Lecture 20 - Schrödinger equation in 3D

What's important:
- Schrödinger equation in 3D
- angular momentum operators

Text: Gasiorowicz, Chap. 10

3D Schrödinger equation

As discussed in Lec. 17, the time-independent Schrödinger equation for a free particle in three dimensions reads:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)u_E(x,y,z)=E\,u_E(x,y,z). \quad (1)$$

Adding a time-independent potential can easily be accommodated through

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)u_E(x,y,z)+V(x,y,z)\,u_E(x,y,z)=E\,u_E(x,y,z) \quad (2)$$

Now, for many situations of interest, the potential:
- is between two objects, both of whose motion must be considered
- depends only on the radial separation *r*, so-called central potentials.

Two-particle wavefunctions in one-dimension were introduced in Lec. 16, where we showed that if the potential energy depended only on the relative separation x_{rel}, the wavefunction could be written as a product of independent wavefunction for the relative motion and the cm motion. The same is true for three dimensions for central potentials $V(r)$. To review the notation (**bold** indicates vectors):

$$\mathbf{R}_{cm} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2) / (m_1 + m_2)$$

and (3)

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2.$$

With this replacement, the arguments of the plane wave

$$\mathbf{p}_1\mathbf{r}_1 + \mathbf{p}_2\mathbf{r}_2 = \mathbf{P}_{cm}\mathbf{R}_{cm} + \mathbf{pr}, \quad (4)$$

where the total and relative wavevectors are

$$\mathbf{P}_{cm} = \mathbf{p}_1 + \mathbf{p}_2 \quad \text{and} \quad \mathbf{p} = (m_2\mathbf{p}_1 - m_1\mathbf{p}_2) / (m_1 + m_2). \quad (5)$$

The total kinetic energy then becomes

$$E = P_{cm}^2 / 2M_{total} + p^2 / 2\mu. \quad (6)$$

Because the kinetic energy separates cleanly into two pieces, and the potential energy depends on relative separation, the wavefunction separates into a plane-wave part describing the cm, and a relative part which satisfies the Schrödinger equation with a reduced mass:

$$U(\mathbf{R}_{cm}, \mathbf{r}) = \exp(i\mathbf{P}_{cm}\mathbf{R}_{cm}/\hbar) \bullet u(\mathbf{r})$$

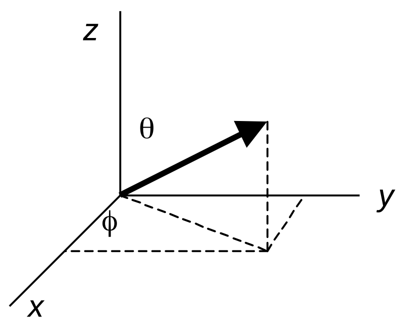
where $u(\mathbf{r})$ satisfies the time-independent SE:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)u(\mathbf{r}) = Eu(\mathbf{r}). \qquad (7)$$

Many of the problems of interest in the remaining part of this course are drawn from atomic and molecular physics, where the mass of the two-particle system is concentrated in the nucleus, such that the total mass is close to the nuclear mass and the reduced mass is close to the electron mass. As a result, we will often write Eq. (7) with μ replaced by m_e; but we should keep in mind that the *exact* solution involves the reduced mass.

Central potentials

That the potential in Eq. (7) depends on r, rather than $\mathbf{r}$, suggests that it may be useful to represent ∇^2 in spherical polars, rather than cartesian coordinates. Recalling the definition



It takes repeated application of the chain rule to establish that:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$
$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad (8)$$

The first term involves only r, giving us some hope that an approach based on the separation of variables might help. As a first step, write the wavefunction $u(r, \theta, \phi)$ as a product state:

$$u(r, \theta, \phi) = R(r) \bullet Y(\theta, \phi) \qquad (9)$$

and substitute into Eq. (7), transposing $E \bullet u(r, \theta, \phi)$ in so doing:

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

So long as $V(r)$ has no derivatives, we can divide by $R(r)$ without worry, leading to (after multiplying by r^2:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr^2}{\hbar^2}\left[E - V(r)\right] = -\frac{1}{Y\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right]Y \qquad (10)$$

To make the expression look less cumbersome, the arguments on RY have been dropped. This looks promising: the LHS depends only on r, and the RHS depends only on θ, ϕ, so both sides must equal a constant, which we define with some foreshadowing as $\ell(\ell+1)$. This gives us two equations:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr^2}{\hbar^2}\left[E - V(r)\right]R = \ell(\ell+1)R \qquad (11)$$

and

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y = Y\ell(\ell+1) \qquad (12)$$

We'll return to the first of these equations, called the *radial equation*, in a few lectures. The solution to the radial equation obviously depends on the choice of $V(r)$. But the angular equation is universal - valid for any central potential. We'll solve the Y functions in the next lecture, but to aid our interpretation, a diversion into the representation of angular momentum is in order.

Angular momentum in polar coordinates

We have already established an operator representation for the linear momentum **p**. In the following lectures, we interpret the functions Y in terms of angular momentum **L**, so it is worthwhile to establish at least a few of the angular momentum operator here, as well as its representation in spherical polar coordinates. Now, the classical form of **L** is

L = **r x p**.

When the usual quantum substitution $p_x \to -i\hbar\,\partial/\partial x$ is performed, the order of **r** and **p** is even more important than in the classical cross product. For example,

$$L_z = xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad (13)$$

In polar coordinates, this operator has the form

$$L_z = -i\hbar\, \partial / \partial\phi \tag{14}$$

which we establish by consistency. Recalling the transformation between coordinate systems

$$x = r \sin\theta \cos\phi \qquad y = r \sin\theta \sin\phi \qquad z = r \cos\theta$$

then

$$L_z = -i\hbar \frac{\partial}{\partial\phi} = -i\hbar \left[\frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z} \right]$$

$$= -i\hbar \left[\frac{\partial r \sin\theta \cos\phi}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial r \sin\theta \sin\phi}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial r \cos\theta}{\partial\phi}\frac{\partial}{\partial z} \right]$$

$$= -i\hbar \left[-r \sin\theta \sin\phi \frac{\partial}{\partial x} + r \sin\theta \cos\phi \frac{\partial}{\partial y} + 0 \cdot \frac{\partial}{\partial z} \right]$$

$$= -i\hbar \left[-y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} \right]$$

The last line is just Eq. (13) again. Similar expressions can be obtained for L_x and L_y:

$$L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \tag{15}$$

$$L_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \tag{16}$$

Eqs. (14) - (16) can be combined to yield:

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right] \tag{17}$$

Eq. (17) has the same form as (13), which is why we have made the identification with $\ell(\ell+1)$. Why we chose this instead of ℓ^2 will become apparent in the next two lectures.