Notes for Quantum Mechanics

Richard Seto

```
Date[]
```

```
{2006, 2, 21, 13, 6, 7.4369200}
```

Lecture 27
The hydrogen atom

We had from lecture 25 $\left\langle \boldsymbol{x} \left| \hat{\boldsymbol{L}}^2 \right| \alpha \right\rangle = -\hbar^2 \left[\frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) \right] \langle \boldsymbol{x} | \alpha \rangle$

The laplacian in spiracle coordinates is $\vec{\nabla}^2 = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) = \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) \right]$

So we wrote

$\left\langle \boldsymbol{x} \left| \frac{\hat{\boldsymbol{p}}^2}{2m} \right| \alpha \right\rangle = \frac{1}{2m} \left\langle \boldsymbol{x} \left| \hat{\boldsymbol{p}}^2 \right| \alpha \right\rangle = -\left(\frac{\hbar^2}{2m} \right) \vec{\nabla}^2 \langle x | \alpha \rangle = -\left(\frac{\hbar^2}{2m} \right) \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \langle x | \alpha \rangle \right) - \frac{1}{\hbar^2} \langle x | \hat{\boldsymbol{L}}^2 | \alpha \rangle \right] =$

$-\left(\frac{\hbar^2}{2m} \right) \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \langle x | \alpha \rangle \right) \right] + \frac{1}{2mr^2} \langle x | \hat{\boldsymbol{L}}^2 | \alpha \rangle$

I would like now to get to the radial part of the wave eqn in 3D in a different way. Lets first look at the relationship between $\hat{\boldsymbol{L}}^2$ and $\hat{p}^2$.

Some identities first (you can prove them if you want)

$\sum_k \epsilon_{ijk} \epsilon_{lmk} = \delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}$

$(\hat{\boldsymbol{x}} \times \hat{\boldsymbol{p}})_k = \sum_{ij} \hat{x}_i \hat{p}_j \epsilon_{ijk}$

$\hat{\boldsymbol{L}}^2 = (\hat{\boldsymbol{x}} \times \hat{\boldsymbol{p}})^2 = \sum_k \sum_{ij} \hat{x}_i \hat{p}_j \epsilon_{ijk} \sum_{lm} \hat{x}_l \hat{p}_m \epsilon_{lmk} = \sum_{ijlmk} \epsilon_{ijk} \epsilon_{lmk} \hat{x}_i \hat{p}_j \hat{x}_l \hat{p}_m = \sum_{ijlm} (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) \hat{x}_i \hat{p}_j \hat{x}_l \hat{p}_m =$

$\sum_{ijlm} \delta_{il} \delta_{jm} \hat{x}_i (\hat{x}_l \hat{p}_j - i\hbar\delta_{jl}) \hat{p}_m - \delta_{im} \delta_{jl} \hat{x}_i \hat{p}_j (\hat{p}_m \hat{x}_l + i\hbar\delta_{lm}) =$

$\sum_{ijlm} \delta_{il} \delta_{jm} \hat{x}_i \hat{x}_l \hat{p}_j \hat{p}_m \quad - i\hbar \sum_{ijlm} \delta_{il} \delta_{jm} \delta_{jl} \hat{x}_i \hat{p}_m \quad - \sum_{ijlm} \delta_{im} \delta_{jl} \hat{x}_i \hat{p}_j (\hat{p}_m \hat{x}_l + i\hbar\delta_{lm}) =$

$\hat{\boldsymbol{x}}^2 \hat{\boldsymbol{p}}^2 - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} - \sum_{ijlm} \delta_{im} \delta_{jl} \hat{x}_i \hat{p}_j \hat{p}_m \hat{x}_l - i\hbar \sum_{ijlm} \delta_{im} \delta_{jl} \delta_{lm} \hat{x}_i \hat{p}_j =$

$\hat{\boldsymbol{x}}^2 \hat{\boldsymbol{p}}^2 - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} - \sum_{ijlm} \delta_{im} \delta_{jl} \hat{x}_i \hat{p}_m \hat{p}_j \hat{x}_l - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} =$

$\hat{\boldsymbol{x}}^2 \hat{\boldsymbol{p}}^2 - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} - \sum_{ijlm} \delta_{im} \delta_{jl} \hat{x}_i \hat{p}_m (\hat{x}_l \hat{p}_j - i\hbar\delta_{jl}) - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} =$

$\hat{\boldsymbol{x}}^2 \hat{\boldsymbol{p}}^2 - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} - (\hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}})^2 + \quad i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} - i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}} = \hat{\boldsymbol{x}}^2 \hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}})^2 - \quad i\hbar \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{p}}$

Now remembering (from QM25work)

 © James J. Kelly, 1998

x'=rsinθcosϕ y'=rsinθsinϕ z'=rcosθ r=$\sqrt{x'^2+y'^2+z'^2}$ θ= acos$\left(\frac{z'}{r}\right)$= acos$\left(\frac{z'}{\sqrt{x'^2+y'^2+z'^2}}\right)$ ϕ = atan$\left(\frac{y'}{x'}\right)$

$\frac{d}{dx}$ =sinθcosϕ $\frac{d}{dr}+\frac{\cos\theta\cos\phi}{r}\frac{d}{d\theta}-\frac{\sin\phi}{r\sin\theta}\frac{d}{d\phi}$

$\frac{d}{dy}$ = sinθsinϕ $\frac{d}{dr}+\frac{\cos\theta\sin\phi}{r}\frac{d}{d\theta}+\frac{\cos\phi}{r\sin\theta}\frac{d}{d\phi}$

$\frac{d}{dz}$ = cosθ $\frac{d}{dr}$ - $\frac{\sin\theta}{r}\frac{d}{d\theta}$

we get that $\hat{\boldsymbol{x}}\cdot\overline{\nabla}=r\sin^2\theta\cos^2\phi\frac{d}{dr}+\sin\theta\cos\theta\cos^2\phi\frac{d}{d\theta}-\cos\phi\sin\phi\frac{d}{d\phi}$ +

$r\sin^2\theta\sin^2\phi\frac{d}{dr}+\sin\theta\cos\theta\sin^2\phi\frac{d}{d\theta}+\cos\phi\sin\phi\frac{d}{d\phi}$

$r\cos^2\theta\frac{d}{dr}$ $-\cos\theta\sin\theta\frac{d}{d\theta}=r\frac{d}{dr}$ so $\langle x'|\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}}|\alpha\rangle=\frac{\hbar}{i}\hat{\boldsymbol{x}}\cdot\overline{\nabla}\langle\boldsymbol{x}'|\alpha\rangle=\frac{\hbar}{i}r'\frac{d}{dr'}\langle\boldsymbol{x}'|\alpha\rangle$

and $\left\langle x'|(\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}})^2\,|\,\alpha\right\rangle=\int d^3\boldsymbol{x}''\left\langle x'\left|\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}}\right|x''\right\rangle\left\langle r'\frac{d}{dr'}'\left|\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}}\right|\alpha\right\rangle=-\hbar^2\int d^3\boldsymbol{x}''r'\frac{d}{dr'}\langle\boldsymbol{x}'|\boldsymbol{x}''\rangle r''\frac{d}{dr''}\langle\boldsymbol{x}''|\alpha\rangle=$

$-\hbar^2 r'\frac{d}{dr'}r'\frac{d}{dr'}\langle\boldsymbol{x}'|\alpha\rangle=-\hbar^2\left(r'^2\frac{d^2}{dr'^2}\langle\boldsymbol{x}'|\alpha\rangle+r'\frac{d}{dr'}\langle\boldsymbol{x}'|\alpha\rangle\right)$

and finally $\left\langle\boldsymbol{x}\left|\hat{\boldsymbol{L}}^2\right|\alpha\right\rangle=\left\langle\boldsymbol{x}\left|\hat{x}^2\hat{\boldsymbol{p}}^2-(\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}})^2-i\hbar\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}}\right|\alpha\right\rangle=r'^2\langle\boldsymbol{x}'|\hat{\boldsymbol{p}}^2|\alpha\rangle+\hbar^2\left(r'^2\frac{d^2}{dr'^2}\langle\boldsymbol{x}'|\alpha\rangle+r'\frac{d}{dr'}\langle\boldsymbol{x}'|\alpha\rangle\right)$

or turning it around

$\frac{1}{2m}\langle\boldsymbol{x}'|\hat{\boldsymbol{p}}^2|\alpha\rangle=-\frac{\hbar^2}{2m}\overline{\nabla}^2\langle x'|\alpha\rangle=-\left(\frac{\hbar^2}{2m}\right)\left[\frac{d}{dr^2}\langle x'|\alpha\rangle+\frac{2}{r}\frac{d}{dr}\langle x'|\alpha\rangle\right]+\frac{1}{2mr^2}\left\langle\boldsymbol{x}\left|\hat{\boldsymbol{L}}^2\right|\alpha\right\rangle$

Now I would like to adopt Liboff's notation and call

$\hat{H}=\frac{1}{2m}\left(\hat{p}_r{}^2+\frac{\hat{\boldsymbol{L}}^2}{r^2}\right)$

$\hat{p}_r{}^2$ can be written several ways in position representation and I give them all here)

$\frac{2m}{-\hbar^2}\left(\frac{1}{2m}\hat{p}_r{}^2\right)=-\frac{\hat{p}_r{}^2}{\hbar^2}=\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}=\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}=\left[\frac{1}{r}\frac{d}{dr}r\right]^2=\frac{1}{r}\frac{d^2}{dr^2}$r Use the one which suits you. The last 2 are easy to remember

So now we write the Schrodinger eqn with some potential V(r) in the position representation as

$\hat{H}\langle\boldsymbol{x}|\alpha\rangle=\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right)+\frac{\hat{\boldsymbol{L}}^2}{r^2}+V(r)\right]\langle x|\alpha\rangle$

We want to look for eigenfuctions and eigenvalues and V(r) is spherically symmetric and $\hat{H}$ commutes with $\hat{\boldsymbol{L}}$ and we can write

$\hat{H}\langle\boldsymbol{x}|\alpha\rangle=\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right)+\frac{\hat{\boldsymbol{L}}^2}{2mr^2}\right)+V(r)\right]\langle x|\text{nlm}\rangle=E_{\text{nlm}}\langle x|\text{nlm}\rangle$

Further we can write $\langle x|\text{nlm}\rangle=\langle r,\theta,\phi|\text{nlm}\rangle=R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)$

$\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right)-\frac{\hat{\boldsymbol{L}}^2}{2mr^2}+V(r)\right]R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)=E_{\text{nlm}}R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)$

We know $\hat{\boldsymbol{L}}^2R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)=R_{\text{nl}}(r)\,\hat{\boldsymbol{L}}^2Y_l^m(\theta,\phi)=\hbar^2l(l+1)R_{\text{nl}}(r)Y_l^m(\theta,\phi)$ so

$\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right)+\frac{\hbar^2l(l+1)}{2mr^2}\right)+V(r)\right]R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)=E_{\text{nlm}}R_{\text{nl}}(r)\,Y_l^m(\theta,\phi)$

$\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right)+\frac{\hbar^2l(l+1)}{2mr^2}\right)+V(r)\right]R_{\text{nl}}(r)=E_{\text{nlm}}R_{\text{nl}}(r)$

This is the radial wave eqn. We have already done the hard part of the θ and ϕ coordinates.

We can solve this thing for all kinds of V(r). i.e. V(r)=0 just gives us a free particle in 3D. V(r)= box potential is the analog of a particle in a box etc. But lets go straight to the Hydrogen atom. What is the picture? In its simplest form we

can just think of a very heavy proton with an electron. Since the protons is ~2000 times heavier than an electron we can effectively think of it as infinitely heavy. If you dont like this just think of m as the reduces mass of the proton and election i.e. $\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_p}$. The potential is just a coulomb potential

$V(r) = -Z\,\frac{e^2}{r}$ We leave the factor of Z in there to deal with a 1 electron atom of heavier things. Later we will work our way up to 2 electron atoms etc. Now we want to think of bound states so E is negative. (remember -13.6 eV?)

So we have

$\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r\right) + \frac{\hbar^2\, l(l+1)}{r^2} - \frac{Ze^2}{r} + |E|\right] R(r) = 0$ for ease I leave off the subscripts n and l for now. They will come back

OK. Its painful but we have to solve this. I wont do it. I will just give you the solution

First lets set $R(r) = \frac{u(r)}{r}$ We then get

$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2\, l(l+1)}{r^2} - \frac{Ze^2}{r} + |E|\right) u(r) = 0$

Now let me define some things:

the Bohr radius $a_0 = \frac{\hbar^2}{me^2} = 5.3\times 10^{-9}\ m$

The Rydberg constant $\mathcal{R} = \frac{me^4}{2\hbar^2} = 13.6\,\text{eV}$

$\kappa = \sqrt{\frac{2\,mE}{\hbar^2}}$ $\lambda^2 = Z^2\frac{\mathcal{R}}{|E|}$ and $\rho = 2\kappa r$ which will be our radial variable for now so u is now u(ρ)

The radial eqn can now be written

$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0$

The solutions are

$u(\rho) = e^{-\rho/2}\,\rho^{l+1}\,F_{nl}(\rho)$ where the F_{nl} are the Laguerre Polynomials.

and λ must be an integer n with l ≤ n-1 (that is a el+1) hence we have

$$E_n = -|E_n| = -\frac{Z^2\mathcal{R}}{n^2}$$

Now the wave functions must be normalized. We remember that the element for 3D is $r^2\,d\cos\theta\,d\phi$ wo this means

$\int_0^\infty |R_{nl}(r)|^2\, r^2\, dr = 1$

After all that we will get

$\langle x|nlm\rangle = (2\kappa)^{3/2} A_{nl}\,\rho^l\, e^{-\rho/2} F_{nl}(\rho)\, Y_l^m(\theta,\ \phi)$

n=1,2,3... l=0,1,2...n-1 m=-l,....+1

For example

$\langle x|n=1\ l=0\ m=0\rangle = \psi_{100} = \frac{1}{\sqrt{8\pi}}\left(\frac{2Z}{a_0}\right)^{3/2} e^{-(Z/a_0)r}$ The ground state of hydrogen.

The energy is $E_n = -\frac{Z^2\mathcal{R}}{n^2} = -Z^2\mathcal{R}$ or -13.6 eV for Z=1

© James J. Kelly, 1998

Here are the first set of wave function in spectroscopic notation where the notation 1s means n=1, l=0

remember: s: l=0 p: l=1 d: l=2 f: l=3 ...

1s $\varphi_{100} = \frac{2}{a_0^{3/2}} e^{-r/a_0} Y_0^0$

2s $\varphi_{200} = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} Y_0^0$

2p $\varphi_{21m} = \frac{2}{\sqrt{3}\,(2a_0)^{3/2}} \frac{r}{2a_0} e^{-r/a_0} Y_1^m$

3s $\varphi_{300} = \frac{2}{3(2a_0)^{3/2}} \left[3 - 2\frac{r}{a_0} + 2\left(\frac{r}{3a_0}\right)^2\right] e^{-r/a_0} Y_0^0$

3p $\varphi_{31m} = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} \left[1 - \frac{r}{6a_0}\right] e^{-r/a_0} Y_1^m$

3d $\varphi_{32m} = \frac{2\sqrt{2}}{27\sqrt{5}\,(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} Y_2^m$

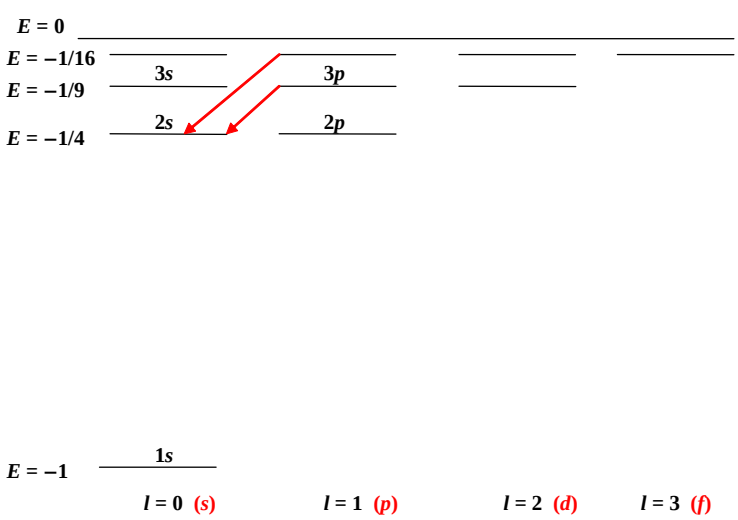
Degeneracies

We see that for any particular n, there are many values of l and m that are OK, i.e. there are $\sum_{l=0}^{n-1} (2l+1)$ states, so for instance for the n=2 state, we have 1 l=0 state and 3 l=1 states =4 total and so on. So this means that there are several states which have the same energy. I.e. there are degeneracies. We will see in the next lecture about how part of this degeneracy is actually not there since we dont quite have the right hamiltonian. These degeneracies also mean that for many electron atoms, the various states can mix and we do not have to use the eigenfuctions ⟨x|nlm⟩ but we can choose any linear combination of those with the same energy. This leads to things like hybridization and the formation of molecules.

Some pictures

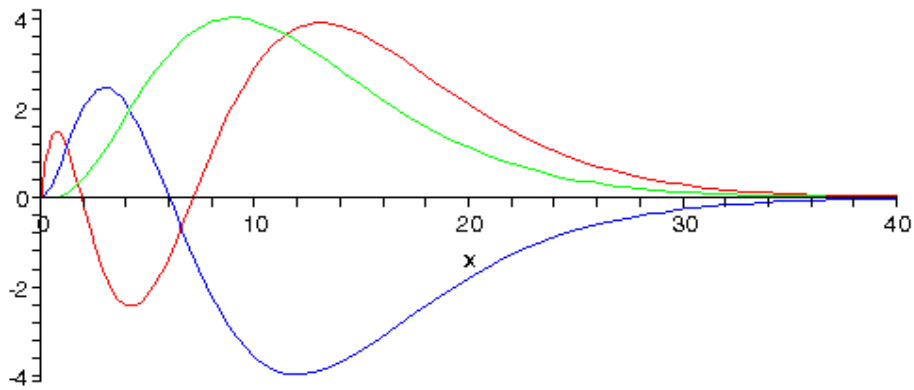
Energy

Levels

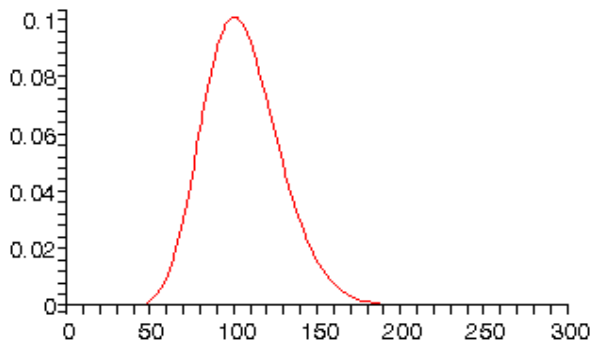


© James J. Kelly, 1998

Radial wave functions in units of a_0 $n = 1$ (green) $n = 1$ (blue) $n = 2$ (red)



Probablility distribution of n=10, L=0



© James J. Kelly, 1998