3.2 Hydrogen Atom

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3.2 Hydrogen Atom

In section 3.1, we solved the two differential equations below where Eq. 3.2.1 is dependent on phi and Eq. 3.2.2 which is dependent on theta

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \qquad (3.2.1)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\Theta = \frac{m^2\Theta}{\sin^2\theta} \qquad (3.2.2)$$

In section 3.2, we will solve the radial dependent differential equation and analyze its results in the context of the Hydrogen atom.

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The differential equation below is the radial dependent component of the 3-D Schrödinger Equation in spherical coordinates

$$-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R+\frac{\lambda\hbar^2}{2mr^2}R+V(r)R=ER \qquad (3.2.3)$$

We will relate our equation to the Hydrogen atom by considering the form of **V(r).**

$$V(r)\sim\frac{1}{r}$$

The potential of the Hydrogen atom, **V(r)** is inversely proportional to **r**

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We will define an operator called the radial-momentum operator

$$p_r = \frac{\hbar}{i}\left(\frac{d}{dr} + \frac{1}{r}\right) \tag{3.2.4}$$

Using this operator we can redefine the differential term of the kinetic energy operator in spherical coordinates as

$$\frac{p_r^{\,2}}{2m} \tag{3.2.5}$$

For the skeptics out there, the next slide will illustrate the equivalence of Eq. 3.2.5 and the differential term of the kinetic energy operator.

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Proof that the radial-momentum operator is equivalent to the differential term of the kinetic energy operator:

$$-\hbar^2 \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr}\right) = -\hbar^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)$$

differential term of the kinetic energy operator

$$p_r{}^2 = -\hbar^2\left(\frac{d}{dr} + \frac{1}{r}\right)\left(\frac{d}{dr} + \frac{1}{r}\right)$$

$$= -\hbar^2\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{1}{r^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\right)$$

$$= -\hbar^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)$$

radial-momentum operator same as the differential term of the kinetic energy operator

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So rewriting the kinetic energy operator in terms of $\mathbf{p_r}$ results in

$$T = \frac{p_r^{\,2}}{2m} + \frac{L^2}{2mr^2} \qquad (3.2.6)$$

Using Eq. 3.2.6, Schrödinger's Equation is given by

$$H\Psi(r) = E\Psi(r)$$

$$L^2\Psi = \lambda\Psi$$

where $\lambda = l(l+1)$

$$\left(\frac{p_r^{\,2}}{2m} + \frac{L^2}{2mr^2} + V(r)\right)\Psi(r) = E\Psi(r)$$

$$\left(\frac{p_r^{\,2}}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)\Psi(r) = E\Psi(r) \qquad (3.2.7)$$

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Let $\Psi(r) = \dfrac{u(r)}{r}$ where **u(r)** is an polynomial of **r**

Consider

$$p_r^{\,2}\Psi(r) = p_r^{\,2}\frac{u(r)}{r} = \left(\frac{d}{dr}+\frac{1}{r}\right)\left(\frac{d}{dr}+\frac{1}{r}\right)\frac{u(r)}{r}$$

$$= \left(\frac{d}{dr}+\frac{1}{r}\right)\left(\frac{1}{r}\frac{du}{dr}-\frac{1}{r^2}u(r)+\frac{1}{r^2}u(r)\right)$$

$$= \left(\frac{d}{dr}+\frac{1}{r}\right)\left(\frac{1}{r}\frac{du}{dr}\right) = \left[\frac{d}{dr}\left(\frac{1}{r}\frac{du}{dr}\right)+\frac{1}{r^2}\frac{du}{dr}\right]$$

$$= \left[-\frac{1}{r^2}\frac{du}{dr}+\frac{1}{r}\frac{d^2u}{dr^2}+\frac{1}{r^2}\frac{du}{dr}\right] = \frac{1}{r}\frac{d^2u}{dr^2} \tag{3.2.8}$$

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Substituting $\Psi(r)=\dfrac{u(r)}{r}$ and Eq. 3.2.8 into Eq. 3.2.7

$$\frac{-\hbar^2}{2mr}\frac{d^2u}{dr^2}+\frac{\hbar^2 l(l+1)}{2mr^2}\frac{u}{r}+V(r)\frac{u}{r}=E\frac{u}{r}$$

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2}+\frac{\hbar^2 l(l+1)}{2mr^2}u+V(r)u=Eu \tag{3.2.9}$$

Define **V(r)** (in cgs units) we have

$$V(r)=\frac{-Zq^2}{r} \tag{3.2.10}$$

where **Z** is the atomic number, **q** is the charge of an electron and **r** is the distance between force center and particle under observation.

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We can take some steps to make Eq. 3.2.9 dimensionless to simplify our analysis. Defining

$$r = a_o \rho \quad \text{and} \quad E = E_o \varepsilon \tag{3.2.11}$$

no units

Substituting Eq. 3.2.11 and Eq. 3.2.10 into Eq. 3.2.9 results in

$$\frac{-\hbar^2}{2m}\frac{1}{a_o{}^2}\frac{d^2u}{d\rho^2} + \frac{\hbar^2 l(l+1)}{2ma_o{}^2\rho^2}u - \frac{Zq^2}{a_o\rho}u = E_o\varepsilon u \tag{3.2.12}$$

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Defining $\boldsymbol{a_o}$ and $\boldsymbol{E_o}$ from Eq. 3.2.11 so that Eq. 3.2.12 is dimensionless

$$\frac{Zq^2}{a_o} = \frac{\hbar^2}{m{a_o}^2} = E_o$$

$$a_o = \frac{\hbar^2}{mq^2 Z} \tag{3.2.13}$$

$$E_o = \frac{Z^2 q^4 m}{\hbar^2} \tag{3.2.14}$$

Substituting Eq. 3.2.13 and Eq. 3.2.14 into Eq. 3.2.12 we get the dimensionless expression of the Schrödinger's Equation

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + \frac{l(l+1)}{2\rho^2} - \frac{1}{\rho}\right]u = \varepsilon u \tag{3.2.15}$$

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a_o is known as the Bohr radius which is considered to be the effective radius of a Hydrogen atom. To calculate the Bohr radius we must consider the cgs units for energy, length and electric charge.

Conversion between SI and cgs.

The cgs unit for length is the centimeter.

$$100\text{cm} = 1\text{m}$$

The cgs unit for energy is the erg.

$$1\text{erg} = 1\text{g}\cdot\text{cm}^2/\text{s}^2$$

$$10^7\,\text{erg} = 1\text{J}$$

The cgs units for electric charge is "electrostatic unit" or esu.

$$1\text{C} = 3\times10^9\,\text{esu}$$

$$a_o = \frac{\hbar^2}{mq^2Z} = \frac{(1.05\times10^{-34}\,\text{J}\cdot\text{s})^2\left(\dfrac{10^7\,\text{erg}}{1\text{J}}\right)^2}{(9.11\times10^{-31}\text{kg})\left(\dfrac{1000\text{g}}{1\text{kg}}\right)\left(1.6\times10^{-19}\,C\right)^2\left(\dfrac{3\times10^9\,\text{esu}}{1\text{C}}\right)^2} \quad (1)$$

$$a_o = 5.29\times10^{-9}\,\text{cm} = 5.29\times10^{-11}\,\text{m}$$

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Now let us assume a power series solution to Eq. 3.2.15 of the form

$$u(\rho) = A_o \rho^n e^{-\frac{\rho}{n}} + A_1 \rho^n \rho^1 e^{-\frac{\rho}{n}} + \ldots + A_q \rho^n \rho^q e^{-\frac{\rho}{n}} + \ldots \qquad (3.2.16)$$

Applying the second derivative to the first term in Eq. 3.2.16,

$$\frac{d^2}{d\rho^2}\left(A_o \rho^n e^{-\frac{\rho}{n}} \right) = \frac{d}{d\rho}\left[A_o n \rho^{n-1} e^{-\frac{\rho}{n}} + A_o \rho^n \left(-\frac{1}{n} \right) e^{-\frac{\rho}{n}} \right]$$

$$= A_o \frac{d}{d\rho}\left[n\rho^{n-1} - \frac{\rho^n}{n} \right] e^{-\frac{\rho}{n}}$$

$$= A_o \left[\frac{\rho^n}{n^2} - 2\rho^{n-1} + n(n-1)\rho^{n-2} \right] e^{-\frac{\rho}{n}} \qquad (3.2.17)$$

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Substituting this result into Eq. 3.2.15 and the first term of Eq. 3.2.16, we get

$$-\frac{1}{2}\frac{\rho^n}{n^2}-\frac{1}{2}n(n-1)\rho^{n-2}+\frac{l(l+1)}{2}\rho^{n-2}=\varepsilon\rho^n \qquad (3.2.18)$$

Equating the coefficients of like powers

$$-\frac{1}{2}\frac{1}{n^2}\rho^n=\varepsilon\rho^n \quad \Rightarrow \quad \varepsilon=-\frac{1}{2n^2} \qquad (3.2.19)$$

Thus

$$E=E_o\varepsilon=\frac{Z^2q^4m}{\hbar^2}\left(-\frac{1}{2n^2}\right)=-\frac{Z^2q^4m}{2\hbar^2n^2} \qquad (3.2.20)$$

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Substituting the appropriate values for the physical constants into Eq. 3.2.20 and setting Z=1 since we are considering the Hydrogen atom, we get

$$E = -\frac{13.6\mathrm{eV}}{n^2} \qquad (3.2.21)$$

Equating the coefficients of **ρ^{n-2}** leads to

$$\frac{n(n-1)}{2} = \frac{l(l+1)}{2} \qquad (3.2.22a)$$

Solving for *l* in terms of *n* we get

$$l^2 + l - n(n-1) = 0$$

$$l = n - 1 \qquad (3.2.22b)$$

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Now, we have defined three quantum numbers – *n*, *l*, *m* – that are needed to specify the particles motion in a hydrogen atom.

What about the wave function of a particle in a hydrogen atom?

To accomplish this we will redefine the power series solution for Schrödinger's Equation

$$u = \rho^s \sum_{q=0}^{\infty} A_q \rho^q e^{-\frac{\rho}{n}} \tag{3.2.23}$$

as

$$u(r) = g(r) e^{-\frac{r}{na_o}} \tag{3.2.24}$$

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Also

$$\frac{du}{dr} = g' e^{-\frac{r}{na_o}} - \frac{1}{na_o} g e^{-\frac{r}{na_o}}$$

$$\frac{d^2u}{dr^2} = g'' e^{-\frac{r}{na_o}} - \frac{2}{na_o} g' e^{-\frac{r}{na_o}} + \frac{1}{(na_o)^2} g e^{-\frac{r}{na_o}} \tag{3.2.25}$$

Substituting the above result into Eq. 3.2.9 where **V(r)** is defined as Eq. 3.2.10 and E is defined as Eq. 3.2.20, dividing out the exponential terms and simplifying the result, we get

$$-\frac{\hbar^2}{2m}\left[g'' - \frac{2}{na_o} g'\right] + \frac{\hbar^2 l(l+1)}{2mr^2} g - \frac{Zq^2}{r} g = 0 \tag{3.2.26}$$

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g(r) is defined as

$$g(r) = r^s \sum_q A_q r^q \tag{3.2.27}$$

So the first and second derivatives of **g(r)** are

$$\begin{aligned} g'(r) &= sr^{s-1}A_o + (s+1)r^s A_1 + \ldots + (s+q)A_q r^{s+q-1} + \ldots \\ g''(r) &= s(s-1)r^{s-2} + (s+1)sA_1 r^{s-1} + \ldots \\ &\qquad \ldots + (s+q)(s+q-1)A_q r^{s+q-2} + \ldots \end{aligned} \tag{3.2.28}$$

We want to make Eq. 3.2.26 dimensionless so again we substitute Eq. 3.2.11 into Eq. 3.2.26

$$\frac{d^2 g}{d\rho^2} - \frac{2}{n}\frac{dg}{d\rho} - \frac{l(l+1)}{\rho^2} g + \frac{2}{\rho} g = 0 \tag{3.2.29}$$

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Substituting Eq. 3.2.11 into Eq. 3.2.27 and Eq. 3.2.28 and substituting that result into Eq. 3.2.29 gives us

$$\begin{aligned}
& s(s-1){a_o}^{s} A_o \rho^{s-2} + \ldots + (s+q)(s+q-1){a_o}^{s+q} A_q \rho^{s+q-2} + \ldots \\
& \quad - l(l+1)\left[A_o \rho^{s-2} + \ldots + A_q {a_o}^{s+q} \rho^{s+q-2} + \ldots\right] \\
& \quad\quad + \frac{2}{n}\left[s A_o {a_o}^{s} \rho^{s-1} + \ldots + (s+q) A_q {a_o}^{s+q} \rho^{s+q-1} + \ldots\right] \\
& \quad\quad\quad + 2\left[A_o {a_o}^{s} \rho^{s-1} + \ldots + A_q {a_o}^{s+q} \rho^{s+q-1} + \ldots\right] = 0
\end{aligned} \tag{3.2.30}$$

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Eq. 3.2.30 must equal zero for all ρ. Therefore the coefficients of the ρ^{s-2} must sum to zero.

$$s(s-1)-l(l+1)=0 \qquad (3.2.31)$$

The coefficients of the general term, ρ^{s+q-1} are

$$(s+q+1)(s+q)A_{q+1}a_o^{\,s+q+1}-\frac{2}{n}A_q a_o^{\,s+q}(s+q)$$
$$-l(l+1)A_{q+1}a_o^{\,s+q+1}+2A_q a_o^{\,s+q}=0 \qquad (3.2.32)$$

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Solving for *s* in terms of *l* using Eq. 3.2.31 we find

$$s = l + 1 \tag{3.2.33}$$

Substituting Eq. 3.2.33 into Eq. 3.2.32 and solving for A_{q+1} we have

$$A_{q+}1 = A_q \left[\frac{\frac{2}{n}(l+1+q)-2}{(l+q+2)(l+q+1)-l(l+1)} \right] \tag{3.2.34}$$

Note: $1/a_o$ factor is absorbed by the A_q term.

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Eq. 3.2.34 can be reexpressed as

$$A_{q+1} = A_q \left[\frac{\frac{2}{n}(l+1+q)-2}{(q+1)(q+2l+2)} \right] \tag{3.2.35}$$

Eq. 3.2.35 can be used to find the coefficients of the higher order terms of Eq. 3.2.23. The general wave function for the Hydrogen atom is defined by Eq. 3.2.36.

$$\Psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) \tag{3.2.36}$$

Eq. 3.2.35 and Eq. 3.2.23 are used to define R(r) in Eq. 3.2.36 and $Y_{lm}(\theta,\Phi)$ is defined in Section 3.1.

References

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