XIII. THE HYDROGEN ATOM

Our goal for the next couple of lectures is to understand the hydrogen atom. Historically, the analysis first appeared as the culmination of Schrödingers series of papers in 1926. Imagine Schrödinger typing up all these complicated equations while ensconsed in a cabin in the Austrian alps.

The Hamiltonian for the Hydrogen atom is clearly the most complicated one we would find here. We are seeking to describe an electron in a central potential exerted by a sole-proton nucleous. It is obviously 3d, and therefore requires not just a second derivative, but rather, a Laplacian:

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ke^2}{|\vec{r}|} \tag{315}$$

coupled with a nasty potential. The Laplacian could be a real burden if we insist on working in cartesian coordinates. Given the potential, how should we handle it?

As a matter of habit, you should adjust your coordinate system to the form of the potential. The Laplacian can always be recast easily in other coordinate systems. In this case, we expect that polar coordinates would be best.

Getting the polar coordinates to work within the Laplacian is easy. What is a gradient if not a way of getting the differential of a function. The first step is to write a differential of $\vec{r}$. In polar coordinates, we can write:

$$d\vec{r} = \hat{r}dr + rd\theta\hat{\theta} + r\sin\theta d\phi\hat{\phi} \tag{316}$$

where the hatted vectors always point in the direction of the change of the unit vector when the parameter under the hat changes. By the requirement that $\nabla f(\vec{r})\cdot d\vec{r} = df$ we have:

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{317}$$

The laplacian is just an application of the nabla on itself. This is a bit dangerous, since we must remember that the unit vectors themselves are functions of location. The dangerous parts arise from a 'cross dependence on parameters. This is a problem with $\hat{\theta}$ and $\hat{r}$:

$$\frac{\partial\hat{\theta}}{\partial\phi} = \cos\theta\hat{\phi}, \quad \frac{\partial\hat{r}}{\partial\phi} = \sin\theta\hat{\phi}, \quad \frac{\partial\hat{r}}{\partial\theta} = \hat{\theta} \tag{318}$$

Therefore:

$$\nabla\cdot\nabla = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta}\cdot\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial\phi}\cdot\left(\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta}\right) \tag{319}$$

and the mixed terms add up to give:

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \cot\theta\frac{\partial}{\partial\theta}\right) \tag{320}$$

which I would like you to read as the r-pices, and the angular stuff (for lack of a better word…). But what is the angular stuff? It is the angular momentum:

$$\hat{L}^2 = (\vec{r}\times\vec{p})^2 = r^2(\hat{r}\times\vec{p})^2 \tag{321}$$

With this insight, let us set aside the SE, not before making a separation of variable ansatz:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{322}$$

We will assume that the θ and ϕ pieces will just give:

$$\hat{L}^2 Y(\theta,\phi) = \ell(\ell+1)Y(\theta,\phi) \tag{323}$$

which would leave the r pieces to solve the relatively simple SE:

$$ER(r) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} - \frac{\ell(\ell+1)}{r^2}R\right) - \frac{Ke^2}{r}R \tag{324}$$

The first thing to do is figure out the angular momentum piece. For that, I'd like to take an algebraic detour, because the equation for the angular parts are pretty nasty. As it turns out, though, the algebraic structure is rather simple.

A. Momentum as generators of translation

Before we attack the issue of angular momenta, let's reconsider the issue of momentum. By now we know that it is almost the definition of momentum being the operator which has the following commutation relation with location:

$$[\hat{x},\, \hat{p}_x] = i\hbar. \tag{325}$$

There is another way of writing this relation. Imagine calculating the matrix element of the location:

$$\langle\psi|\, \hat{x}\, |\phi\rangle = \int dx \psi^*(x) x \phi(x) \tag{326}$$

Now consider making a unitary transformation that looks as follows:

$$\hat{U}_a = \exp(i\hat{p}a/\hbar) \tag{327}$$

This is unitary since:

$$\left(\hat{U}_a\right)^\dagger = \hat{U}_a^{-1} = \hat{U}_{-a} \tag{328}$$

which can be seen by simply taking the hermitian conjugate of the exponent, and remembering that $\hat{p}$ is hermitian, and therefore:

$$\left(\hat{U}_a\right)^\dagger \hat{U}_a = I. \tag{329}$$

Let me now prove to you that:

$$\langle\psi|\, \hat{U}_a^\dagger \hat{x} \hat{U}_a\, |\phi\rangle = \int dx \psi^*(x+a)(x)\phi(x+a) = \int dx \psi^*(x)(x-a)\phi(x) \tag{330}$$

The way to realize that this is going to happen is to recall:

$$\hat{p}_x = \frac{i}{\hbar}\frac{\partial}{\partial x} \tag{331}$$

Therefore:

$$\hat{U}_a\, |\phi\rangle = \exp\left(a\frac{\partial}{\partial x}\right)\phi(x) = \left(1 + \frac{\partial \phi}{\partial x}a + \frac{1}{2!}\frac{\partial^2 \phi}{\partial x^2}a^2 + \frac{1}{3!}\frac{\partial^3 \phi}{\partial x^3}a^3 \ldots\right) \tag{332}$$

and once we recognize that this is just the Taylor series we get:

$$= \hat{U}_a\, |\phi\rangle = \phi(x+a) \tag{333}$$

The same is true for the dagger'd $\hat{U}_a$ once it is applied to the left ($\langle\psi|\, \hat{U}_a^\dagger = \left(\hat{U}_a\, |\psi\rangle\right)$).

We can also see this from an algebraic perspective just using the commutator. let's write the operator as a product of many many operators each one close to being the identity.

$$\hat{U}_a = \exp(\frac{a}{N}i\hat{p}_x/\hbar) \cdot \exp(\frac{a}{N}i\hat{p}_x/\hbar) \cdot \exp(\frac{a}{N}i\hat{p}_x/\hbar) \ldots \cdot \exp(\frac{a}{N}i\hat{p}_x/\hbar) \tag{334}$$

with exaclty N terms in the product, and N a ginormous number.Why is this good? It allows us to write:

$$\exp(\frac{a}{N}i\hat{p}_x/\hbar) = I + \frac{a}{N}\frac{i}{\hbar}\hat{p}_x + \mathcal{O}(N^{-2}) \tag{335}$$

and it is understood that $\mathcal{O}$ is going to be thrown out, since it is really small. Now, let's treat the x operator sandwiched between a $\hat{U}_{a/N}$ and its dagger at a time:

$$\hat{U}_{-a}\hat{x}\hat{U}_N = \hat{U}_{-a/N}\hat{U}_{-a/N}\ldots\hat{U}_{-a/N}\hat{x}\hat{U}_{a/N}\hat{U}_{a/N}\ldots\hat{U}_{a/N} \tag{336}$$

okay. Deep breath! the first layer of this sandwich:

$$\hat{U}_{-a/N}\hat{x}\hat{U}_{a/N} = (I - \frac{ia}{N\hbar}\hat{p}_x)\hat{x}(I + \frac{ia}{N\hbar}\hat{p}_x) = \hat{x} + \frac{ia}{N\hbar}[\hat{x},\, \hat{p}_x] + \mathcal{O}(N^{-2}) = \hat{x} - \frac{a}{N} + \mathcal{O}(N^{-2}) \tag{337}$$

and we neglect anything that smells like a higher power of $1/N$. This turns out to be quite simple. In fact, it is so simple, you can't help but want to repeat it. And:

$$\hat{U}_{-a/N}(\hat{x} - \frac{a}{N})\hat{U}_{a/N} = \hat{x} - 2\frac{a}{N} \tag{338}$$

and after the N'th wrapper of the santwich is resolved, we get our expected answer:

$$\hat{U}_{-a}\hat{x}\hat{U}_{a} = \hat{x} - a. \tag{339}$$

this is a neat algebraic construction. But I would like to turn it on its head. I'd like to say that if:

$$e^{-i\delta\hat{A}}\hat{B}e^{i\delta\hat{A}} = \hat{B} - \delta\hat{C} \tag{340}$$

then:

$$[\hat{A}, \hat{B}] = i\hat{C} \tag{341}$$

This is going to be our way of extracting commutators for the angular momentum operators.

B. Algebra from rotation

Angular momentum is a complicated operator. Really complicated. So let's start simple. Let's only consider angular momentum in the z direction. Clasically, what is angular momentum in the z-direction measuring?

$$L_z = I_z\omega_z = I_z\dot{\phi} \tag{342}$$

where ϕ is again the azimuthal angle. For a particle moving on a ring (just as in the mid-term) this would simply be:

$$L_z = rm\dot{\phi}r = rp_{ring} \tag{343}$$

Now, taking the ring as our example, we see that in the same way that:

$$[\hat{p}_{ring}, \hat{x}_{ring}] = -i\hbar \tag{344}$$

we can write:

$$-i\hbar = [r\hat{p}_{ring}, \hat{x}_{ring}/r] = [\hat{L}_z, \phi]. \tag{345}$$

So indeed, we deduce what we could have guessed: in quantum mechanics, the relation between a coordinate, and its associated momentum, is a 'unit' commutation relation. This also gives us the form of the angular momentum in real space:

$$\hat{L}_z = \frac{i}{\hbar}\frac{\partial}{\partial\phi}. \tag{346}$$

But now we can apply our previous interpretation of this commutation relation. Namely, looking at wavefunctions of tops (i.e., things that are described using an angle):

$$\langle\psi|\, e^{-\frac{i}{\hbar}\delta\phi\hat{L}_z}\hat{\phi}e^{\frac{i}{\hbar}\delta\phi\hat{L}_z}\,|\xi\rangle = \langle\psi|\,(\hat{\phi} - \delta)\,|\xi\rangle \tag{347}$$

Note that $\delta\phi$ is just a number, which you should construe as a really small angle. With cartesian coordinates, this seemed innocent. But now we have in our hands a tool that doesn't translate the system - we have something that *rotates* it!

So let's consider a particle moving in a 3d space deascribed with a polar coordinate system. let's ask the following question: what happens when we put an operator that is a component of a vector between the exponents? For instance:

$$e^{-\frac{i}{\hbar}\delta\phi\hat{L}_z}\hat{\vec{x}}e^{\frac{i}{\hbar}\delta\phi\hat{L}_z} =? \tag{348}$$

where $\hat{x} = r\sin\theta\cos\phi$. Actually, this is kind of easy - we can write:

$$e^{-\frac{i}{\hbar}\delta\phi\hat{L}_z}\hat{\hat{x}}e^{\frac{i}{\hbar}\delta\phi\hat{L}_z} = r\sin\theta\cos(\phi-\delta\phi) = r\sin\theta\cos\phi + \delta\phi r\sin\theta\sin\phi = \hat{x} + \delta\phi\hat{y} \tag{349}$$

neat! beacuse this allows us to read the commutator:

$$\left[\hat{L}_z,\, \hat{x}\right] = i\hbar\hat{y} \tag{350}$$

you can already see that by the very same activity we can figure out:

$$\left[\hat{L}_z,\, \hat{y}\right] = -i\hbar\hat{x} \tag{351}$$

And here is the crucial question of the day - what is $\left[\hat{L}_z,\, \hat{L}_x\right]$. $\hat{\mathbf{L}}$ is also a vector, so just like the radius vector, we also have:

$$\left[\hat{L}_z,\, \hat{L}_x\right] = i\hbar\hat{L}_y \tag{352}$$

and:

$$\left[\hat{L}_z,\, \hat{L}_y\right] = -i\hbar\hat{L}_x \tag{353}$$

Now, we could repeat this process with $\hat{L}_y$ being the rotating vector, but we already have the answers above, or, for the missing $[L_x, L_y]$ commutator, we can also figure thigs our by simple taking a permutation of the axes: $x \to y$, $y \to z, z \to x$, and we get:

$$\left[\hat{L}_x,\, \hat{L}_y\right] = i\hbar\hat{L}_z \tag{354}$$

In fact, we can summarize everything as:

$$\left[\hat{L}_\alpha,\, \hat{L}_\beta\right] = i\hbar\hat{L}_\gamma\epsilon^{\alpha\beta\gamma} \tag{355}$$

with the ϵ being the Levi-Civita tensor. it is zero if there is any repition, and 1 or -1 depending on the determinant of the matrix:

$$LC = \delta_{1\alpha} + \delta_{2\beta} + \delta 3\gamma. \tag{356}$$

with $\alpha = 1, 2, 3$ means x, y, z respectively. This gives: $\epsilon^{xyz} = \epsilon^{yzx} = \epsilon^{zxy} = 1$ and $\epsilon^{yxz} = \epsilon^{zyx} = \epsilon^{xzy} = 1$. So cycling the letters from xyz leaves the tensor the same, and exchanging any two, changes the sign. This is just like an antisymmetric dressed up version of the Kronecker delta.