QM II
Phys 652

Lecture #4

Hydrogen atom

Recall: $\Delta \Psi(r,\theta,\varphi) + \frac{2\mu}{\hbar^2}\left(E - U(r)\right]\Psi(r,\theta,\varphi) = 0$

$$\Psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)\,; \quad Y(\theta,\varphi) \Rightarrow Y_e^m(\theta,\varphi)$$

$$\vec{L}^2 Y_e^m(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_e^m(\theta,\varphi)\,; \quad L_z Y_e^m(\theta,\varphi) = = \hbar m\, Y_e^m(\theta,$$

Now it's time to consider the radial part $R(r)$: from Lecture #2

$$\frac{d}{dr}\left(r^2 \frac{dR(r)}{dr}\right)\cdot\frac{1}{R(r)} + \frac{2\mu r^2}{\hbar^2}\left(E - U(r)\right) = \underbrace{\lambda}_{\ell(\ell+1)}$$

multiply by $R(r)$ and $\frac{-\hbar^2}{2\mu r^2}$:

$$-\frac{\hbar^2}{2\mu r^2}\left(2r\frac{dR(r)}{dr} + r^2\frac{d^2R(r)}{dr^2}\right) + \Big(U(r) + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}}_{\text{centrifugal potential}}\Big)\cdot R(r) = E\,R(r) \qquad (5.1)$$

$$\underbrace{U_{eff}}_{\text{effective potential}}(r) = U(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$$

Simplify Eq. (5.1) by introducing $u(r)$ such that $R(r) = \frac{u(r)}{r}$ => then =>

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{2\cancel{r}}{\cancel{r}}\frac{du(r)}{dr} - \frac{2r}{r^2}u(r) + \underbrace{r^2\frac{d}{dr}\left(\frac{du(r)}{dr}\cdot\frac{1}{r} - \frac{1}{r^2}u(r)\right)}\right) + V_{eff}(r)\frac{u(r)}{r} = E\frac{u(r)}{r}$$

$$\parallel$$

$$\frac{d^2u(r)}{dr^2}\cdot\frac{1}{r} - \frac{du(r)}{dr}\cdot\frac{1}{r^2} + \frac{2}{r^3}u(r) - \frac{1}{r^2}\frac{du(r)}{dr}$$

$$-\frac{\hbar^2}{2\mu r^2}\left(2\frac{du(r)}{dr} \cancel{- \frac{2}{r}u(r)} + r\frac{d^2u(r)}{dr^2} - \frac{du(r)}{dr} \cancel{+ \frac{2}{r}u(r)} - \frac{du(r)}{dr}\right) + V_{eff}(r)\frac{u(r)}{r} = E\frac{u(r)}{r}; \Rightarrow$$

$$-\frac{\hbar^2}{2\mu r^2}r\frac{d^2u(r)}{dr^2} + V_{eff}(r)\frac{u(r)}{r} = E\frac{u(r)}{r} \Rightarrow$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(r)}{dr^2} + V_{eff}(r)u(r) = Eu(r) \quad (5.2)$$

looks like a 1D problem, but $r \geq 0$! (not $-\infty < r + \infty$)

much simpler than (5.1)

Replace $u(r) \to u_{\kappa,l}(r)$
$E \to E_{\kappa,l}$

V_{eff} depends on l, we'll see later that we'll need κ

At $r \to 0 \Rightarrow R(r) = \frac{u(r)}{r}$ should be finite $\Rightarrow$

$u_{k,\ell}(0) = 0$

To move any further $\Rightarrow$ need to specify a potential $V(r)$ in (5.2) and find $u_{k,\ell}(r) \Rightarrow$ the most common example is the hydrogen atom

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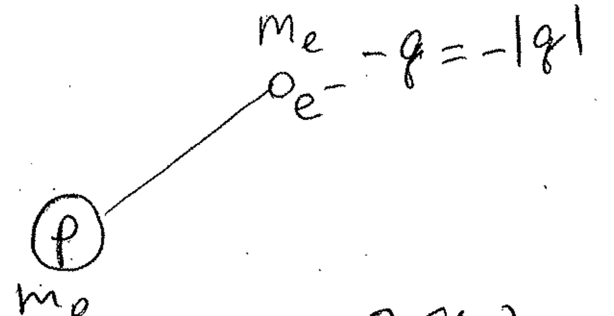
proton and electron interact via Coulomb force (electrostatic interaction)



$+q = |q|$

$$V(r) = -\underbrace{\frac{q^2}{4\pi\varepsilon_0}}\frac{1}{r} = -\frac{e^2}{r}$$

$q = 1.6 \cdot 10^{-19}$ Coulomb SI system $\varepsilon_0 = 8.85 \cdot 10^{-12} \frac{F}{m}$

$m_e = 9.1 \cdot 10^{-31}$ kg
$m_p = 1.7 \cdot 10^{-27}$ kg $(m_e << m_p) \Rightarrow \mu = \frac{m_e m_p}{m_e + m_p} \approx m_e$

Since the proton is so much heavier, the center of mass almost coinsides with the proton, and so the "center-of-mass" particle (recall Lecture #1) is a proton, and the "relative" particle is an electron.

So, now Eq. (5.2) is: $(u_{k,\ell}(0) = 0)$

$$-\frac{\hbar^2}{2\mu}\frac{d^2 u_{k,\ell}(r)}{dr^2} + \left(\frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right)u_{k,\ell}(r) = E_{k,\ell}\, u_{k,\ell}(r) \quad (5.3)$$

First of all $\Rightarrow$ make all variables dimensionless

(recall harmonic oscillator problem)

$\Downarrow$

choose

$$a_0 = \frac{\hbar^2}{\mu e^2} \quad \text{— Bohr radius}$$

(for H-atom $a_0 \simeq 0.5\,\mathring{A}$)

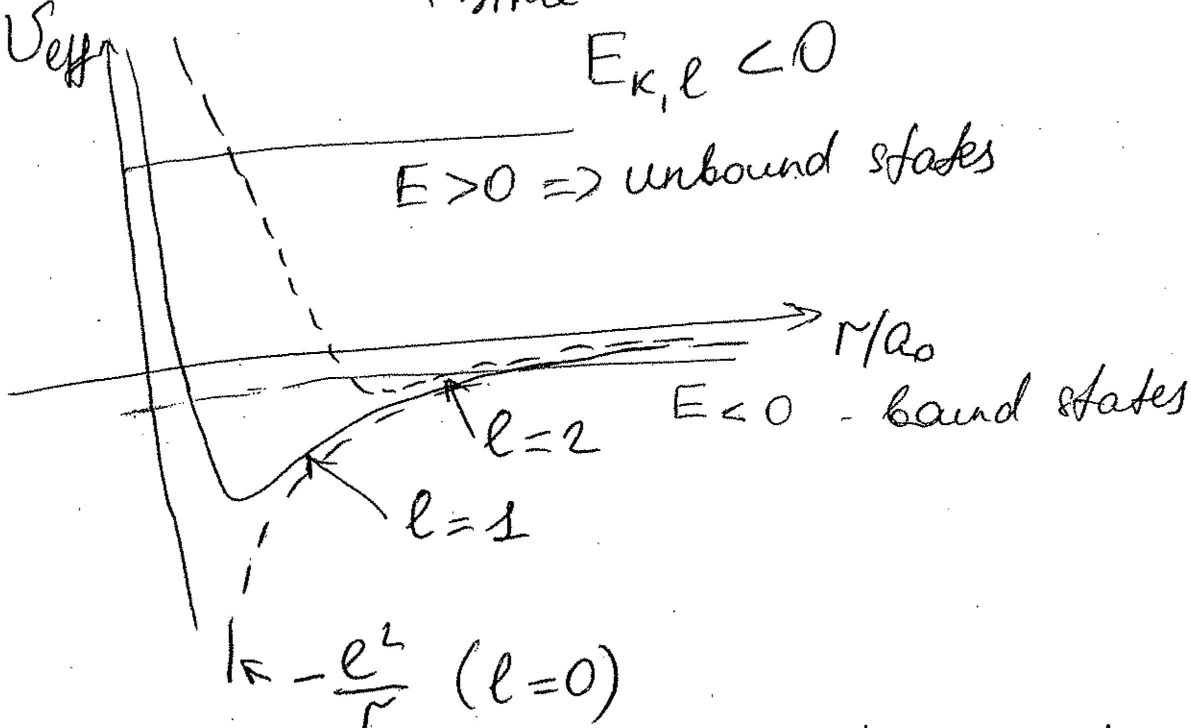
$$E_I = \frac{\mu e^4}{2\hbar^2} \quad \text{- ionization energy}$$

$\Leftarrow$ introduce new variables

$$\rho = \frac{r}{a_0}$$

$$\lambda_{k,l} = \sqrt{-E_{k,l}/E_I}$$

since we are looking for bound states, $E_{k,l} < 0$



With the new variables ρ, $\lambda_{k,l}$, the Eq. (5.3) is:

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{k,l}^2\right] u_{k,l}(\rho) = 0 \qquad (5.4)$$

1) Investigate the asymptotic behavior

$\rho \to \infty$: $\frac{1}{\rho^2}, \frac{1}{\rho} \to 0 \Rightarrow$

Eq. (5.4) reduces to $\left[\frac{d}{d\rho^2} - \lambda_{\kappa,\ell}^2\right] u_{\kappa,\ell}(\rho) = 0 \Rightarrow$

$$u_{\kappa,\ell}(\rho) = \underbrace{C_1 e^{\rho\lambda_{\kappa,\ell}}}_{\to\infty \text{ as } \rho\to\infty \Rightarrow \text{ unphysical} \Rightarrow C_1 = 0} + C_2 e^{-\rho\lambda_{\kappa,\ell}}$$

So, at $\rho \to \infty \Rightarrow u_{\kappa,\ell}(\rho) \sim e^{-\rho\lambda_{\kappa,\ell}}$

2) Go back to Eq. (5.4) and look for solution in the form $u_{\kappa,\ell}(\rho) = e^{-\rho\lambda_{\kappa,\ell}} y_{\kappa,\ell}(\rho) \Rightarrow$

$$\left(\frac{d^2}{d\rho^2} - 2\lambda_{\kappa,\ell}\frac{d}{d\rho} + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) y_{\kappa,\ell}(\rho) = 0 \qquad (5.5)$$

Since $u_{\kappa,\ell}(0) = 0 \Rightarrow y_{\kappa,\ell}(0) = 0$

As in the harmonic oscillator problem, look for $y_{\kappa,\ell}(\rho)$ as a power series:

$$y_{\kappa,\ell}(\rho) = \rho^s \sum_{q=0}^{\infty} C_q \rho^q \quad (C_0 \neq 0) \Rightarrow \text{substitute into (5.5)}$$

$$\frac{d y_{\kappa,\ell}(\rho)}{d\rho} = \sum_{q=0}^{\infty} (q+s) C_q{}^{q+s-1}$$

(6)

$$\frac{d^2 y_{\kappa,\ell}(\rho)}{d\rho^2} = \sum_{q=0}^{\infty} (q+s)(q+s-1) C_q \rho^{q+s-2}$$

Then, Eq. (5.5) is:

$$\underbrace{\sum_{q=0}^{\infty} (q+s)(q+s-1) C_q \rho^{q+s-2}}_{1} - 2\lambda_{\kappa,\ell} \underbrace{\sum_{q=0}^{\infty} (q+s) \cdot C_q \rho^{q+s-1}}_{2} + 2 \underbrace{\sum_{q=0}^{\infty} C_q \rho^{q+s-1}}_{3} - \ell(\ell+1) \underbrace{\sum_{q=0}^{\infty} C_q \rho^{q+s-2}}_{4} = 0 \qquad (5.6)$$

The lowest power of ρ is $(s-2)$ (in 1 and 4 at $q=0$)

collect these terms $\Rightarrow$

$$\left(s(s-1) C_0 - \ell(\ell+1) C_0 \right) \rho^{s-2} = 0 \Rightarrow$$

since $C_0 \neq 0 \Rightarrow s(s-1) - \ell(\ell+1) = 0 \Rightarrow$

$$s = \begin{cases} \ell+1 \\ -\ell \end{cases}$$

$$y_{\kappa,\ell}(\rho) = \underbrace{\rho^{-\ell} \sum_{q=0}^{\infty} C_q \rho^q}_{} \quad \text{or} \quad \boxed{\rho^{\ell+1} \sum_{q=0}^{\infty} C_q \rho^q}$$

unphysical since $y_{\kappa,\ell}(0) = 0$ $\Rightarrow$ discard!

Now change q to $q-1$ in 2 and 3 $\Rightarrow$

$$2: \sum_{q=0}^{\infty} (q+s) C_q \rho^{q+s-1} \Rightarrow \sum_{q=1}^{\infty} (q-1+s) C_{q-1} \rho^{q+s-2}$$

③: $\sum_{q=0}^{\infty} C_q \rho^{q+s-1} \Rightarrow \sum_{q=1}^{\infty} C_{q-1} \rho^{q+s-2}$

Then, Eq. (5.6) is:

$$\sum_{q=1}^{\infty} \Big[\big((q+s)(q+s-1) - \ell(\ell+1)\big) C_q + C_{q-1} \cdot (-2\lambda_{k,\ell} \cdot (q-1+s) + 2)\Big] \rho^{q+s-2} = 0 \quad (5.7)$$

(Note that the $q=0$ term in ① and ④ was taken care of before, when we found that $s = \ell+1$)

From (5.7) $\Rightarrow$ obtain the <u>recurrence relation</u>

$$\big[(q+s)(q+s-1) - \ell(\ell+1)\big] C_q = \big[2\lambda_{k,\ell}(q+s-1) - 2\big] \cdot C_{q-1};$$

Since $s = \ell + 1 \Rightarrow$

$$\big[\underbrace{(q+\ell+1)(q+\ell) - \ell(\ell+1)}\big] C_q = \big[2\lambda_{k,\ell}(q+\ell) - 2\big] \cdot C_{q-1};$$

$$(q+\ell)^2 + q + \cancel{\ell} - \ell^2 - \cancel{\ell} = q^2 + 2q\ell + \cancel{\ell^2} + q - \cancel{\ell^2} = \underline{q(q+2\ell+1)}$$

$$\underline{q(q+2\ell+1) C_q = 2\big(\lambda_{k,\ell}(q+\ell) - 1\big) C_{q-1}}$$

If we know $C_0 \Rightarrow$ can find all other coefficients

Next step: check the convergence of the series

$$\frac{C_q}{C_{q-1}} = \frac{2\left(\lambda_{\kappa,l}(q+l)-1\right)}{q(q+2l+1)} \underset{q\to\infty}{=} \frac{2\lambda_{\kappa,l}}{q}$$

If we allow this power series to have infinite number of terms, i.e. $\sum_{q=0}^{\infty} C_q \rho^q$, then this power series would describe an exponential function

$e^{2\rho\lambda_{\kappa,l}} = \sum_{q=0}^{\infty} \frac{(2\lambda_{\kappa,l})^q}{q!}\rho^q$, and so altogether

our solution $u_{\kappa,l}(\rho) = e^{-\rho\lambda_{\kappa,l}} y_{\kappa,l}(\rho) =$

$= e^{-\rho\lambda_{\kappa,l}} \rho^{l+1} e^{2\rho\lambda_{\kappa,l}} = \rho^{l+1} e^{\rho\lambda_{\kappa,l}} \to \infty$

as $\rho \to \infty$ $\Downarrow$

unphysical

$\Downarrow$

need to terminate our power series!

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Declare that there exist a $q_{max} = \kappa$, so that $\underline{\lambda_{\kappa,l}(\kappa+l) - 1 = 0}$ $(C_\kappa = 0)$

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Recall that this is a dimensionless energy $\nearrow$ $\underline{\lambda_{\kappa,l} = \frac{1}{\kappa+l}}$ $\Rightarrow$ $\underline{E_{\kappa,l} = -\frac{E_I}{(\kappa+l)^2}}$

$\uparrow$

allowed energy levels $(\kappa = 1, 2, 3, \ldots)$