(w) = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ll'} \tag{38}$$

However, with the use of Equation 38, one can multiply $P_l^m(w)$ with the appropriate normalization factor, and obtain a normalized solution $F_{lm}(w)$ to Equation 30 - up to an uncertain phase factor of modulus 1.

The corresponding physical solutions to equation 29 $\Theta_{lm}(\theta)$ are given by

$$\Theta_{lm}(\theta) = \begin{cases} (-1)^m \left[\frac{(2l+1)}{2} \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta), & m \geq 0 \\ (-1)^m \Theta_{l|m|}(\theta) & m < 0. \end{cases} \tag{39}$$

These functions are normalized, namely

$$\int_0^{\pi} \Theta^{\star}_{l'm}(\theta)\Theta_{lm}(\theta)\sin(\theta)d\theta = \delta_{ll'}. \tag{40}$$

We can now (finally) write the simultaneous eigenfunctions $Y_{lm}(\theta, \phi)$ common to the operators $\mathbf{L}^2$ and L_z (see equations 25 and 26) as

$$Y_{lm}(\theta,\phi) = \begin{cases} (-1)^m \left[\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\phi}, & m \geq 0 \\ (-1)^m Y^{\star}_{l,-m}(\theta,\phi) & m < 0. \end{cases} \tag{41}$$

(where we have adopted the commonly use convention for the phase). These functions are known as **spherical harmonics**.

The spherical harmonics are normalized to unity on a unit sphere, and are orthogonal:

$$\int Y^{\star}_{l'm'}(\theta,\phi)Y_{lm}(\theta,\phi)d\Omega \equiv \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin(\theta) Y^{\star}_{l'm'}(\theta,\phi)Y_{lm}(\theta,\phi) = \delta_{ll'}\delta_{mm'} \tag{42}$$

They further form a **complete set**, namely, every (arbitrary) function $f = f(\theta, \phi)$ can be expanded as

$$f(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta,\phi) \tag{43}$$

The lowest order spherical harmonics are summarized in table 1.

l	m	$Y_{lm}(\theta,\phi)$
0	0	$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
1	0	$Y_{1,0} = \left(\frac{3}{8\pi}\right)^{1/2} \cos\theta$
	±1	$Y_{1,1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$
2	0	$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	±1	$Y_{2,\pm1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$
	±2	$Y_{2,\pm2} = \mp \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
3	0	$Y_{3,0} = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	±1	$Y_{3,\pm1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\left(5\cos^2\theta - 1\right) e^{\pm i\phi}$
	±2	$Y_{3,\pm2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
	±3	$Y_{3,\pm3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

Table 1: The first few spherical harmonics, Y_{lm}.

3.3. The angular momentum ladder operators

Let us study the effect of the operators L_x and L_y on the eigenfunctions Y_{lm}. For this purpose, it is convenient to introduce the two operators:

$$L_\pm = L_x \pm iL_y. \tag{44}$$

These operators are **not** Hermitian, but are mutually adjoint, since $L_+^\dagger = L_x - iL_y = L_-$ and $L_-^\dagger = L_x + iL_y = L_+$ (and we used the fact that L_x and L_y are Hermitian).

Since both L_x and L_y commute with $\mathbf{L}^2$, so do $L_\pm$,

$$[\mathbf{L}^2, L_\pm] = 0. \tag{45}$$

Using the commutation relations between the components of the angular momentum (Equations 8 - 10), it is straightforward to show that the ladder operators L_+ and L_- satisfy:

$$L_\pm L_\mp = \mathbf{L}^2 - L_z^2 \pm \hbar L_z; \tag{46}$$

$$[L_+, L_-] = 2\hbar L_z; \tag{47}$$

$$[L_z, L_\pm] = \pm\hbar L_\pm. \tag{48}$$

Equation 48 can be used with the eigenvalue Equation 26 to obtain

$$L_z(L_\pm Y_{lm}) = (m \pm 1)\hbar(L_\pm Y_{lm}) \tag{49}$$

Similarly, using the fact that $L_\pm$ commute with $\mathbf{L}^2$, from Equation 25 we have

$$\mathbf{L}^2(L_\pm Y_{lm}) = l(l+1)\hbar^2(L_\pm Y_{lm}) \tag{50}$$

This implies that when acting on the common eigenfunction Y_{lm} of $\mathbf{L}^2$ and L_z, the operator L_+ produces a new common eigenfunction, for which the eigenvalue of $\mathbf{L}^2$ does not change, (remains $l(l+1)\hbar^2$), but the eigenvalue of L_z increases by $\hbar$, to become $(m+1)\hbar$. Similarly, L_-Y_{lm} is a simultaneous eigenfunction of $\mathbf{L}^2$ and L_z with eigenvalues $l(l+1)\hbar^2$ and $(m-1)\hbar$. This explains their names - **raising** and **lowering** operators.

We therefore find that

$$L_\pm Y_{lm} = C^\pm_{lm} Y_{l,m\pm1}, \tag{51}$$

where $C^\pm_{lm}$ are constants, whose value we want to find. To determine the value of these constants, we return to Equation 17, and write $L_\pm$ in spherical polar coordinates,

$$L_\pm = \hbar e^{\pm i\phi}\left[\pm\frac{\partial}{\partial\theta} + i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right] \tag{52}$$

This can be applied to the functions Y_{lm} derived above. The result is

$$L_\pm Y_{lm}(\theta,\phi) = \hbar[l(l+1) - m(m\pm1)]^{1/2} Y_{l,m\pm1}(\theta,\phi) \tag{53}$$

Let us switch now to Dirac's notation. In this notation, the state described by the spherical harmonic $Y_{lm}(\theta,\phi)$ is denoted by the ket $|l,m\rangle$.

The expectation values of $L_\pm$ are zero: this follows from the orthonormality of the spherical harmonics, which can be written as $\langle l,m|l',m'\rangle = \delta_{ll'}\delta_{mm'}$:

$$\langle l,m|L_\pm|l,m\rangle = \hbar[l(l+1) - m(m\pm1)]^{1/2}\langle l,m|l,m\pm1\rangle = 0. \tag{54}$$

Using $L_x = \frac{1}{2}(L_+ + L_-)$ and $L_y = \frac{1}{2i}(L_+ - L_-)$, this result implies that the expectation values $\langle L_x\rangle = \langle L_y\rangle = 0$. On the other hand,

$$\langle L_x^2\rangle = \langle L_y^2\rangle = \langle \mathbf{L}^2 - L_z^2\rangle = \frac{1}{2}[l(l+1) - m^2]\hbar^2. \tag{55}$$

Interestingly, even when $m = \pm l$ - the orbital angular momentum is “parallel” or “anti-parallel” to the z-axis, its x- and y- components are still not zero, although the average values of L_x and L_y vanish.

4. Schrödinger equation in three dimensions, central potential

The knowledge we gained on angular momentum is particularly useful when treating real life problems. As our world is three dimensional, we need to generalize the treatment of Schrödinger equation to 3-d.

The time-independent Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi \tag{56}$$

where, in 3-d,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{57}$$

In many problems in physics, the potential is **central**, namely, $V = V(r)$; this means that the potential is **spherically symmetric**, and is not a function of θ or ϕ. In this type of systems - the best representative may be the hydrogen atom to be discussed shortly, it is best to work in spherical coordinates, r, θ, ϕ.

In spherical coordinates, the laplacian becomes

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right). \tag{58}$$

Comparing to Equation 17, we see that the last two terms of the laplacian are equal to $-\mathbf{L}^2/\hbar^2 r^2$. Thus, we can write the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r) \tag{59}$$

and the time-independent Schrödinger equation is

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r)\right\}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \tag{60}$$

In order to proceed, we note that all of the angular momentum operators: L_x, L_y, L_z and $\mathbf{L}^2$ do not operate on the radial variable, r; this can be seen directly by their description in spherical coordinates, equation 17. This means that all these operators commute with $V(r)$: $[L_z, V(r)] = 0$, etc. Furthermore, since L_x, L_y and L_z commute with $\mathbf{L}^2$, we conclude that all of the angular momentum operators commute with the Hamiltonian,

$$[\hat{H}, L_x] = [\hat{H}, L_y] = [\hat{H}, L_z] = [\hat{H}, \mathbf{L}^2] = 0 \tag{61}$$

This means that it is possible to obtain solutions to Schrödinger equation (Equation 60) which are common eigenfunctions of $\hat{H}$, $\mathbf{L}^2$ and L_z.

We already know simultaneous eigenfunctions of $\mathbf{L}^2$ and L_z: these are of course the spherical harmonics, $Y_{lm}(\theta, \phi)$. Thus, a full solution to Schrödinger equation can be written as

$$\psi(r, \theta, \phi) = R_{El}(r) Y_{lm}(\theta, \phi). \tag{62}$$

$R_{El}(r)$ is a radial function of r, which we need to find. The subscripts E and l mark the fact that in general, we obtain different functions for different values of the energy(E) and the orbital angular momentum quantum number l. It is independent, though, on the magnetic quantum number m, as can be seen by inserting this solution into Schrödinger equation (in which the operator $\mathbf{L}^2$ appears explicitly, but not L_z).

We may put the solution in Equation (62) in Schrödinger equation (60), and use the fact that $\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$ (Equation 25), to obtain an equation for $R_{El}(r)$,

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right] R_{El}(r) = E R_{El}(r) \tag{63}$$

To be physically acceptable, the wave functions must be square integrable, and normalized to 1:

$$\int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi |\psi_{Elm}(r, \theta, \phi)|^2 = 1. \tag{64}$$

We already know that the spherical part, $Y_{lm}(\theta, \phi)$ is normalized; see Equation 42. Thus, the radial part of the eigenfunctions must satisfy the normalization condition

$$\int_0^\infty dr r^2 |R_{El}(r)|^2 = 1. \tag{65}$$

We may further simplify Equation 63 by changing a variable,

$$u_{El}(r) = r R_{El}(r) \tag{66}$$

Thus, $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, and $\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \frac{u}{r} = \frac{1}{r} \frac{\partial^2 u}{\partial r^2}$. Overall, Equation 63 becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{El}}{dr^2} + V_{eff}(r) u_{El}(r) = E u_{El}(r) \tag{67}$$

where

$$V_{eff}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \tag{68}$$

is an **effective potential**; in addition to the interaction potential, $V(r)$ it contains a **repulsive centrifugal barrier**, $(\hbar^2/2m)[(l(l+1)/r^2]$.

With the inclusion of this potential, Equation 67 has an identical form to the 1-d (time-independent) Schrödinger equation. The only difference is that it is physically meaningful only for $r > 0$, and we must provide the boundary condition at $r = 0$. The boundary conditions are provided by the physical requirement that the function $R_{El}(r)$ remains finite at the origin, $r = 0$. Since $R_{El}(r) = u_{El}(r)/r$, this implies

$$u_{El}(0) = 0. \tag{69}$$

5. The hydrogen atom

Perhaps the most important demonstration of the above analysis (and of quantum mechanics in general) is the ability to predict the energy levels and wave functions of the hydrogen atom. This is the simplest atom, that contains one proton and one electron. The proton is heavy ($m_p/m_e = 1836$) and is essentially motionless - we can assume it being at the origin, $r = 0$). The proton has a positive charge $+q$, and the electron a negative charge, $-q$. We can therefore use Coulumb's law to calculate the potential energy:

$$V(r) = -\frac{q^2}{4\pi\epsilon_0}\frac{1}{r} \tag{70}$$

(in SI units).

The radial equation (67) becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2u_{El}}{dr^2} + \left[-\frac{q^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{l(l+1)\hbar^2}{2mr^2}\right]u_{El}(r) = Eu_{El}(r) \tag{71}$$

Before proceeding to solve this equation, we note the following. At $r \to \infty$, $V_{eff}(r) \to 0$. This means that for any value of positive energy ($E > 0$), one could find an acceptable eigenfunction $u_{El}(r)$. Therefore, there is a *continuous spectrum* for $E > 0$, describing scattering between electron and proton (this will be dealt with in next year's QM...). We focus here on solutions for which $E < 0$. These are called **bound states**.

We proceed by some change of variables: We write

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \tag{72}$$

(note that $E < 0$, and so κ is *real*). Equation 71 becomes

$$\frac{1}{\kappa^2}\frac{d^2u_{El}}{dr^2} = \left[1 - \frac{mq^2}{2\pi\epsilon_0\hbar^2\kappa^2 r} + \frac{l(l+1)}{\kappa^2 r^2}\right]u_{El} \tag{73}$$

We next introduce

$$\rho = \kappa r; \quad \rho_0 = \frac{mq^2}{2\pi\epsilon_0\hbar^2\kappa} \tag{74}$$

and write Equation 73 as

$$\frac{d^2 u_{El}}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u_{El} \tag{75}$$

We proceed along lines which are somewhat similar to those taken in deriving the SHO. We begin by examining the asymptotic behavior. We note that when $\rho \to \infty$, Equation 75 is approximately $d^2u_{El}/d\rho^2 \approx u_{El}$, which admits the general solution

$$u(\rho) = Ae^{-\rho} + Be^{\rho}.$$

However, in order for u_{El} to remain finite as $\rho \to \infty$, we must demand $B = 0$, implying $u_{El}(\rho) \sim Ae^{-\rho}$.

On the other hand, as $\rho \to 0$, the centrifugal term dominates (apart when $l = 0$, but, as will be seen, the result is valid there too), and one can write

$$\frac{d^2 u_{El}}{d\rho^2} \approx \frac{l(l+1)}{\rho^2} u_{El}$$

with the general solution

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}.$$

Again, the second term, ρ^{-l} diverges as $\rho \to 0$, implying that we must demand $D = 0$. Thus,

$$u_{El}(\rho) \sim C\rho^{l+1}$$

for small ρ.

This discussion motivates another change of variables, writing

$$u_{El}(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \tag{76}$$

where $v(\rho) \equiv v_{El}(\rho)$, and the subscripts El are omitted for clarity.

With this change of variables, we have

$$\frac{du}{d\rho} = \rho^l e^{-\rho}\left[(l+1-\rho)v + \rho\frac{dv}{d\rho}\right]$$

and

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho}\left\{\left[-2l - 2 + \rho + \frac{l(l+1)}{\rho}\right] v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\}$$

and Equation 75 becomes

$$\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}+[\rho_0-2(l+1)]\,v=0. \tag{77}$$

We search for solution $v(\rho)$ is terms of power series:

$$v(\rho)=\sum_{j=0}^{\infty}c_j\rho^j. \tag{78}$$

We can thus write:

$$\frac{dv}{d\rho}=\sum_{j=0}^{\infty}jc_j\rho^{j-1}=\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j, \tag{79}$$

and

$$\frac{d^2v}{d\rho^2}=\sum_{j=0}^{\infty}j(j+1)c_{j+1}\rho^{j-1} \tag{80}$$

similar to the analysis of the SHO, we insert these results into Equation 77, and equate the coefficients of each individual power law of ρ to write:

$$j(j+1)c_{j+1}+2(l+1)(j+1)c_{j+1}-2jc_j+[\rho_0-2(l+1)]c_j=0,$$

or

$$c_{j+1}=\left[\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right]c_j \tag{81}$$

Similar to the SHO case, we note that for $j\gg\{l,\rho_0\}$ we have

$$c_{j+1}\approx\frac{2}{j}c_j$$

which gives $c_j=(2^j/j!)c_0$, and $v(\rho)=c_0\sum_j\frac{2^j}{j!}\rho^j=c_0e^{2\rho}$, from which $u(\rho)=c_0\rho^{l+1}e^{\rho}$; this of course is unacceptable, as it diverges at large ρ.

This means that the series **must terminate**, namely there is a maximum integer, $j_{\rm max}$ for which $c_{(j_{\rm max}+1)}=0$. From Equation 81 this gives

$$2(j_{\rm max}+l+1)-\rho_0=0. \tag{82}$$

We can now define the **principle quantum number,** n via

$$n\equiv j_{\rm max}+l+1. \tag{83}$$

Thus, $\rho_0=2n$. But ρ_0 determines the energy via equations 72 and 74:

$$E=-\frac{\hbar^2\kappa^2}{2m}=-\frac{mq^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}. \tag{84}$$

We therefore conclude that the allowed energies are

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{q^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \qquad n = 1, 2, 3, ...} \tag{85}$$

This is the well-known **Bohr's formula**.

Using again equation 74, one finds

$$\kappa = \left(\frac{mq^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}, \tag{86}$$

where

$$\boxed{a \equiv \frac{4\pi\epsilon_0\hbar^2}{mq^2} = 5.29\times 10^{-11}\ \mathrm{m}} \tag{87}$$

is known as the **Bohr's radius**.

The **ground state** (namely, the state of lowest energy) is obtained by putting $n = 1$ in Equation 85. Putting the values of the physical constants, one finds that

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{q^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\ \mathrm{eV} \tag{88}$$

This is the **binding energy** of the hydrogen atom - the amount of energy one needs to give to the electron in the hydrogen atom that is in its ground state to ionize the atom (=release the electron).

Furthermore, $E_2 = E_1/2^2 = E_1/4 = -3.4$ eV, etc.

5.1. The wavefunctions

Returning to Equation 62, the wavefunctions are given by

$$\psi(r,\theta,\phi) = R_{El}(r)Y_{lm}(\theta,\phi).$$

where (using Equations 66 and 76)

$$R_{El}(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho). \tag{89}$$

Here, $v(\rho)$ is given by the polynomial of degree $j_{\max} = n - l - 1$ (see Equation 83).

In the **ground state**, $n = 1$; Equation 83 forces $l = 0$ and $j_{\max} = 0$. Since $l = 0$, we known that $m = 0$ as well (see Equation 35). This means that the wave function is given by

$$\Psi_{100} = R_{10}(r)Y_{00}(\theta, \phi) \tag{90}$$

Using the recursion formula (Equation 81), with $j = 0$, leads to $c_1 = 0$; that is, $v(\rho) = 0$ is simply a constant. This implies that

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a} \tag{91}$$

where a is given by Equation 87. The normalization constant is derived from $\int_0^\infty |R_{10}|^2 r^2 dr = 1$, and is $c_0 = 2/\sqrt{a}$. Using $Y_{00} = 1/\sqrt{4\pi}$ (see Table 1), the ground state of the hydrogen atom is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \tag{92}$$

The next energy level is $n = 2$, which represents the first excited state. There are, in fact **four different states** with this same energy: one state with $l = 0$, in which case also $m = 0$; and $l = 1$, in which case $m = -1, 0, +1$. For $l = 0$, Equation 81 gives $c_1 = -c_0$, $c_2 = 0$, namely $v(\rho) = c_0(1 - \rho)$. This implies

$$R_{20}(r) = \frac{c_0}{2a}\left(1 - \frac{r}{2a}\right)e^{-r/2a}. \tag{93}$$

For $l = 1$, the recursion formula terminates the series after a single term, $v(\rho)$ is constant, and one finds

$$R_{21}(r) = \frac{c_0}{4a^2}re^{-r/2a} \tag{94}$$

and so on.

In fact, one can write

$$v(\rho) = L^{2l+1}_{n-l-1}(2\rho), \tag{95}$$

where

$$L^p_{q-p} = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \tag{96}$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^p (e^x x^q) \tag{97}$$

is known as the qth **Laguerre polynomial.** I list in table 5.1 the first few radial eigenfunctions of the hydrogen.

$R_{10} = \frac{2}{a^{3/2}} e^{-r/a}$
$R_{20} = \frac{1}{\sqrt{2}a^{3/2}} \left(1 - \frac{1}{2}\frac{r}{a}\right) e^{-r/2a}$ $R_{21} = \frac{1}{\sqrt{24}a^{3/2}} \frac{r}{a} e^{-r/2a}$
$R_{30} = \frac{2}{\sqrt{27}a^{3/2}} \left[1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right] e^{-r/3a}$ $R_{31} = \frac{8}{27\sqrt{6}a^{3/2}} \left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right) e^{-r/3a}$ $R_{32} = \frac{4}{81\sqrt{30}a^{3/2}} \left(\frac{r}{a}\right)^2 e^{-r/3a}$
$R_{40} = \frac{1}{4a^{3/2}} \left[1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right] e^{-r/4a}$ $R_{41} = \frac{\sqrt{5}}{16\sqrt{3}a^{3/2}} \left[1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right]\left(\frac{r}{a}\right) e^{-r/4a}$ $R_{42} = \frac{1}{64\sqrt{5}a^{3/2}} \left[1 - \frac{1}{12}\frac{r}{a}\right]\left(\frac{r}{a}\right)^2 e^{-r/4a}$ $R_{43} = \frac{1}{768\sqrt{35}a^{3/2}} \left(\frac{r}{a}\right)^3 e^{-r/4a}$

Table 2: The first few radial wavefunctions for the hydrogen, $R_{El}(r)$.

According to the standard interpretation of the wavefunction, the quantity

$$|\psi_{nlm}(r,\theta,\phi)|^2 d\vec{r} = \psi^{\star}_{nlm}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) r^2 dr \sin\theta d\theta d\phi \tag{98}$$

represents the probability of finding the electron in the volume element $d\vec{r}$, when the system is in the stationary state specified by the quantum numbers (n, l, m).

Since $\psi(r,\theta,\phi) = R_{El}(r)Y_{lm}(\theta,\phi)$ (see Equation 62), the position probability density $|\psi_{nlm}(r,\theta,\phi)|^2$ is composed of a **radial part** that depends only on r, and an **angular part** that depends only on θ (recall that the dependence on ϕ disappears).

We can write the radial part as

$$D_{El}(r) = r^2 |R_{El}(r)|^2, \tag{99}$$

which is known as the **radial distribution function.** In figure 2 I plot the first few radial functions R_{El} and the radial distribution function.

Finally, in figures 3 – 5 I give a few examples of the full probability density of finding the electron in (r, θ) for a hydrogen atom, namely

$$P(r,\theta,\phi) = |\psi_{nlm}(r,\theta,\phi)|^2 d\vec{r} = \psi^{\star}_{nlm}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) r^2 dr \sin\theta d\theta d\phi \tag{100}$$

for few values of the quantum numbers n, l, and m. As is obvious from the discussion above, this probability is independent on ϕ, but only on r and θ.

As a final remark, I would add that in the usual spectroscopic notation the quantum number l is replaced by a letter, according to the following table: Thus, the energy levels

value of l	0	1	2	3	4
	↕	↕	↕	↕	↕
Code letter	s	p	d	f	g

are denoted by two symbols: the first is the principal quantum number n, and the second is a letter corresponding to l.

The ground state ($n = 1$) is denoted by $1s$; The first excited state ($n = 2$) contains one $2s$ state, and three $2p$ state, corresponding to $m = -1, 0, +1$ - so total 4 states; the second excited state contains one $3s$ state, three $3p$ states and five $3d$ states, with $m = -2, -1, 0, +1, +2$, so total of 9 states; etc.

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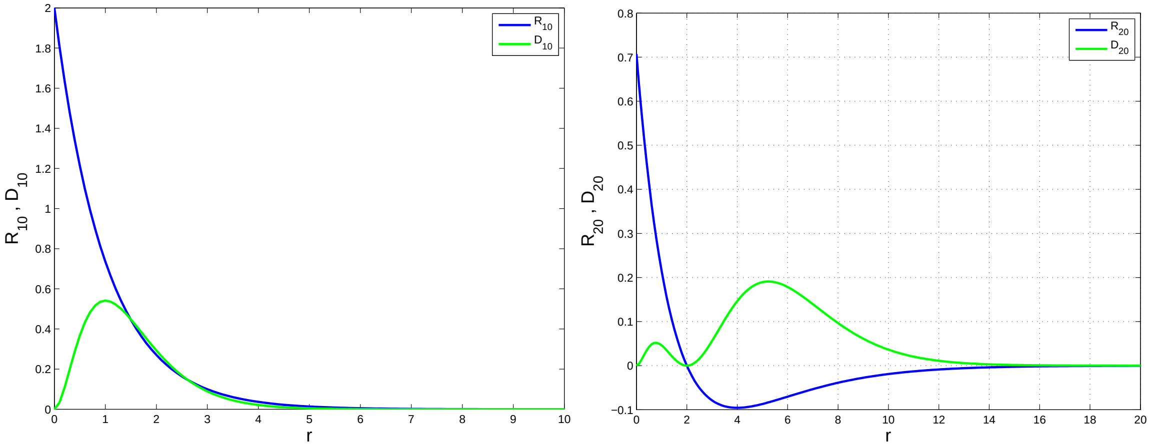
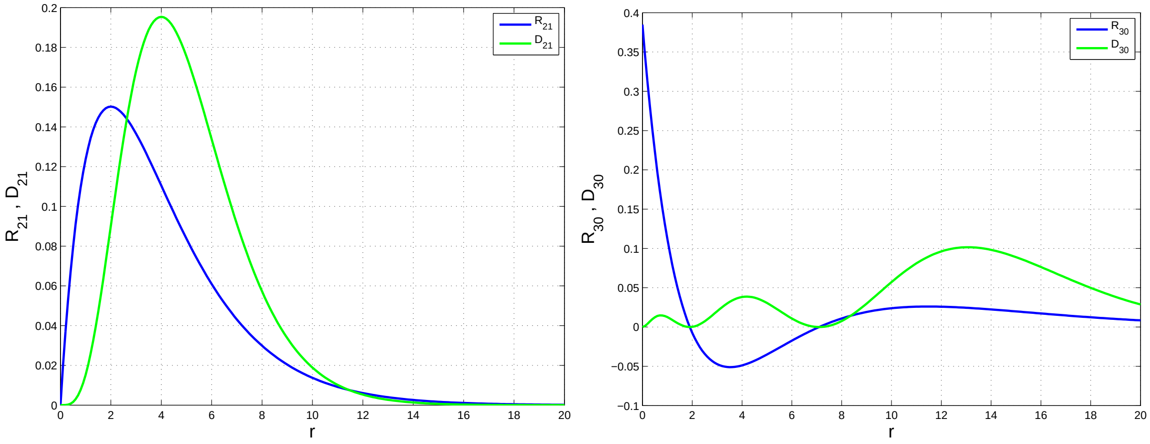


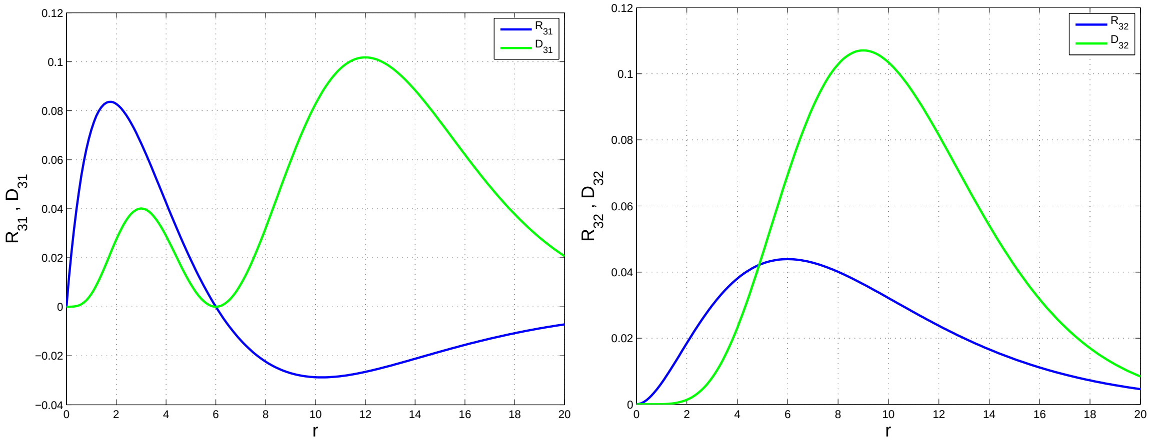
(a) R_{10}

(b) R_{20}



(c) R_{21}

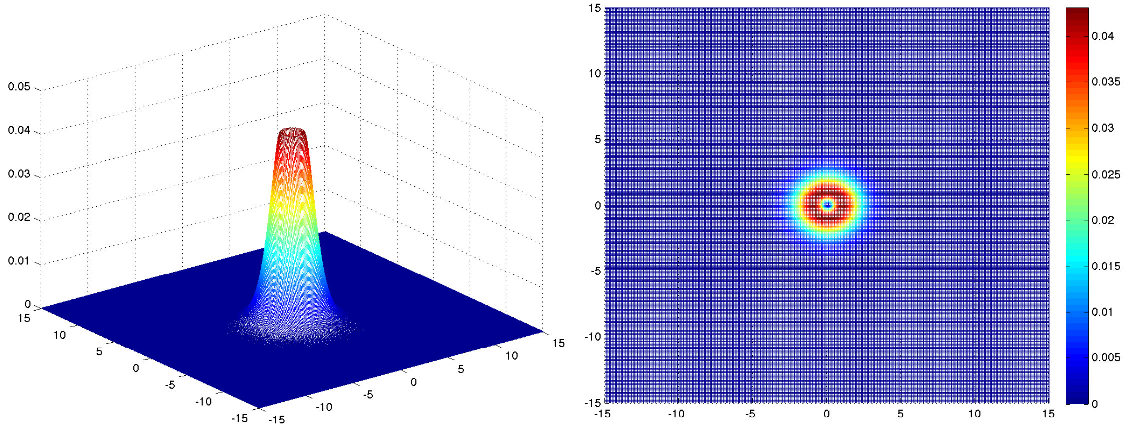
(d) R_{30}



(e) R_{31}

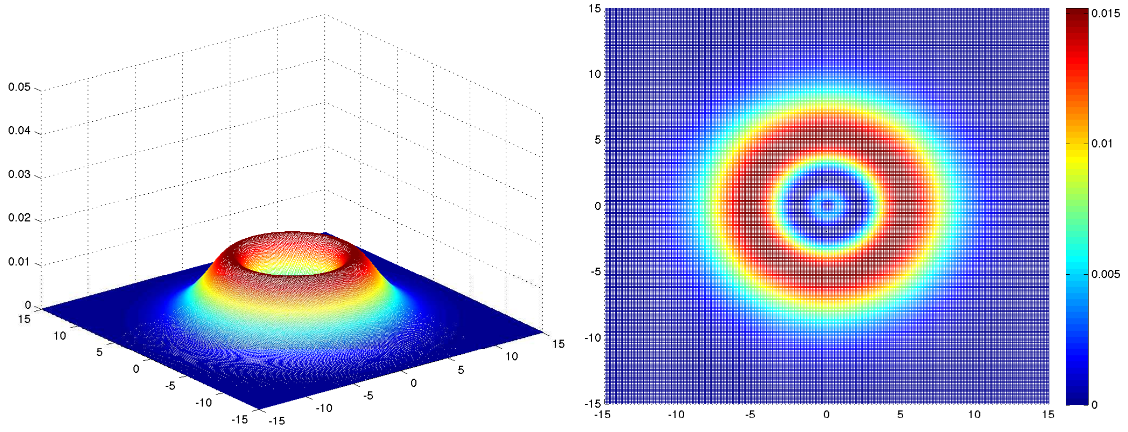
(f) R_{32}

Fig. 2.— Radial functions $R_{El}(r)$ (blue) and radial distribution functions $D_{El}(r) = r^2 R_{El}^2(r)$ (green) for the hydrogen atom. The radii r are normalized to the Bohr's radius a.



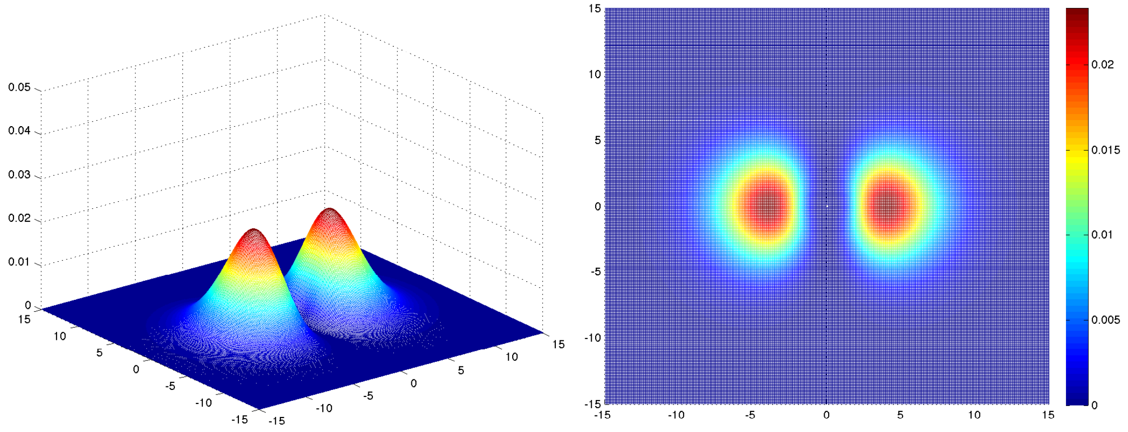
(a) $|\Psi_{100}|^2 d\vec{r}$

(b) $|\Psi_{100}|^2 d\vec{r}$



(c) $|\Psi_{200}|^2 d\vec{r}$

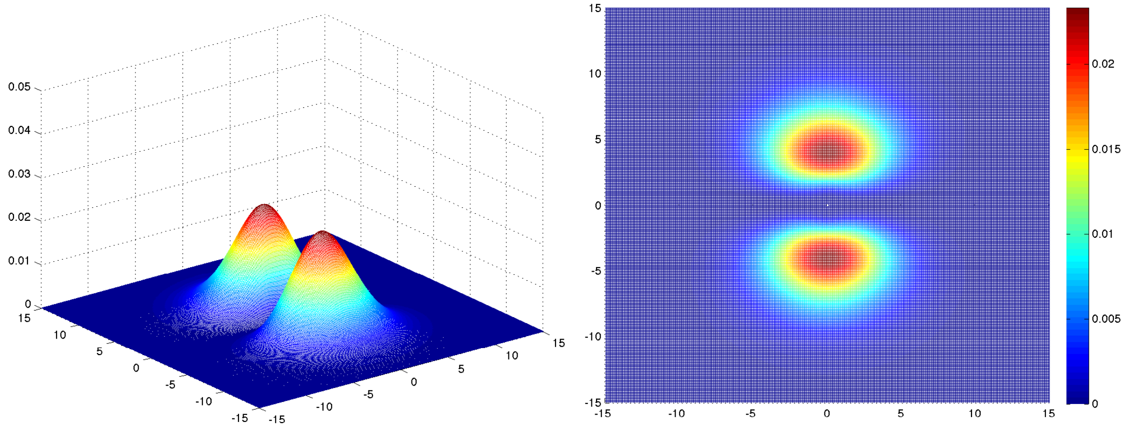
(d) $|\Psi_{200}|^2 d\vec{r}$



(e) $|\Psi_{210}|^2 d\vec{r}$

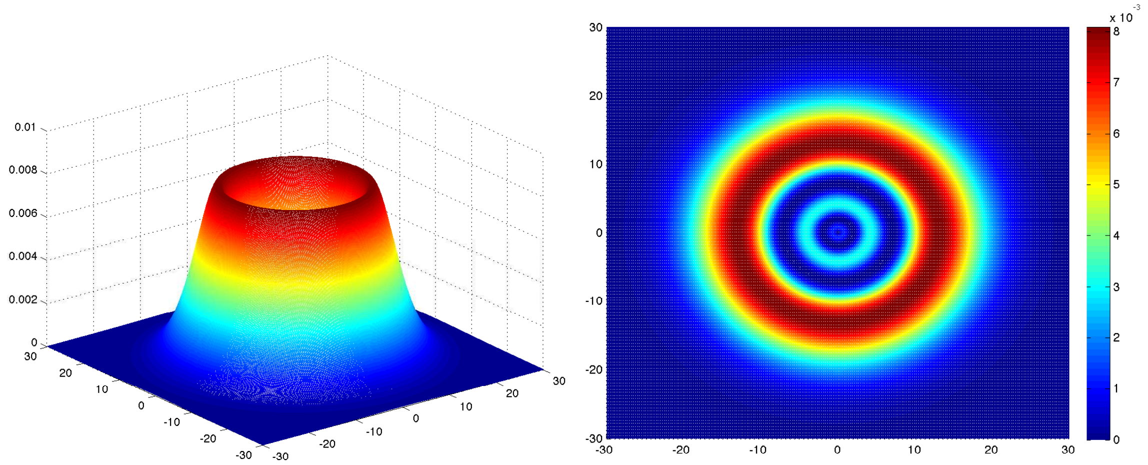
(f) $|\Psi_{210}|^2 d\vec{r}$

Fig. 3.— Probability density $P(r, \theta, \phi)$ of finding the electron in the Hydrogen atom at r, θ. The radius r is normalized to Bohr's radius a. Left are 3-d plots; right: same plots in 2d.



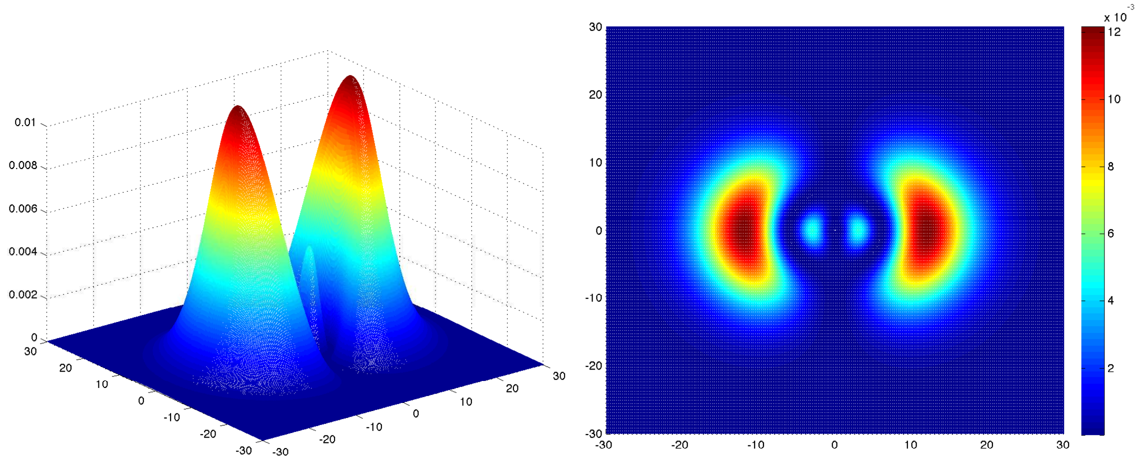
(a) $|\Psi_{211}|^2 d\vec{r}$

(b) $|\Psi_{211}|^2 d\vec{r}$



(c) $|\Psi_{300}|^2 d\vec{r}$

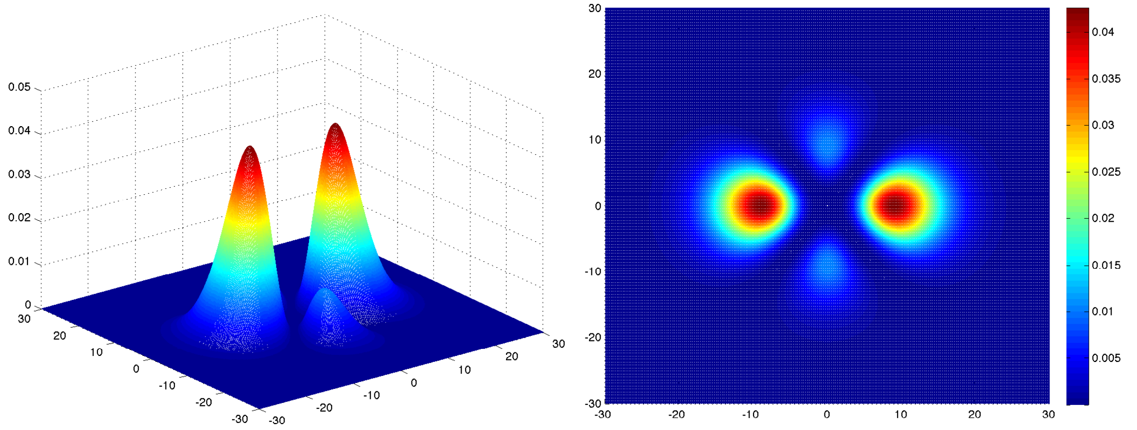
(d) $|\Psi_{300}|^2 d\vec{r}$



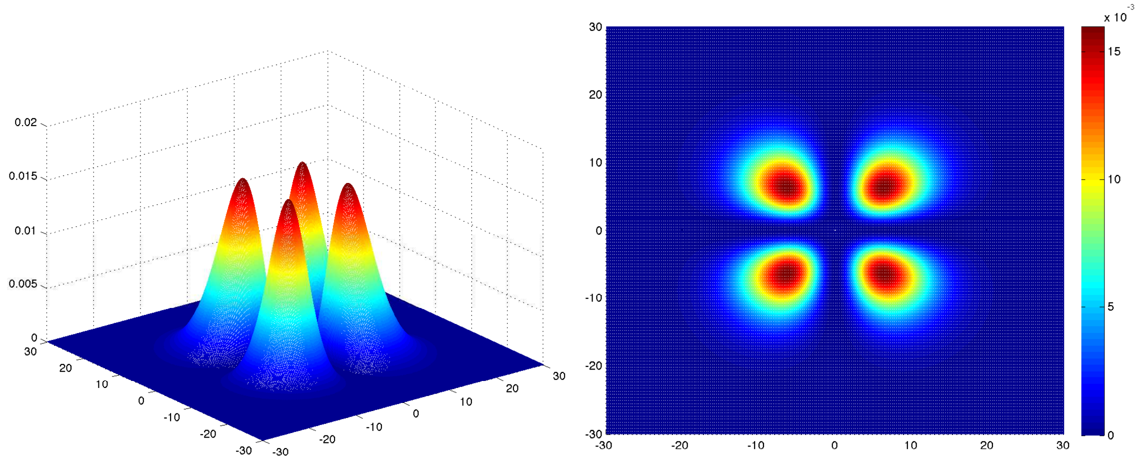
(e) $|\Psi_{310}|^2 d\vec{r}$

(f) $|\Psi_{310}|^2 d\vec{r}$

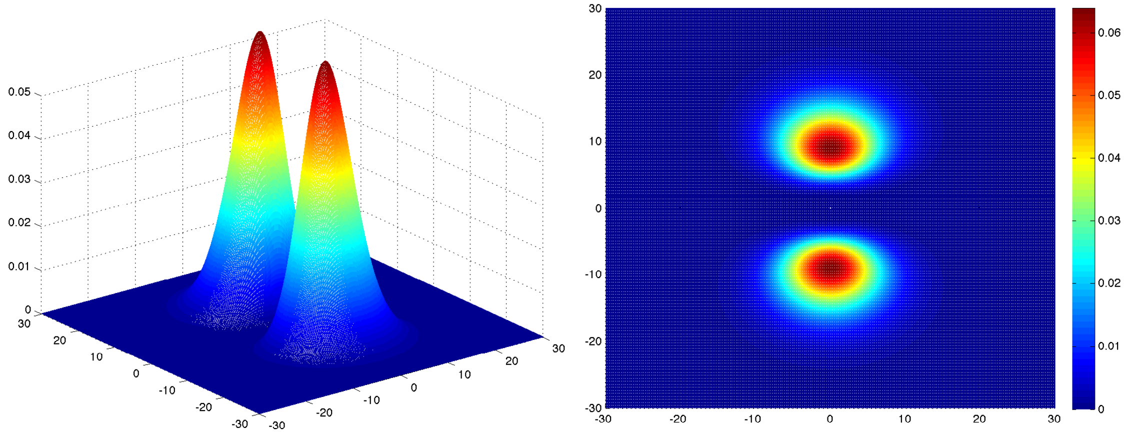
Fig. 4.— Same as in Figure 3.



(a) $|\Psi_{320}|^2 d\vec{r}$ (b) $|\Psi_{320}|^2 d\vec{r}$



(c) $|\Psi_{321}|^2 d\vec{r}$ (d) $|\Psi_{321}|^2 d\vec{r}$



(e) $|\Psi_{322}|^2 d\vec{r}$ (f) $|\Psi_{322}|^2 d\vec{r}$

Fig. 5.— Same as in Figure 3.