Quantum Physics

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Chapter 1

Hydrogen Atom.

1.1 Two Body problem and quantum mechanics.

We consider two particles described by $\vec{r_1}, \vec{r_2}, \vec{p}_1, \vec{p}_2, m_1$ and m_2 that interact with a potential $V(\vec{r_2} - \vec{r_1})$. Then the Hamiltonian is given by:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\vec{r_2} - \vec{r_1})$$

Now as usually done in classical physics we want to decompose the motion into the motion of the center of mass and a rotation around it. So we introduce:

$$\vec{P} = \vec{p}_1 + \vec{p}_2, \vec{R} = \frac{m_1\vec{r_1} + m_2\vec{r_2}}{m_1 + m_2}, \vec{r} = \vec{r_1} - \vec{r_2}, \vec{p} = \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1 + m_2}, M = m_1 + m_2, \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Then the Hamiltonian is re-written as:

$$H = \underbrace{\frac{P^2}{2M}}_{H_{\text{CM}}} + \underbrace{\frac{p^2}{2\mu} + V(\vec{r})}_{H_{\text{rel}}}$$

And the commutation relations are given by:

$$[R_i, P_i] = i\hbar\delta_{ij}, [r_i, p_j] = i\hbar\delta_{ij}, [r_i, P_j] = 0, [R_i, p_j] = 0$$

We immediately see that $[H, P] = 0$, this is a result of the invariance by translation of the problem. Hence $\vec{P}$ is a constant of the problem and $\vec{P}$ and H share a common basis. The egein-values of the momentum of the center of mass are planes waves of the form:

$$e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \quad \text{and} \quad H_{\text{rel}}\psi(\vec{r}) = E\psi(\vec{r}) \Rightarrow E_{\text{tot}} = \frac{\hbar^2 k^2}{2M} + E$$

Now if we look at the specific case of the hydrogen atom since $m_p \gg m_e$ we have:

$$\mu = \frac{m_e m_p}{m_e + m_p} = m_e\left[1 - \frac{m_e}{m_p}\right]$$

1.2 Central force movement.

Say we have a potential of the form $V(\vec{r}) = V(r)$ then we want to solve the T.I.S.E.:

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

Remember also that $[L^2, H] = [L^2, L_i] = 0$, so $[\vec{L}, H] = 0$. So we can now look for solution that eigenstates of L^2 and L_z which we know to be the spherical harmonics. So we decompose a given eigenstate in a radial component and a spherical harmonic component:

$$R_l(r)Y_{l,m}(\theta, \varphi)$$

Now plugging this into the T.I.S.E. we get:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]R_l(r) = ER_l(r)$$

And normalization gives:

$$\int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \mathrm{d}r |R_l(r)|^2 |Y_{l,m}(\theta,\varphi)|^2 = \int_0^{+\infty} r^2 |R_l(r)|^2 \mathrm{d}r =$$

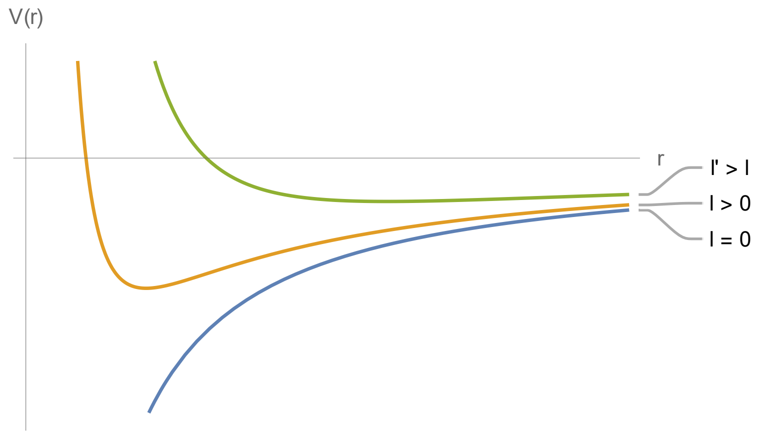
Now to try and simplify the problem and reduce it to a 1D schrodinger equation we introduce a new function $u_l(r) = rR_l(r)$ we then have:

$$\int_0^{+\infty} |u_l(r)|^2 = 1$$

We also replace it in the T.I.S.E. which gives:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right] u_l(r) = Eu_l(r)$$

We see that we get a central force term plus a centrifugal term. The role of this centrifugal force is to make the potential diverge to infinity when r goes to 0. A typical plot of this (for a coulomb potential) is as follows:



1.2.1 Behavior close to the origin.

We now write $u_l(r) \overset{r\to 0}{\sim} Cr^s$ and we assume that $V(r)$ does not go to infinity faster than $\frac{1}{r}$. Then we see that for the solution to be well defined we need the first two terms to cancel otherwise the solution diverges. So we get:

$$-\frac{\hbar^2}{2m}s(s-1) + \frac{\hbar^2}{2m}l(l+1) = 0 \Leftrightarrow s = -l \vee s = l+1$$

We see that the first solution is impossible if $l \neq 0$ since u_l wouldn't be normalizable. It is also impossible when $l = 0$ because in that case $u_l(r) \sim c$ and so $R_l(r) \sim \frac{C}{r}$, but then $\Delta R_l = -4\pi C\delta$ which is not a viable solution to the Schrodinger equation. So the only viable solution is $s = l+1$. So we now need to solve the following equation:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right] u_l(r) = Eu_l(r) \quad \wedge \quad u_l(0) = 0$$

We know that there are discrete energies solution to this problem and actually for the coulomb potential case the energies will be given by: $n' + l + 1 = n$. We call n the principal quantum number.

1.3 Hydrogen Atom.

For the hydrogen atom the potential is given by: $V(r) = \frac{-q^2}{4\pi\varepsilon_0 r}$ to simplify the writing we introduce $e^2 = \frac{q^2}{4\pi\varepsilon_0}$ so that $V(r) = -\frac{e^2}{r}$. Then the T.I.S.E. is given by:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{l(l+1)\hbar}{2mr^2} - \frac{e^2}{r}\right] u_l(r) = Eu_l(r)$$

We want to make the problem dimensionless so we introduce $a_0 = \frac{\hbar^2}{me^2} = 0.53\ \mathring{A}$ as a unit for length, $E_I = \frac{e^2}{2a_0} = \frac{m^2e^4}{2\hbar^2} = 13.6$ eV as a unit for energy. We now introduce the dimensionless parameters $\rho = \frac{r}{a_0}$ and $\varepsilon = -\frac{E}{E_I}$ and plugging them in the T.I.S.E. we get:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \varepsilon\right] u_l(\rho) = 0$$

When $\rho \to \infty$ the equation simplifies to something that gives $e^{\pm\sqrt{\varepsilon}\rho}$ the plus being non-normalizable we keep only the minus and we introduce a new variable: $u_l(\rho) = y_l(\rho)e^{-\sqrt{\varepsilon}\rho}$ and plugging this in and introducing $\lambda = \sqrt{\varepsilon}$ we get:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - 2\lambda\frac{\mathrm{d}}{\mathrm{d}\rho} + \left[\frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right]\right] y_l = 0 \wedge y_l(0) = 0$$

To solve this we pass by the series decomposition of y_l:

$$y_l(\rho) = \rho^s \sum_{q=0}^{\infty} c_q \rho^q \text{ with } s > 0 \text{ in order for } y_l(0) = 0$$

Then the derivatives are given by:

$$\frac{\mathrm{d}y_l(\rho)}{\mathrm{d}\rho} = \sum_{q=0}^{+\infty} c_q \rho^{q+s-1}(q+s) \wedge \frac{\mathrm{d}^2 y_l(\rho)}{\mathrm{d}\rho^2} = \sum_{q=0}^{+\infty} c_q (q+s)(q+s-1)e^{q+s-2}$$

Then plugging this into the differential equation and using the uniqueness of the series expansion we get the following recursion relation:

$$c_q\left[q(q+2l+1)\right] = 2\left[(q+l)\lambda - 1\right]c_{q-1} \Rightarrow \frac{c_q}{c_{q-1}} \overset{q\to\infty}{\sim} \frac{2\lambda}{q} \Rightarrow y_l(\rho) \overset{q\to\infty}{\sim} e^{2\lambda\rho}$$

However if this was true then it would mean that $u_l(\rho) \overset{\rho\to\infty}{\sim} e^{\lambda\rho}$ which is impossible. Therefore it must be that c_q terminates for a certain $n' \in \mathbb{N}$. Hence:

$$(n' + 1 + l)\lambda - 1 = 0 \Rightarrow c_{n'+1} = 0$$

Then the energy is given by:

$$\varepsilon = \lambda^2 = \frac{1}{(n'+1+l)^2} \Leftrightarrow E = \frac{-E_I}{(n'+1+l)^2}$$

Now note that the degeneracy of a given energy is given by the amount of ways we can write $n = n' + 1 + l$ changing n' and l. So for n given there are n possible values that l can take, for every l there are $(2l+1)$ values that m can take. So the degeneracy of a state of principal quantum number n is given by:

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