Quantum Physics

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Contents

1 Hydrogen Atom. **5**
1.1 Two Body problem and quantum mechanics. 5
1.2 Central force movement. 5
1.2.1 Behavior close to the origin. 6
1.3 Hydrogen Atom. 6

2 Approximation Methods. **9**
2.1 Variational Method. 9
2.1.1 Infinite potential well. 9
2.1.2 Helium atom. 9
2.1.3 Other Levels. 10
2.2 Stationary perturbation method. 10
2.2.1 The case where E_0 is not degenerated. 10
2.2.2 The case where E_0 is degenerated. 11

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:

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

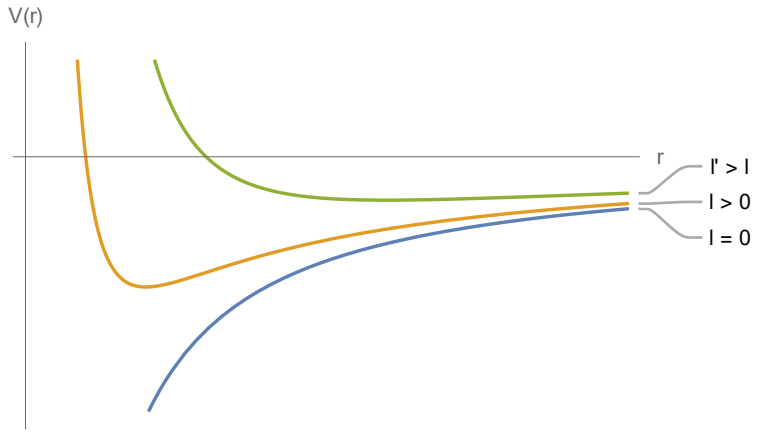
Now to try and simplify the problem and reduce it to a 1D schrodinger equation we introduce a new function $u_l(r) = rR_l(r)$ we then have:

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

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:

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

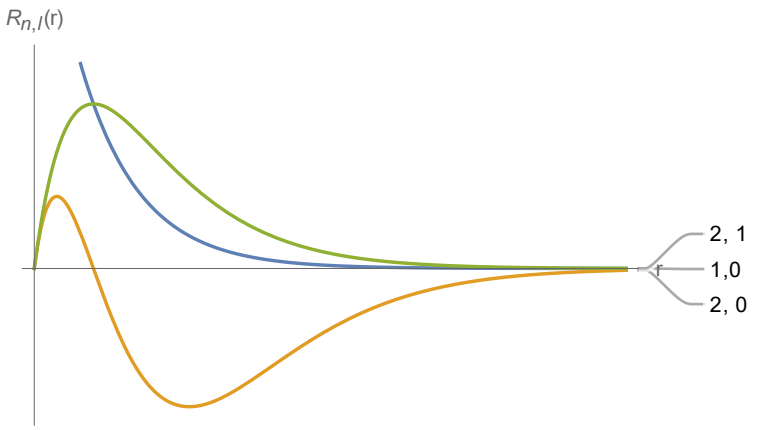
Now note that the degeneracy of a given energy is given by the amount of ways we can write $n = n' + 1 + l$ changing n' and l. So for n given there are n possible values that l can take, for every l there are $(2l+1)$ values that m can take. So the degeneracy of a state of principal quantum number n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

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

Then the first eigenstates are given by:

$$R_{n=1,l=0} = 2(a_0)^{-3/2}e^{-r/a_0}, R_{n=2,l=0} = r(a_0)^{-3/2}(1 - \frac{r}{2a_0})e^{-r/2a_0}, R_{n=2,l=1} = (2a_0)^{-3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$$

Which look like:



Now note that:

$$\langle\psi_{n,l,m}|\frac{1}{r}|\psi_{n,l,m}\rangle \Rightarrow [H, \vec{r}\cdot\vec{p}] = -i\hbar\left[\frac{p^2}{m} + \frac{e^2}{r}\right] \Rightarrow \langle\psi_{n,l,m}|[H,A]|\psi_{n,l,m}\rangle = 0\,\forall A$$

So we get that:

$$\langle\frac{p^2}{m}\rangle + \langle\frac{e^2}{r}\rangle = 0, \langle\frac{p^2}{2m} - \frac{e^2}{r}\rangle = E \Rightarrow \langle\frac{e^2}{r}\rangle = -2E, \langle\frac{p^2}{2m}\rangle = -E$$

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Chapter 2

Approximation Methods.

2.1 Variational Method.

Let E_0 be the energy of the fondamental eigen state of the Hamiltonian H. Then we have that:

$$\forall \left|\psi\right\rangle, \left\langle\psi\right| H \left|\psi\right\rangle \geq E_0$$

From this we get the intuition that we can approximate E_0 by minimizing $\left\langle\psi\right| H \left|\psi\right\rangle$. Hence we introduce a family of wave functions $\left(\left|\psi(\alpha)\right\rangle\right)_\alpha$ indexed by the parameter α, then $\left\langle\psi(\alpha_0)\right| H \left|\psi(\alpha_0)\right\rangle$ is often a good approximation of E_0 if $\frac{\mathrm{d}}{\mathrm{d}\alpha} \left\langle\psi(\alpha)\right| H \left|\psi(\alpha)\right\rangle |_{\alpha_0} = 0$.

2.1.1 Infinite potential well.

The fundamental state of the infinite potential well is: $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$ and $E_0 = \frac{\pi^2 \hbar^2}{2mL^2}$. Now we take the following wave function: $\psi(x) = \frac{30}{L^5} x(x-L)$ (which respects the boundary conditions). We have that:

$$\left\langle\psi\right| H \left|\psi\right\rangle = \frac{5\hbar^2}{mL^2}$$

Knowing that $\frac{\pi^2}{2} = 4.93$ this is already a very good approximation.

2.1.2 Helium atom.

The Hamiltonian of the helium atom is given by:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r_1} - \vec{r_2}|}$$

If we neglect the interaction term we get a separable Hamiltonian: $H = H_1 + H_2$. Then we have that:

$$E_0 = 2(4 \times E_I) = 108.8 \text{ eV}$$

And the fundamental state is given by:

$$\psi(\vec{r_1}, \vec{r_2}) = e^{-2r_1/a_0} e^{-2r_2/a_0}$$

We add an 'ecrantage' factor ξ to model the interaction term:

$$\psi_\xi(\vec{r_1}, \vec{r_2}) = \underbrace{\frac{\xi^2}{\pi a_0^2}}_{\text{normalization}} e^{-\xi r_1/a_0} e^{-\xi r_2/a_0}$$

Then the Hamiltonian is written as:

$$H = \left(\frac{p_1^2}{2m} - \frac{\xi e^2}{r_1}\right) + \left(\frac{p_2^2}{2m} - \frac{\xi e^2}{r_2}\right) + (\xi - 2)e^2 \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\vec{r_1} - \vec{r_2}|}$$

Now looking individually at the contribution of each term:

- The first 2 terms gives and $\xi^2 E_I$ each.

- The third term gives $4\xi(\xi-2)E_I$.
- The last term gives: $\iint \left(\frac{\xi^2}{\pi a_0^2}\right)^2 e^{-2\xi r_1/a_0} e^{-2\xi r_2/a_0} \frac{1}{|\vec{r_1}-\vec{r_2}|} \mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}$.

We know that:

$$\frac{1}{r} = \frac{4\pi}{(2\pi)^3}\int \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2}\mathrm{d}^3\vec{k} \Leftrightarrow \nabla^2\frac{1}{r} = 4\pi\delta(\vec{r})$$

And we need to compute:

$$\left(\frac{\xi^2}{\pi a_0^2}\right)^2 \int \frac{1}{k^2} \underbrace{\left(\int e^{i\vec{k}\cdot\vec{r}} e^{-2\xi r/a_0}\mathrm{d}^3\vec{r}\right)^2}_{\frac{16\xi/a_0}{(k^2+(2\xi/a_0)^2)^2}} \mathrm{d}^3\vec{k} = \frac{5}{4}\xi E_I$$

Hence putting everything together we get that:

$$\langle\psi|_\xi H |\psi\rangle_\xi = 2E_I(\xi^2 - \frac{27}{8}\xi) \text{ which is minimal for } \xi = \frac{27}{16} \lesssim 2$$

This then gives that: $E_{\min} = -\frac{729}{128}E_I = -77.5$ eV and the experimental value is $E_0 = -78.6$ eV.

2.1.3 Other Levels.

Theorem:

$|\psi\rangle$ is an eigenstate of H if and only if the differential of $|\phi\rangle \mapsto \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$ cancels in $|\psi\rangle$.

Proof:

We first prove the left to right implication. Suppose that $|\psi\rangle$ is an eigenstate of H then:

$$\langle\delta\psi| H |\psi\rangle + \langle\psi| H |\delta\psi\rangle = E_\psi \langle\delta\psi|\rangle \psi + E_\psi \langle\psi|\delta\psi\rangle \Rightarrow \langle\delta\psi| H - E_\psi |\psi\rangle + \langle\psi| H - E_\psi |\delta\psi\rangle = 0$$

Now we suppose the right hand side. Let $|\delta\psi\rangle = \eta(H-E_\psi)|\psi\rangle \Rightarrow \langle\psi|(H-E_\psi)^2|\psi\rangle = 0 \Rightarrow ||(H-E_\psi)^2|\psi\rangle|| = 0$.

2.2 Stationary perturbation method.

Take a Hamiltonian $H = H_0 + \underbrace{W}_{\text{perturbation}} = H_0 + \lambda V$ where $\lambda \ll 1$, and the eigenvalues of V are of the same order of magnitude as those of H_0. We then write:

$$\begin{cases} E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots \\ |\psi\rangle = |\psi_0\rangle + \lambda|\psi_1\rangle + \lambda^2|\psi_2\rangle + \cdots \end{cases}$$

Then the Schrodinger equation gives for the successive orders of λ:

- $H_0|\psi_0\rangle = E_0|\psi_0\rangle$.
- $H_0|\psi_1\rangle + V|\psi_0\rangle = E_0|\psi_1\rangle + E_1|\psi_0\rangle$.
- $H_0|\psi_2\rangle + V|\psi_1\rangle = E_0|\psi_2\rangle + E_1|\psi_1\rangle + E_2|\psi_0\rangle$.

Furthermore the normalization of $|\psi\rangle$ gives:

$$\langle\psi_0|\psi_0\rangle = 1 \wedge \langle\psi_1|\psi_0\rangle + \langle\psi_0|\psi_1\rangle = 0 \Leftrightarrow \mathrm{Re}(\langle\psi_0|\psi_1\rangle) = 0$$

2.2.1 The case where E_0 is not degenerated.

For simplicity we write: $|\psi_0\rangle = |n\rangle$ and $E_0 = E_n$. Then we have that:

$$\langle n| H_0 |\psi_1\rangle + \langle n| V |\psi_0\rangle = E_0\langle n|\psi_1\rangle + E_1\langle n|\psi_0\rangle \Leftrightarrow E_1 = \langle n| V |n\rangle$$

Then takes an eigenstate $\langle n|' \neq \langle n|$ then we have:

$$\langle n'| H_0 |\psi_1\rangle + \langle n'| V |\psi_0\rangle = E_0\langle n'|\psi_1\rangle + E_1\cancelto{0}{\langle n'|\psi_0\rangle} \Leftrightarrow \langle n'|\psi_1\rangle = \frac{\langle n'| V |n\rangle}{E_n - E_{n'}}$$

Furthermore if we impose that $\langle\psi|\rangle\, n \in \mathbb{R}$ then the condition $\mathrm{Re}(\langle\psi_0|\psi_1\rangle) = 0$ gives: $\langle n|\psi_1\rangle = 0$. Hence we get that at the first order:

$$|\psi\rangle = |n\rangle + \sum_{n'\neq n} \frac{\langle n'|\, V\, |n\rangle}{E_n - E_{n'}}\, |n'\rangle$$

Repeating the same process for the second order we get that:

$$E^2 = \langle n|\, V\, |\psi^1\rangle = \sum_{n'\neq n} \frac{|\,\langle n'|\, V\, |n\rangle\,|^2}{E_n - E_{n'}}$$

Which gives:

$$E = E_n + \langle n|\, W\, |n\rangle + \sum_{n'\neq n} \frac{|\,\langle n'|\, V\, |n\rangle\,|^2}{E_n - E_{n'}}$$

Example for the non-degenerated harmonic oscillator.

We have the following Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 X^2 - qEX$$

Then $\langle n|\, qEX\, |n\rangle = 0$ which means that there is no first order correction. However at the second order we get:

$$E = \hbar\omega(n + \frac{1}{2}) + \sum_{n'\neq n} \frac{|\,\langle n'|\, qEX\, |n\rangle\,|^2}{E_n - E_{n'}} = \hbar\omega(n + \frac{1}{2}) - \frac{q^2E^2}{2m\omega^2}$$

In this specific case it turns out that the second order is actually the exact answer.

2.2.2 The case where E_0 is degenerated.

Let $|\psi_0\rangle \in \ker(H - E_0 I)$ and we write: $\left|\psi^i_{n,q}\right\rangle$ with $q \in [\![1, g_n]\!]$ instead of $|\psi_i\rangle$. Then we have that:

$$\left|\psi^0_{n,q}\right\rangle = \sum_{r=1}^{g_n} A_{q,r}\, |n, r\rangle$$

Now applying the same method as before we have that: $\sum_{r=1}^{g_n} A_{q,r}\, \langle n, r'|\, V\, |n, r\rangle = E^1_{n,q} A_{q,r'}$. Then to solve the following problem one needs to diagonalize $V_{|\ker(H - E_n I)}$.