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

Prof. Marissa Weichman

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
- the rigid rotor
- quantum angular momentum and spin

If you need more review of any of these topics, Chapters 2 and 4 of Griffiths "Introduction to Quantum Mechanics," are an excellent resource.

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 eigenstates of this system, we solve the 1D time-independent Schrödinger equation:

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

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

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 write down the full time-dependent wavefunction 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 eigenstates of the free particle are not actually physically realizable, because they have infinite spatial extent. They are therefore only normalizeable over a finite window.

Nevertheless, these eigenstates provide us with a nice continuous basis with which to describe arbitrary wavefunctions of particles exploring free space. For instance, we can describe a wavepacket composed of waves with a distribution of k values:

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

where $\phi(k)$ is, e.g., a Gaussian envelope.

2 Particle in a Box

The particle in a box (PIB) is 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 PIB Hamiltonian is given by:

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

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

The eigenstate 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. 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 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 an arbitrary potential well can be approximated by a quadratic potential for small displacements from the bottom of the well, centered at x_0:

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

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

The time-independent Schrödinger equation for the harmonic oscillator with $V(x) = \frac{1}{2}kx^2$ and spring constant $k = m\omega^2$ is:

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

This differential equation can be solved to find $\psi_n(x)$, but the solutions do not have a 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 n^{th} Hermite polynomial, and $\alpha = \sqrt{km/\hbar^2}$. The n^{th} wavefunction has n nodes and decays into the walls of the potential according to its Gaussian envelope.

Despite the complicated explicit form of the harmonic oscillator eigenstates, this system 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 describe any system with evenly spaced energy levels using the harmonic oscillator formalism. 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 harmonic oscillator problem 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 write:

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

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

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

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

Note that we can also 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 $\hat{a}$ and $\hat{a}^\dagger$ we find:

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

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

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

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

$$= \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2} \tag{25}$$

$$\rightarrow \quad \hat{H} = \hbar\omega\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right] \tag{26}$$

So we've recovered a simpler form of the Hamiltonian. 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 is 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

$$\left[\hat{a}, \hat{a}^\dagger\right] = 1 \quad \rightarrow \quad \hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + 1 \tag{27}$$

So how does all this help us solve the Schrödinger equation? Let's examine what happens if we apply our new operators to $|n\rangle$, which we define as the n^{th} eigenstate of the harmonic oscillator Hamiltonian:

$$\hat{H}\left[\hat{a}^\dagger|n\rangle\right] = \hbar\omega\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right]\hat{a}^\dagger|n\rangle \tag{28}$$

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

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

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

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

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

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

$\hat{a}^\dagger |n\rangle$ is therefore an eigenstate 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 $|n\rangle$ looks like, we can generate all other eigenstates up the ladder of energy levels by repeatedly applying $\hat{a}^\dagger$ to $|n\rangle$.

With similar math, we can show that $\hat{a}\,|n\rangle$ generates an eigenstate 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:

$$\hat{a}^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{35}$$

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle \tag{36}$$

$$\hat{a}^\dagger\hat{a}\,|n\rangle = n\,|n\rangle \tag{37}$$

$$\hat{H}\,|n\rangle = \hbar\omega\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right]|n\rangle = \hbar\omega\left[n + \frac{1}{2}\right]|n\rangle = E_n\,|n\rangle \quad \checkmark \tag{38}$$

This formalism therefore allows us to generate all the eigenstates 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 Radial Potentials & Quantum Angular Momentum

Let's now touch on quantum mechanical angular momentum and how its definition arises when we consider particles in spherically symmetric potentials. Griffiths Chapter 4 is a good resource for more review on this topic.

4.1 The Hamiltonian in 3D

Let's consider a 3D system where the Hamiltonian is spherically symmetric $V(x, y, z) = V(r)$:

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(r) \tag{39}$$

$$\equiv -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{40}$$

where ∇^2 is the Laplacian operator. In spherical coordinates, the Laplacian is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{41}$$

We can therefore recast the Hamiltonian as a sum of three separate parts:

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]\right] \quad -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad +V(r) \tag{42}$$

$$= \hat{KE}_{\text{radial}} \quad + \hat{KE}_{\text{angular}} \quad +V(r) \tag{43}$$

In classical mechanics, the 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, a sort of angular mass. 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.

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

$$\hat{L}^2 = 2I \cdot \hat{KE}_{\text{angular}} = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[\sin\theta \frac{\partial}{\partial\theta} \right] + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{44}$$

Note that for a spherically symmetric potential, all of the angular information encoded in $\hat{H}$ is contained in the $\hat{L}^2$ term in Eqn. 42. This means that the energy eigenstates will factor as $\Psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$, where $Y(\theta, \phi)$ is also an eigenstate of $\hat{L}^2$. This is one reason why $\hat{L}^2$ is so important: *its eigenstates are the angular part of the eigenstates of any spherically symmetric Hamiltonian*, including the rigid rotor and the H atom!

To give a specific example of a system with a radial potential, consider the rigid rotor Hamiltonian, taking Eqn. 42 with r fixed and $V(r) = 0$. We therefore have $\hat{H} = -\frac{\hat{L}^2}{2I}$. The energy eigenstates and eigenvalues of this system are given by:

$$\hat{H}\ Y_J^m(\theta, \phi) = E_J\ Y_J^m(\theta, \phi), \qquad E_J = \frac{\hbar^2}{2I} J(J+1) \tag{45}$$

where $Y_J^m(\theta, \phi)$ are the eigenstates of $\hat{L}^2$, also called "spherical harmonics," which take the form:

$$\hat{L}^2\ Y_J^m(\theta, \phi) = \hbar^2 J(J+1)\ Y_J^m(\theta, \phi) \tag{46}$$

$$Y_J^m(\theta, \phi) = \Theta(\theta)\Phi(\phi) \tag{47}$$

$$\propto P_J^{|m|}(\cos\theta)\, e^{im\phi} \tag{48}$$

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

$$m = 0,\ \pm 1,\ \pm 2,\ \ldots,\ \pm J \tag{50}$$

where $P_J^{|m|}(\cos\theta)$ are Legendre polynomials, expressed as functions of $\cos\theta$.

The integer values of the J and m quantum numbers arise from performing a separation of variables for θ and ϕ when solving for the eigenfunctions of Eqn. 44 (see Griffiths Chapter 4.1 for the details). J and m capture, respectively, the total number of nodes of each wavefunction and the angular orientation of these nodes, typically taken with respect to the lab-frame $\hat{z}$ axis.

We will say more about the Cartesian projections of the angular momentum operator below. But for now, let's just note that the $Y_J^m(\theta, \phi)$ are also eigenfunctions of $\hat{L}_z$, the projection of the angular momentum on the lab-frame z axis, with:

$$\hat{L}_z\ Y_J^m(\theta, \phi) = \hbar m\ Y_J^m(\theta, \phi) \tag{51}$$

4.2 Cartesian Components of Quantum Angular Momentum

The Cartesian components of $\hat{L}$ often crop up, and it's very useful to understand how they behave. Classically, $\underline{L} = \underline{r} \times \underline{p}$, where $\underline{r}$ is the position vector of a particle relative to the origin, and $\underline{p}$ is the particle's linear momentum. Therefore:

$$\underline{L} = \underline{r} \times \underline{p} = \det \begin{bmatrix} \underline{\hat{x}} & \underline{\hat{y}} & \underline{\hat{z}} \\ x & y & z \\ p_x & p_y & p_z \end{bmatrix} \tag{52}$$

$$= [L_x, L_y, L_z] = [yp_z - zp_y, zp_x - xp_z, xp_y - yp_x] \tag{53}$$

We can define quantum operator analogs of the Cartesian components of $\underline{L}$ simply by putting hats on $[x, y, z]$ and $[p_x, p_y, p_z]$:

$$\hat{L}_x = \hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y, \qquad \hat{y} = y, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}, \quad \text{etc.} \tag{54}$$

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

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

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

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \tag{57}$$

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

$$\hat{L}^2 = \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right] \cdot \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right] = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{58}$$

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

$$[\hat{L}^2, \hat{L}_{x,y,z}] = 0 \tag{59}$$

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.

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. See Griffiths Chapter 4.3 for details.

5 Spin

In the above, we considered *orbital* angular momentum, $\hat{L}$ that arises from the motion of the center of mass of a quantum object. We can also think about *spin*, $\hat{S}$, which arises from rotation of an object about its own center of mass. The funny thing is that quantum mechanical spin exists intrinsically even for elementary particles that are structureless points, like the electron. It's not helpful to think too hard about this; there is no classical analog here!

Mathematically, the quantum operator $\underline{\hat{S}}$ behaves much like $\underline{\hat{L}}$. We have:

$$\underline{\hat{S}} = \left[\hat{S}_x, \hat{S}_y, \hat{S}_z\right] \tag{60}$$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{61}$$

where the Cartesian components $\hat{S}_{x,y,z}$ have the same commutation relations we saw for the Cartesian components of $\underline{\hat{L}}$.

We label the eigenvectors of $\hat{S}^2$ as $|S, m\rangle$ with two quantum numbers, S and m, which are analogous to the J and m quantum numbers of $\hat{L}^2$:

$$\hat{S}^2 |S, m\rangle = \hbar^2 S(S+1) |S, m\rangle \tag{62}$$

$$\hat{S}_z |S, m\rangle = \hbar m |S, m\rangle \tag{63}$$

Note, however that while the $|S, m\rangle$ eigenfunctions behave mathematically like angular momentum eigenstates, they are *not* spherical harmonics. There is no θ, ϕ dependence to be found here. Their quantum numbers are also defined somewhat differently. In particular, while J could take on any positive integer value, S can take on half-integer values as well:

$$S = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots \tag{64}$$

$$m = [-S, -S+1, \ldots, S-1, S] \tag{65}$$

The quantum number S is fixed and immutable for a given particle. Fermions have half-integer spin, while bosons have integer spin. To give some familiar examples, electrons are fermions with $S = 1/2$. Protons are fermions with nuclear spin $S = 1/2$, while deuterium nuclei are bosons with $S = 1$ and carbon-12 nuclei are bosons with $S = 0$.

As we will see in the next lecture, $S = 1/2$ particles have only two allowed values of m, $m = [-\frac{1}{2}, \frac{1}{2}]$. They are therefore a canonical two-level system, and make a nice toy model to work with:

$$|+\rangle, |-\rangle \equiv |\tfrac{1}{2}, \tfrac{1}{2}\rangle, |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \tag{66}$$

$$\hat{S}_z |+\rangle = +\tfrac{\hbar}{2} |+\rangle \tag{67}$$

$$\hat{S}_z |-\rangle = -\tfrac{\hbar}{2} |-\rangle \tag{68}$$

Much more on this to come!