CHM 502 - Module 3 - A Review of Model Quantum Systems

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Let's spend a little time reviewing solutions to the most commonly discussed quantum systems. We'll touch on, in particular,

- the free particle

- the particle in a box

- the quantum harmonic oscillator

- quantum angular momentum and the rigid rotor

If you need more review of any of these topics, Chapter 2 of Griffiths "Introduction to Quantum Mechanics," is an excellent resource. You can also reference my lecture notes from my undergraduate quantum course, CHM 305, which can be found here.

1   The Free Particle

The simplest quantum problem is that of a particle of mass m exploring a flat potential energy surface in one dimension. To find the eigenfunctions of this system, we solve the 1D time-independent Schrödinger equation:

$$\hat{H} = \hat{KE} + V(x)^{\,0} \tag{1}$$

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) \tag{2}$$

The solution, of course, is a function that is proportional to its own second derivative, which is a sine or cosine, or equivalently a complex exponential:

$$\psi(x) = e^{ikx} \tag{3}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} = p/\hbar \tag{4}$$

We can also easily write down the full time-dependent Hamiltonian as:

$$\Psi(x,t) = e^{ikx}e^{-iEt/\hbar} = e^{ikx}e^{-i\omega t} \tag{5}$$

Note that this looks exactly like a plane wave: an oscillating amplitude or displacement that is sinusoidal in both time and space, with angular frequency $\omega = 2\pi\nu$ and wavevector $k = 2\pi/\lambda$.

The plane-wave energy eigenfunctions of the free particle are not actually physically realizable, because they have completely delocalized, infinite spatial extent. They are therefore not normalizeable.

Nevertheless, these eigenfunctions provide us with a nice continuous basis with which to describe arbitrary wavefunctions of particles exploring free space. For instance, we can write down the wavefunction of a wavepacket which carries a range of k vectors:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) \cdot e^{i(kx - \omega t)} \, dk \tag{6}$$

where $\phi(k)$ is typically a Gaussian envelope.

2   Particle in a Box

The particle in a box is essentially a free particle confined to a finite region of space. It represents a simple example of quantum confinement, which gives rise to discrete energy eigenvalues. The Hamiltonian is:

$$\hat{H}\psi(x) = \left[\frac{\hat{p}^2}{2m} + V(x) \right] \psi(x) \tag{7}$$

$$V(x) = \begin{cases} 0 & 0 < x < L \\ +\infty & \text{elsewhere} \end{cases} \tag{8}$$

The eigenvector solutions are just free particle wavefunctions subject to the boundary condition that the wavefunction is pinned to 0 at the edges of the box where the potential explodes to infinity. We therefore find a series of sinusoidal solutions that oscillate such that a half-integer number of wavelengths fall perfectly within the box:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L} \right), \quad n = 1, 2, 3, \ldots \tag{9}$$

Plugging these wavefunctions into the Hamiltonian gives rise to the following discrete energy eigenvalues:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{10}$$

3   Harmonic Oscillator

The harmonic oscillator problem assumes a quadratic potential well. This is a useful model system because a well of any shape can be approximated by a quadratic potential, for small displacements from the bottom of the well, centered at x_0:

$$V(x) = V(x_0) + \left(\frac{dV}{dx} \right)_{x_0} (x - x_0) + \left(\frac{d^2V}{dx^2} \right)_{x_0} (x - x_0)^2 + \mathcal{O}\left[(x - x_0)^3 \right] \tag{11}$$

where $\left(\frac{dV}{dx} \right)_{x_0} = 0$ at the bottom of the well.

We therefore write down the time-independent Schrödinger equation for the harmonic oscillator assuming $V(x) = \frac{1}{2}kx^2$, with spring constant $k = m\omega^2$:

$$\hat{H}\psi_n(x) = \left[\frac{\hat{p}^2}{2m} + \frac{1}{2}kx^2\right]\psi_n(x) = E_n\psi_n(x) \tag{12}$$

This differential equation can be solved, but the solutions do not have a particularly compact form. They can be expressed as:

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2/2}, \quad n = 0, 1, 2\ldots \tag{13}$$

where N_n is a normalization constant, $H_n(x)$ is the nth Hermite polynomial, and $\alpha = \sqrt{km/\hbar^2}$. The nth wavefunction has n nodes and decays into the walls of the potential according to its Gaussian envelope.

One special property of the harmonic oscillator is the fact that, despite the complicated explicit form of its eigenfunctions, it has an evenly spaced ladder of energy eigenvalues:

$$E_n = \hbar\omega\left[n + \frac{1}{2}\right], \quad n = 0, 1, 2\ldots \tag{14}$$

This uniformly spaced eigenvalue spectrum is peculiar to the harmonic oscillator. We can therefore represent any system with evenly spaced energy levels as a harmonic oscillator. This will come in handy later on when we consider the quantization of the electromagnetic field.

3.1 The ladder operator approach

A better way to approach the solutions to the harmonic oscillator is to work within the ladder operator formalism, which sidesteps having to directly solve any differential equations. We'll go through this very quickly here, but Griffiths Section 2.3 is a great reference if you need more review.

Let's start by inspecting the harmonic oscillator Hamiltonian, which we'll rewrite as:

$$\hat{H} = \frac{1}{2m}\left[\hat{p}^2 + (m\omega\hat{x})^2\right] \tag{15}$$

Based on the form of this Hamiltonian, we might hope that we can factor it, given that $\hat{x}$ and $\hat{p}$ appear as a sum of their squares. For instance, if we were working with numbers rather than operators, we could do:

$$u^2 + v^2 = (u + iv) \cdot (u - iv) \tag{16}$$

Unfortunately, $\hat{p}$ and $\hat{x}$ are operators, not numbers, and famously do not commute. Regardless, let's take some inspiration from trying to factor the Hamiltonian and define the following operators:

$$\hat{a} = \frac{1}{\sqrt{2\hbar m\omega}}\left[m\omega\hat{x} + i\hat{p}\right] \tag{17}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}\left[m\omega\hat{x} - i\hat{p}\right] \tag{18}$$

As a quick aside, we can also conveniently express $\hat{x}$ and $\hat{p}$ as linear combinations of these two new operators:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left[\hat{a}^\dagger + \hat{a}\right] \tag{19}$$

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}\left[\hat{a}^\dagger - \hat{a}\right] \tag{20}$$

If we then consider the product of the $\hat{a}$ and $\hat{a}^\dagger$ we find:

$$\hat{a}^\dagger\hat{a} = \frac{1}{2\hbar m\omega}\left[m\omega\hat{x} - i\hat{p}\right]\cdot\left[m\omega\hat{x} + i\hat{p}\right] \tag{21}$$

$$= \frac{1}{2\hbar m\omega}\left[(m\omega\hat{x})^2 + \hat{p}^2 - im\omega\hat{p}\hat{x} + im\omega\hat{x}\hat{p}\right] \tag{22}$$

$$= \frac{1}{2\hbar m\omega}\left[(m\omega\hat{x})^2 + \hat{p}^2 - im\omega\left[\hat{p}\hat{x} - \hat{x}\hat{p}\right]\right] \tag{23}$$

$$= \frac{1}{2\hbar m\omega}\left[(m\omega\hat{x})^2 + \hat{p}^2 - im\omega\left[-i\hbar\right]\right] \tag{24}$$

$$= \frac{1}{\hbar\omega}\cdot\frac{1}{2m}\left[(m\omega\hat{x})^2 + \hat{p}^2\right] - \frac{1}{2} \tag{25}$$

$$= \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2} \tag{26}$$

$$\rightarrow \quad \hat{H} = \hbar\omega\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right] \tag{27}$$

So we've recovered a simpler form of the Hamiltonian in terms of the $\hat{a}$ and $\hat{a}^\dagger$ operators. Note that the Hamiltonian doesn't factor perfectly, as we have an extra term of $\frac{1}{2}\hbar\omega$ representing the zero point energy of the system. This a consequence of the uncertainty principle and the fact that $\hat{x}$ and $\hat{p}$ do not commute.

With a bit more math, we can also find that

$$\left[\hat{a}, \hat{a}^\dagger\right] = 1 \tag{28}$$

So how does all this help us solve the Schrödinger equation? Let's examine what happens if we apply our new operators to $|n\rangle$, the nth solution to the HO Schrödinger equation.

$$\hat{H}\left[\hat{a}^{\dagger}\left|n\right\rangle\right] = \hbar\omega\left[\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right]\hat{a}^{\dagger}\left|n\right\rangle \tag{29}$$

$$= \hbar\omega\left[\hat{a}^{\dagger}\hat{a}\hat{a}^{\dagger} + \frac{1}{2}\hat{a}^{\dagger}\right]\left|n\right\rangle \tag{30}$$

$$= \hbar\omega\hat{a}^{\dagger}\left[\hat{a}\hat{a}^{\dagger} + \frac{1}{2}\right]\left|n\right\rangle \tag{31}$$

$$= \hbar\omega\hat{a}^{\dagger}\left[\hat{a}^{\dagger}\hat{a} + 1 + \frac{1}{2}\right]\left|n\right\rangle \tag{32}$$

$$= \hat{a}^{\dagger}\left[\hbar\omega\left[\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right] + \hbar\omega\right]\left|n\right\rangle \tag{33}$$

$$= \hat{a}^{\dagger}\left[\hat{H} + \hbar\omega\right]\left|n\right\rangle \tag{34}$$

$$= \hat{a}^{\dagger}\left[E + \hbar\omega\right]\left|n\right\rangle = \left[E + \hbar\omega\right]\hat{a}^{\dagger}\left|n\right\rangle \tag{35}$$

$\hat{a}^{\dagger}\left|n\right\rangle$ is therefore an eigenfunction of the Hamiltonian with energy eigenvalue $E + \hbar\omega$. We have shown that we can use $\hat{a}^{\dagger}$ as a *raising* ladder operator or *creation operator*. As long as we know what $\left|n\right\rangle$ looks like, we can generate all other eigenvectors up the ladder of energy levels by repeatedly applying $\hat{a}^{\dagger}$ to $\left|n\right\rangle$.

With similar math, we can show that $\hat{a}\left|n\right\rangle$ generates an eigenfunction of the Hamiltonian with energy eigenvalue $E - \hbar\omega$, and therefore constitutes a *lowering* ladder operator, or *annihilation operator*.

We won't go through all the details here, but by normalizing the wavefunctions generated from the raising and lowering operators (e.g. making sure that $\langle n|\hat{a}^{\dagger}\hat{a}|n\rangle = 1$) one can show that:

$$\hat{a}^{\dagger}\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle \tag{36}$$

$$\hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle \tag{37}$$

$$\hat{a}^{\dagger}\hat{a}\left|n\right\rangle = n\left|n\right\rangle \tag{38}$$

$$\hat{H}\left|n\right\rangle = \hbar\omega\left[\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right]\left|n\right\rangle = \hbar\omega\left[n + \frac{1}{2}\right]\left|n\right\rangle = E_n\left|n\right\rangle \quad \checkmark \tag{39}$$

This formalism therefore allows us to generate all the eigenfunctions and eigenvalues for this system without having to deal with tedious integrals of Hermite polynomials. One can also evaluate various expectation values using the expressions for $\hat{x}$ and $\hat{p}$ in terms of ladder operators.

4 Angular Momentum

Finally, let's review the principles of quantum mechanical angular momentum and the rigid rotor Hamiltonian. Griffiths Section 4.3 is a great resource for more review on this topic.

It becomes useful to cast problems in terms of angular momentum in cases where the Hamilto-

nian is spherically symmetric $V(x, y, z) = V(r)$. In three dimensions :

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(r) \tag{40}$$

$$\equiv -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{41}$$

Where ∇^2 is the Laplacian operator.

In spherical coordinates, the Laplacian can be re-expressed as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial}{\partial \theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2} \tag{42}$$

In spherical coordinates, we can therefore recast the Hamiltonian as a sum of three separate parts:

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]\right] \qquad -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial}{\partial \theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right] \qquad +V(r) \tag{43}$$

$$= \hat{KE}_{\text{radial}} \qquad\qquad +\hat{KE}_{\text{angular}} \qquad\qquad\qquad\qquad +V(r) \tag{44}$$

We know from classical mechanics that angular kinetic energy is given by $KE_{\text{angular}} = \frac{L^2}{2I}$, where L is angular momentum and $I = mr^2$ is the moment of inertia. This is in direct analogy to the kinetic energy for linear motion $KE = \frac{p^2}{2m}$, with L standing in for p, and I for m, as a sort of angular mass.

This allows us to write down an expression for the angular momentum quantum operator:

$$\hat{L}^2 = 2mr^2 \cdot \hat{KE}_{\text{angular}} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial}{\partial \theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right] \tag{45}$$

Note that all of the angular information encoded in $\hat{H}$ in Eqn. 43 is contained in the $\hat{L}^2$ term, for the case of a spherically symmetric potential. This means that the eigenvector solutions to this Hamiltonian will factor into $\Psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$, and the angular component of the wavefunctions $Y(\theta, \phi)$ will also be the eigenvectors of $\hat{L}^2$. This is why $\hat{L}^2$ is such an important quantum operator: *its eigenvectors are the angular components to the solutions of any spherically symmetric Hamiltonian*, including the rigid rotor and the hydrogen atom.

The $Y(\theta, \phi)$ solutions to $\hat{L}^2$ are called spherical harmonics, and take the form:

$$Y_J^m(\theta, \phi) = \Theta(\theta)\Phi(\phi) \tag{46}$$

$$\propto P_J^{|m|}(\cos\theta)\, e^{im\phi} \tag{47}$$

$$J = 0, 1, 2\ldots \tag{48}$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm J \tag{49}$$

where $P_J^{|m|}(\cos\theta)$ are Legendre polynomials, expressed as functions of $\cos\theta$. The quantum numbers J and m capture, respectively, the total number of nodes of each wavefunction and the angular orientation of these nodes.

For the rigid rotor Hamiltonian, where r is fixed, and $V(r) = 0$, we have $\hat{H} = -\frac{\hat{L}^2}{2I}$, and the $Y_J^m(\theta, \phi)$ make up the energy eigenfunctions with corresponding energy eigenvalues

$$E_J = \frac{\hbar^2}{2I}J(J+1) \tag{50}$$

Finally, it's worth mentioning that the Cartesian components of $\hat{L}$ often crop up, and it's useful to know a bit about how they behave.

Classically, $\vec{L} = \vec{r} \times \vec{p}$, where $\vec{r}$ is the position vector of a moving particle relative to the origin, and $\vec{p}$ is its linear momentum perpendicular to $\vec{r}$. Therefore:

$$\vec{L} = \vec{r} \times \vec{p} = \det \begin{bmatrix} \hat{x} & \hat{y} & \hat{z} \\ r_x & r_y & r_z \\ p_x & p_y & p_z \end{bmatrix} \tag{51}$$

$$= [L_x, L_y, \textrm{Ł}_z] = [yp_z - zp_y, zp_x - xp_z, xp_y - yp_x] \tag{52}$$

We can define quantum operator analogs of the components of $\vec{L}$ simply by replacing $[x, y, z]$ and $[p_x, p_y, p_z]$ with their quantum operator analogs, e.g.

$$\hat{L}_x = \hat{y} \cdot \hat{p}_z - \hat{z} \cdot \hat{p}_y, \qquad \hat{y} = y, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}, \quad \textrm{etc.} \tag{53}$$

One can show that these Cartesian components of angular momentum have interesting commutation relations:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \tag{54}$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \tag{55}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \tag{56}$$

We can also relate our $\hat{L}^2$ operator to these components using

$$\hat{L}^2 = \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right] \cdot \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right] = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{57}$$

And one can show that $\hat{L}^2$ commutes with each of its Cartesian components:

$$[\hat{L}^2, \hat{L}_{x,y,z}] = 0 \tag{58}$$

These commutation relations tell us that we can simultaneously measure the square of the total angular momentum of a system, $\hat{L}^2$, as well as its projection on *one* of the three Cartesian axes. However, if you try to find the projection of $\hat{L}^2$ on more than one Cartesian axis simultaneously you will run afoul of the uncertainty principle.

While we won't get into it here, note that there is also a ladder formalism to treat the eigenvectors and eigenvalues of $\hat{L}^2$ and its Cartesian components, similar to that used for the harmonic oscillator.