Quantum Physics 1

Class 20

Three-dimensional Schrodinger Equation

Angular Solutions

Angular Momentum

And

Magnetic Quantum NUmber

The Schrodinger Equation

Reminder

$$\hat{H}\psi = \hat{E}\psi$$

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi + V(\vec{r},t)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right)$$
$$+(E-V)\Psi = 0$$

Solutions for Central Potentials

Assuming: *V=V(r)*, dividing through by $\mathrm{R\Theta\Phi}$,
and multiplying through by $\sin^2\theta\, \mathrm{r}^2 2\mathrm{m}/\hbar^2$,
we can separate the azimuthal term:

$$\sin^2\theta\left(\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2m}{\hbar^2}\right)(E-V)r^2\right)$$
$$+\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)=-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=m_l^2$$

Which has solutions: $\boldsymbol{\Phi(\phi)=e^{\pm i m_l \phi}}$.
In order for Φ to be single-valued for any ϕ ,
$\mathrm{m_l}$ must be an integer.

θ solution for central potential

We are now left with the other two variables, r and θ.
Separating the angular terms from the radial terms:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - r^2\frac{2m\big(E - V(r)\big)}{\hbar^2} =$$

$$+\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right] = l(l+1)$$

Making the substitution x=cosθ, the θ side of the relation is known as the Legendre Equation:

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

and the solutions are the Associated Legendre Polynomials

θ solution for central potential

$$\Theta_{lm}(x) = (1 - x^2)^{|m|/2} \frac{d^{|m|}P_l}{dx^{|m|}}$$

$$With\, P_l(x) = \sum_{j=0}^{N} (-1)^j \frac{(2l-2j)!x^{l-2j}}{2^l l!(l-2j)!(l-1)!}$$

$$where\ N = \frac{l}{2} for\ l\ even\ and\ N = \frac{l-1}{2} for\ n\ odd.$$

from which we can find

$\Theta_{00} = 1,$

$\Theta_{10} = x, \quad \Theta_1^{\pm 1} = (1 - x^2)^{1/2},$

$\Theta_2^0 = 1 - 3x^2, \quad \Theta_2^{\pm 1} = (1 - x^2)^{1/2} x$

Associated Legendre functions

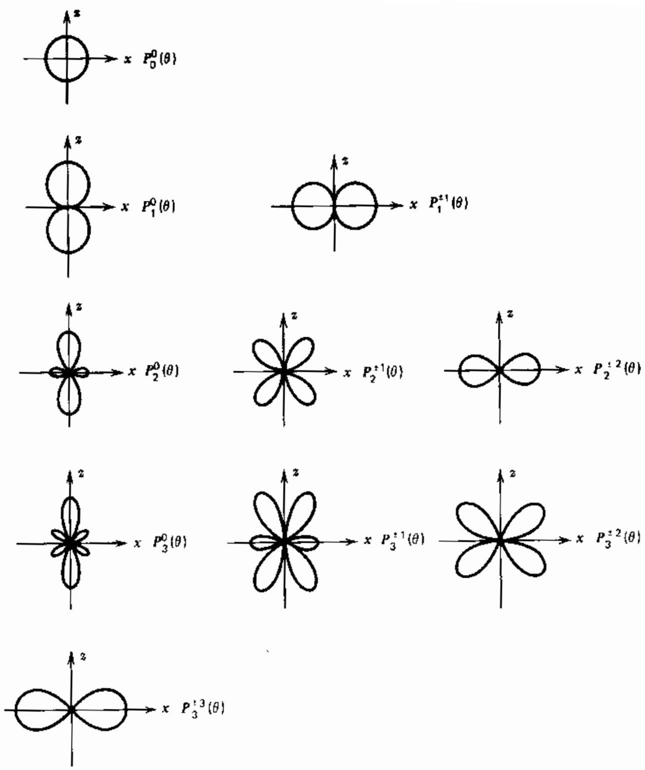
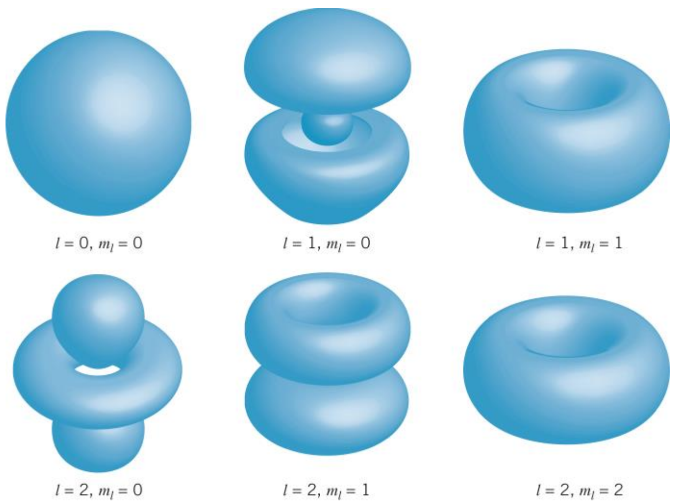


Fig. 12-3. Shapes of the associated Legendre polynomials as a function of θ, the angle between the z-axis and the equatorial plane, denoted here by the x-axis.

from Gasiorowicz



From Krane

See http://falstad.com/qmatom

θ and φ together – Spherical harmonics

Angular solutions put together

The θ and φ solutions can now be combined

$$F_{lm}(\theta, \varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi)$$

and when normalized, yields the

Spherical Harmonics:

$$Y_l^m \equiv \left(\frac{2l+1}{4\pi}\right)\frac{(l-m)!}{(l+m)!}\Theta_l^m(\cos\theta)e^{im\varphi}$$

The orthonormality relation is:

$$\iint Y_l^m Y_{l'}^{m'} d\theta d\varphi = \delta_{ll'}\delta mm'$$

Krane has a nice listing of the spherical harmonics

Spherical Harmonic Functions

l	m	$Y_{lm}(\varphi,\theta)$
0	0	$(4\pi)^{-1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	1	$-(3/8\pi)^{1/2}\sin\theta\, e^{i\varphi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta-1)$

Angular solutions

- Note that for a given value of l there will only be solutions for

$$m_l = -l, -l+1, -l+2, .., 0, .., l-1, l$$

- Note that these solutions only require a central potential.

Angular momentum and magnetic quantum numbers: l and m_l

Another look at the 3D Schrodinger equation

Another way to construct the 3D Schrodinger equation is to compare it to the classical equation:

$$\mathrm{T} + \mathrm{V} = \frac{p^2}{2m} + V = E$$

Breaking p up into components:

$$p^2 = p_x^2 + p_y^2 + p_z^2 = p_r^2 + p_t^2 \; \textit{(radial and tangential)}$$

and in terms of angular momentum: $p_t = \frac{L}{r}$.

$$\frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V = E$$

Angular momentum

If we now compare this expression to the Laplacian version we see that L^2 should be an operator and we can test if it has eigenvalues and functions.

We already know from our prior math that the angular part of the Laplacian has the same eigenfunctions as the Hamiltonian.

Let′s look more closely at the L operator.

We think: $\hat{L}^2\psi = L^2\psi$.

Classically: $\vec{L} = \vec{r} \times \vec{p}$, so let′s do the math.

Angular momentum operators

In Cartesian coordinates:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_x = yp_z - zp_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = zp_x - xp_z = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = xp_y - yp_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Angular momentum in spherical coordinates (1)

$$L_x = \frac{\hbar}{i}\left(-\sin\varphi\,\frac{\partial}{\partial\theta} - \cot\theta\,\cos\varphi\,\frac{\partial}{\partial\varphi}\right)$$

$$L_y = \frac{\hbar}{i}\left(-\cos\varphi\,\frac{\partial}{\partial\theta} - \cot\theta\,\sin\varphi\,\frac{\partial}{\partial\varphi}\right)$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

Commutator: Reminder

A simultaneous eigenstate is one whose state function

is an eigenstate of two operators:

$\hat{Q}\psi_{q,r} = q\psi_{q,r}$ and $\hat{R}\psi_{q,r} = r\psi_{q,r}$

Because they are eigenstates:

$\langle Q \rangle = q \quad \Delta Q = 0$ and $\langle R \rangle = r \quad \Delta R = 0$

$$\left[\hat{Q}, \hat{R}\right] = \hat{Q}\hat{R} - \hat{R}\hat{Q} = 0$$

1) Operators that commute define a complete set of simultaneous eigenfunctions.
2) Two operators that share a complete set of eigenfunctions commute.

Useful commutator/operator relations

$$[A, B] = AB - BA$$
$$[A, B] = -[B, A]$$
$$[A, B + C] = [A, B] + [A, C]$$
$$[A, BC] = [A, B]C + B[A, C]$$
$$\big[A, [B, C]\big] + \big[B, [C, A]\big] + \big[C, [A, B]\big] = 0$$

What can we tell about L?

We can learn quite a bit about angular momentum without doing any integrals.
We can show that L_z, and L_x cannot have a complete set of common eigenstates by considering the commutator $[L_z, L_x]$.

$L_z = xp_y - yp_x; \quad L_x = yp_z - zp_y; \quad L_y = zp_x - xp_z$

$L^2 = L_x^2 + L_y^2 + L_z^2$

$[L_x, L_z] = \left[yp_z - zp_y, xp_y - yp_x\right]$

$= \left[yp_z, xp_y\right] - \left[yp_z, yp_x\right] - \left[zp_y, xp_y\right] + \left[zp_y, yp_x\right]$

$= \left[yp_z, xp_y\right] + 0 + 0 + \left[zp_y, yp_x\right]$

$= x\left[yp_z, p_y\right] + \left[yp_z, x\right]p_y + \left[zp_y, yp_x\right] = -x\left[p_y, yp_z\right] - \left[x, yp_z\right]p_y + \left[zp_y, yp_x\right]$

$= -xy\left[p_y, p_z\right] - x\left[p_y, y\right]p_z - y\left[x, p_z\right]p_y - \left[x, y\right]p_z p_y + \left[zp_y, yp_x\right] =$

$= 0 - x\left[p_y, y\right]p_z + 0 - 0 + \left[zp_y, yp_x\right] = x\left[y, p_y\right]p_z + \left[zp_y, yp_x\right]$

$= x\left[y, p_y\right]p_z + y\left[zp_y, p_x\right] + \left[zp_y, y\right]p_x = x\left[y, p_y\right]p_z - y\left[p_x, zp_y\right] - \left[y, zp_y\right]p_x$

$= x\left[y, p_y\right]p_z - yz\left[p_x, p_y\right] - y\left[p_x, z\right]p_y - z\left[y, p_y\right]p_x - \left[y, z\right]p_y p_x$

$= x\left[y, p_y\right]p_z - 0 - 0 - z\left[y, p_y\right]p_x - 0 = i\hbar\{xp_z - zp_x\} = -i\hbar L_y$

Similarly: $\left[L_x, L_y\right] = i\hbar L_z$ and $\left[L_y, L_z\right] = i\hbar L_x$

What can we tell about L?

- We can also show (homework!) that $[L^2,L_z]=0$.
- This tells us that there exists a complete set of eigenfunctions for both operators, or that we can measure both quantities simultaneously with infinite accruracy.
- (We already knew that because we did the work to find the eigenfunctions and values, but we could have avoided that work if all we wanted was to know whether it could be done.)

Angular Momentum in Spherical coordinates (2)

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

- We have already found the eigenfunctions of this operator. They are the spherical harmonics.
- We have previously found that the eigenvalues of L^2 are $l(l+1)$ with l=integers 0, 1, 2, 3... if the potential is central.
- Angular momentum manifests itself as a magnetic dipole moment when the particle with L has charge.
- It is most useful to know the projection of the dipole onto an applied magnetic field. (Let's say in the z direction.)