Tutorial 12 - Radial Equation & Hydrogen Atom

Question 1:

We consider a quantum spinning top with a hamiltonian given by

$$\hat{H} = \frac{\hat{L}_x^2 + \hat{L}_y^2}{2I}.$$

At time $t = 0$ the system is prepared in the state

$$\psi(\theta, \phi) = A\left(3Y_1^1 + 5Y_7^3 - Y_7^1\right).$$

1. Find eigenstates and eigenvalues of $\hat{H}$.
2. What are the possible values of $\hat{L}^2$ and $\hat{L}_z$?
3. Calculate $|\psi(t)\rangle$ and $\langle H\rangle$.
4. At some time $t > 0$ we measure $\hat{L}^2$ and $\hat{L}_z$ and get $2\hbar^2$ and $\hbar$ respectively. What is the wave function after this measurement?

Solution:

1. We can write the hamiltonian in terms of $\hat{L}_\pm$ as

   $$\hat{H} = \frac{\hat{L}^2 - \hat{L}_z^2}{2I},$$

   thus, recalling that

   $$\hat{L}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle \quad \text{and} \quad , \hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle,$$

   we find

   $$\boxed{\hat{H} |\ell, m\rangle = \frac{\hbar^2}{2I}\left(\ell(\ell+1) - m^2\right) |\ell, m\rangle}.$$

2. The possible values of $\hat{L}^2$ are determined from the different ℓs of the states that constitute $|\psi\rangle$, which are $\hat{L}^2 = 2\hbar^2, 56\hbar^2$ (for $\ell = 1, 7$). In the same manner, $\hat{L}_z = \hbar, 3\hbar$ (for $m = 1, 3$). Normalizing $|\psi\rangle$ we have $|A| = 1/\sqrt{35}$, thus

   $$P\left(\hat{L}^2 = 2\hbar^2\right) = P(\ell = 1) = \boxed{\frac{9}{35}},$$

   $$P\left(\hat{L}^2 = 56\hbar^2\right) = \boxed{\frac{26}{35}},$$

   $$P\left(\hat{L}_z = \hbar\right) = \boxed{\frac{2}{7}},$$

   $$P\left(\hat{L}_z = 3\hbar\right) = \boxed{\frac{5}{7}}.$$

3. The eigenvalues of the hamiltonian $E_{\ell,m}$, for the different states are

$$E_{11} = \frac{\hbar^2}{2I}; \quad E_{73} = \frac{47\hbar^2}{2I}; \quad E_{71} = \frac{55\hbar^2}{2I},$$

thus

$$\boxed{|\psi(t)\rangle = \frac{1}{\sqrt{35}}\left(3|1,1\rangle e^{-iE_{11}t/\hbar} + 5|7,3\rangle e^{-iE_{73}t/\hbar} - |7,1\rangle e^{-iE_{71}t/\hbar}\right)},$$

and

$$\boxed{\langle H\rangle = \frac{1}{35}\left(9E_{11} + 25E_{73} + E_{71}\right) = \frac{1239\hbar^2}{70I}}.$$

4. That means we measured $\ell = 1$ and $m = 1$, for which there is only a single possible eigenstate $|1,1\rangle$, thus

$$\boxed{|\psi(t > t_{\text{measure}})\rangle = |1,1\rangle e^{-iE_{11}t/\hbar}}.$$

Question 2:

Consider a particle moving in a spherically symmetric potential. The particle is in a state $|\ell, m\rangle$ - an eigenstate of $\hat{L}^2$ and $\hat{L}_z$.

1. Calculate $\sigma_{L_x^2} + \sigma_{L_y^2}$.
2. For which values of ℓ and m does this sum vanish?

Solution:

1. We need to calculate $\langle L_x\rangle$, $\langle L_x^2\rangle$, $\langle L_y\rangle$, $\langle L_y^2\rangle$. Recalling that

$$\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right); \quad \hat{L}_y = \frac{1}{2i}\left(\hat{L}_+ - \hat{L}_-\right),$$

and

$$L_\pm |\ell, m\rangle = \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}\,|\ell, m \pm 1\rangle,$$

we have

$$\underline{\left\langle \hat{L}_x \right\rangle = \left\langle \hat{L}_y \right\rangle = 0.}$$

Next we need

$$\hat{L}_x^2 = \frac{1}{4}\left(\hat{L}_+^2 + \hat{L}_-^2 + 2\hat{L}_+\hat{L}_- - \left[\hat{L}_+, \hat{L}_-\right]\right); \quad \hat{L}_y^2 = -\frac{1}{4}\left(\hat{L}_+^2 + \hat{L}_-^2 - 2\hat{L}_+\hat{L}_- + \left[\hat{L}_+, \hat{L}_-\right]\right),$$

where

$$\left[\hat{L}_+, \hat{L}_-\right] = \left[\hat{L}_x + i\hat{L}_y, \hat{L}_x - i\hat{L}_y\right] = -2i\left[\hat{L}_x, \hat{L}_y\right] = 2\hbar\hat{L}_z.$$

Noting that

$$\begin{aligned}\hat{L}_+\hat{L}_- |\ell, m\rangle &= \hbar^2\sqrt{(\ell+m)(\ell-m+1)}\sqrt{(\ell-(m-1))(\ell+(m-1)+1)}\,|\ell, m\rangle \\ &= \hbar^2 (\ell+m)(\ell-m+1)\,|\ell, m\rangle,\end{aligned}$$

we find

$$\begin{aligned}\left\langle \hat{L}_x^2\right\rangle &= \frac{1}{2}\left\langle\left(\hat{L}_+\hat{L}_- - \hbar\hat{L}_z\right)\right\rangle = \frac{\hbar^2}{2}\left[(\ell+m)(\ell-m+1) - m\right] = \frac{\hbar^2}{2}\left[\ell(\ell+1) - m^2\right], \\ \left\langle \hat{L}_y^2\right\rangle &= \frac{1}{2}\left\langle\left(\hat{L}_+\hat{L}_- - \hbar\hat{L}_z\right)\right\rangle = \left\langle \hat{L}_x^2\right\rangle = \frac{\hbar^2}{2}\left[\ell(\ell+1) - m^2\right].\end{aligned}$$

Therefore

$$\boxed{\sigma_{L_x^2} + \sigma_{L_y^2} = 2\left\langle \hat{L}_x^2\right\rangle = \hbar^2\left[\ell(\ell+1) - m^2\right]}.$$

2. Looking at the equation, recalling that $|m| \leq \ell$,

$$\ell(\ell+1) = m^2,$$

we see immediately that

$$\ell(\ell+1) \geq m^2,$$

with the equality for the case of $\boxed{m = \ell = 0}$. So that for $\ell \neq 0$ the min uncertainty is for $m = \pm\ell$.

Central Force

We've seen that the time-independent Schrödinger equation,

$$\hat{H}\psi = E\psi,$$

can be written as

$$\frac{1}{2mr^2}\left[-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + L^2\right]\psi + V(r)\psi = E\psi,$$

in the case of a *central potentials*, $V(\boldsymbol{r}) = V(r)$.
Writing the wave function as

$$\psi(r, \theta, \phi) = R(r) Y_\ell^m(\theta, \phi),$$

where Y_ℓ^m are the eigenfunctions of the angular momentum operator, we get the radial equation

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

Changing variables to $u \equiv rR(r)$, we have

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right] u(r) = Eu(r).$$

But this is just the one-dimensional Schrödinger equation with an *effective potential*

$$V_{\text{eff}}(r) \equiv V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2},$$

which includes the so-called *centrifugal* term as in the pseudo-force in classical mechanics. In this parameterization, the normalization of the radial function becomes

$$1 = \int_0^\infty |R|^2 r^2 dr = \int_0^\infty |u|^2 dr.$$

An important difference from the one-dimensional case is that we require different boundary conditions. In particular, unless $V(r)$ contains $\delta(r)$, then we require

$$\lim_{r\to 0} u(r) \to 0 \quad \text{and} \quad \lim_{r\to\infty} u(r) \to 0.$$

Question 3:

Consider a particle of mass m and angular momentum $\ell = 0$, moving under an attractive potential of a spherical shell:

$$V(r) = -a\delta(r - R),$$

where $a, R > 0$.

1. Write down the radial equation of $u(r)$ for bound states ($E < 0$) and write the necessary conditions to solve it.

2. Find a closed equation for the allowed energies.

3. Find a necessary and sufficient condition on R and a for the existence of a bound state.
4. Under this condition, how many energy values can be measured?

Solution:

1. The radial equation is

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} - a\delta\left(r-R\right)u\left(r\right) = Eu\left(r\right)},$$

since $V\left(r\right)$ does not contain $\delta\left(r\right)$, we require

$$\boxed{\lim_{r\to 0} u\left(r\right) \to 0} \quad \text{and} \quad \boxed{\lim_{r\to\infty} u\left(r\right) \to 0}.$$

In addition, at the point $r = R$, we require that

$$\boxed{u\left(R^+\right) = u\left(R^-\right)},$$

$$\boxed{u'\left(R^+\right) - u'\left(R^-\right) = -\frac{2ma}{\hbar^2}u\left(R\right) = -gu\left(R\right)}, \quad \text{where } g \equiv \frac{2ma}{\hbar^2}.$$

2. Solving the Schrödinger equation for all $r \neq R$, and $E < 0$

$$\frac{d^2u}{dr^2} = -\frac{2mE}{\hbar^2}u = \kappa^2 u, \quad \text{where } \kappa \equiv \frac{\sqrt{-2mE}}{\hbar},$$

we get

$$u\left(r\right) = \begin{cases} Ae^{\kappa r} + Be^{-\kappa r}, & 0 < r < R, \\ Ce^{-\kappa r}, & r > R, \end{cases}$$

where we already dropped the divergent term at $r \to \infty$.
The boundary at $r = 0$ condition yields

$$A = -B,$$

thus

$$u\left(r\right) = \begin{cases} \tilde{A}\sinh\kappa r, & 0 < r < R, \\ Ce^{-\kappa r}, & r > R, \end{cases}$$

while the boundary conditions at $r = R$ give us

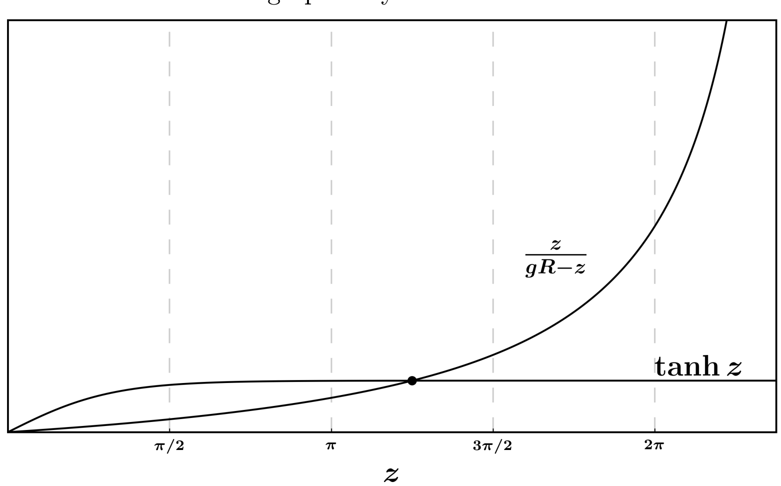
$$\tilde{A}\sinh\kappa R = Ce^{-\kappa R},$$

$$-\kappa\left(Ce^{-\kappa R} + \tilde{A}\cosh\kappa R\right) = -g\tilde{A}\sinh\kappa R,$$

which together read

$$\tanh z = \frac{z}{gR - z}, \quad \text{where } z \equiv \kappa R.$$

This equation has one solution as can be seen graphically



3. It is clear from the plot above that in order for a bound state to exist the slope of the right-hand-side must be lower than that of the tanh function, namely

$$\frac{\partial}{\partial z}\tanh z\bigg|_{z=0} > \frac{\partial}{\partial z}\left(\frac{z}{gR-z}\right)\bigg|_{z=0} \quad\to\quad gR>1 \quad\to\quad \boxed{aR>\frac{\hbar^2}{2m}}.$$

4. There is only a single allowed energy.

The Hydrogen Atom

The hydrogen atom consists of a massive proton, orbited by a much less massive electron. Assuming that the proton is motionless at the origin, the radial Schrödinger equation reads

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\epsilon_0 r}+\frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]u(r)=Eu(r).$$

This equation is solved by

$$R_{n\ell}(r)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n(n+\ell)!}}e^{-\frac{\rho}{n}}\left(\frac{2\rho}{n}\right)^{\ell}\left[L_{n-\ell-1}^{2\ell+1}\left(\frac{2\rho}{n}\right)\right],\qquad \text{with}\ \begin{cases}\rho\equiv\frac{r}{a_0},\\ a_0\equiv\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\approx 0.53\text{Å},\end{cases}$$

where

$$L_q^p(x)\equiv(-1)^p\left(\frac{d}{dx}\right)^p L_{p+q}(x)$$

are the *associated Laguerre polynomials,* and

$$L_q(x)\equiv\frac{e^x}{q!}\left(\frac{d}{dx}\right)^q\left(e^{-x}x^q\right)$$

is the qth *Laguerre polynomial.* Thus we can also write

$$L_q^p(x)=\frac{x^{-p}e^x}{q!}\left(\frac{d}{dx}\right)^q\left(e^{-x}x^{p+q}\right).$$

The allowed energies follow

$$E_n=-\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}=\frac{E_1}{n^2},\quad n=1,2,3,\ldots$$

which is the famous *Bohr formula*, where the ground state, $n=1$, reads

$$\boxed{E_1=-\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2=-13.6\text{ eV}}.$$

Thus, The spatial wave functions are labeled by three quantum numbers (n,ℓ,m):

$$\psi_{n\ell m}(r,\theta,\phi)=R_{n\ell}(r)\,Y_\ell^m(\theta,\phi),$$

or in general the state $|n,\ell,m\rangle$. For arbitrary n, we can have

$$\ell=0,1,2,\ldots,n-1,$$

each of which has $2\ell+1$ possible values of m, thus the total degeneracy of the energy level E_n is

$$g_n(n)=\sum_{\ell=0}^{n-1}(2\ell+1)=n^2.$$

Question 4:

Consider a hydrogen atom that at time $t = 0$ is in a state

$$|\psi\rangle = \frac{1}{\sqrt{14}} \left(2\,|1,0,0\rangle - 3\,|2,0,0\rangle + |3,2,2\rangle\right).$$

1. Is this an eigenstate of the parity operator $\hat{P} f(\boldsymbol{r}) = f(-\boldsymbol{r})$? What is the average of $\hat{P}$ in this state?
2. Find $|\psi(t)\rangle$.
3. Find $\langle x\rangle(t)$.
4. Find $\left\langle \hat{H} \right\rangle(t)$, $\left\langle \hat{L}^2 \right\rangle(t)$ and $\left\langle \hat{L}_z \right\rangle(t)$.

Solution:

1. In spherical coordinates parity transformation, $\boldsymbol{r} \to -\boldsymbol{r}$, translates into

   $$r \to r; \quad \theta \to \pi - \theta; \quad \phi \to \phi + \pi,$$

   thus, it only affects the angular part, or Y_ℓ^m in terms of position basis. Looking at the relevant spherical harmonics:

   $$Y_0^0 = \frac{1}{\sqrt{4\pi}} \quad \text{and} \quad Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi},$$

   we see that Y_0^0 is independent of the parity transformation, while

   $$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2(\pi-\theta)\, e^{2i(\phi+\pi)} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}.$$

   Therefore, $|\psi\rangle$ is an eigenstate of $\hat{P}$.

2. All we need to do is to relate the relevant energies to each term. Recalling that

   $$E_n = \frac{E_1}{n^2}, \quad n = 1,2,3,\ldots$$

   where the ground state reads

   $$E_1 = -\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2,$$

   we have

   $$|\psi(t)\rangle = \frac{1}{\sqrt{14}}\left(2\,|1,0,0\rangle e^{-i\frac{E_1}{\hbar}t} - 3\,|2,0,0\rangle e^{-i\frac{E_2}{\hbar}t} + |3,2,2\rangle e^{-i\frac{E_3}{\hbar}t}\right).$$

3. We need to calculate

   $$\langle x\rangle(t) = \int \psi^*(\boldsymbol{r},t)\,\hat{x}\psi(\boldsymbol{r},t)\,d^3r,$$

   but $\psi(\boldsymbol{r})$ is an even function, hence the integral vanishes and $\boxed{\langle x\rangle(t) = 0}$.

4. We know that $|\psi\rangle$ is an eigenstate of both $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$, with eigenvalues of E_n, $\hbar^2\ell(\ell+1)$ and $\hbar m$, correspondingly, thus

   $$\boxed{\left\langle \hat{H}\right\rangle = \frac{1}{14}\left(4E_1 + \frac{9}{4}E_2 + \frac{1}{9}E_3\right) = -\frac{229}{1008}\frac{m_e e^2}{4\pi\hbar^2\epsilon_0}},$$

   $$\boxed{\left\langle \hat{L}^2\right\rangle = \frac{\hbar^2}{14}(0+0+6) = \frac{3\hbar^2}{7}},$$

   $$\boxed{\left\langle \hat{L}_z\right\rangle = \frac{\hbar}{14}(0+0+2) = \frac{\hbar}{7}}.$$