5. Hydrogen atom

5.1. Hydrogen atom — according to the Schrödinger theory

\[ V(r) = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} \]

Solve the Schrödinger Eq.

\[ \psi_{nlm}(r, \theta, \phi) = \frac{\mu_{2l}(r)}{r} \psi_{lm}(\theta, \phi) = \psi_{nlm}(r, \theta, \phi) \quad (1) \]

\[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dr^2} + \left[ -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{\mu_{2l}}{r^2} \right] \psi(r) = E \psi(r) \quad (2) \]

\[ E_n = -\frac{\mu_{2l}}{2\hbar^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \frac{1}{2n^2} = -\frac{E_{\text{pl}}}{2n^2} \quad n = 1, 2, 3, \ldots \quad (3) \]

In atomic units, the quantities \( m = \hbar = e = 1 \), then the square bracket \( \mu = 1 \),

\[ E_n = -\frac{1}{2n^2} \quad [\text{in atomic units}] \]

1 atomic unit in energy = \( 2 \times 13.6 \text{ eV} \)

Thus the binding energy of hydrogen atom is

\[ E_n = -\frac{13.6 \text{ eV}}{n^2} \quad n = 1, 2, \ldots \quad (4) \]

In the above model, the proton mass is assumed to be infinite.

**Generalization:** If the mass of proton is considered, the mass \( m \) in Eq. (3) should be replaced by the reduced mass \( m^* \).

1. If the charge of the nucleus is \( Z \), the binding energy (4) is multiplied by \( Z^2 \).

2. In a medium, the effective interaction is reduced by \( \kappa \), which is the dielectric constant, the binding energy is reduced by \( (1/\kappa^2) \).

Carry out homework § 4 problems 5 to see how these results appear in real examples.
5.2. Beyond the Schrödinger theory

(1) each has spin, thus the total wavefunction has the form

\[
R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \begin{cases} \chi^+ \\ \chi^- \end{cases}
\]

where \( \chi \) is spin \( \frac{1}{2} \) function.

Total electron angular momentum

\[ \vec{J} = \vec{\ell} + \vec{S} \quad S = \frac{1}{2} \]

Need to learn how to add two angular momenta.

(2) spin-orbit coupling \( \rightarrow \) leading to fine structure

\[
\begin{array}{c}
\text{Schrödinger} \\
\text{spin-orbit coupling}
\end{array}
\]

\[
\begin{array}{c}
2s \\
2p
\end{array}
\]

\[
\begin{array}{c}
0.365 \text{cm}^{-1} \\
2.1 \text{eV}
\end{array}
\]

\[
\begin{array}{c}
2p_\frac{1}{2}, 2p_\frac{3}{2} > 10.951 \text{ MHz} \\
= 4.5 \times 10^5 \text{ eV}
\end{array}
\]

\[
1 \text{ eV} = 8,065.48 \text{ cm}^{-1}
\]

\[
= 2.42 \times 10^8 \text{ MHz}
\]

(3) Lamb shift

\[
\begin{array}{c}
1057 \text{ MHz} \\
2p_{\frac{3}{2}}
\end{array}
\]

\[ \approx 4.36 \times 10^{-6} \text{ eV} \]

(4) hyperfine structure of the ground state of hydrogen

\[
\begin{array}{c}
\vec{F} = \vec{J} + \vec{S} \\
\ell \text{ spin } (\frac{1}{2}) \text{ of the proton}
\end{array}
\]

\[
\begin{array}{c}
21 \text{ cm} \\
\text{radio astronomy}
\end{array}
\]

\[
\begin{array}{c}
F = 1 \\
F = 0
\end{array}
\]

\[ = 1420 \text{ MHz} \]
5.3 Solving the radial eq. of a hydrogen atom

Only key steps are outlined (SI units)

\[-\frac{\hbar^2}{2m} \frac{d^2\psi}{dr^2} + \left[ -\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\ell (\ell + 1) \hbar^2}{2m r^2} \right] \psi = E \psi \quad (5)\]

Define \[\lambda = \frac{1}{\hbar} \sqrt{-2mE}\]

\[\rho = \lambda r \quad \rho_0 = \frac{m e^2}{2\pi\varepsilon_0 \hbar^2} \lambda\]

(5) \[\Rightarrow \frac{d^2\psi}{d\rho^2} = \left[ -\frac{\rho_0}{\rho} + \frac{\ell (\ell + 1)}{\rho^2} \right] \psi \quad (6)\]

Asymptotic form \(\rho \to \infty\)

\[\frac{d^2\psi}{d\rho^2} = 0 \quad \psi = A e^{-\rho} + B e^{\rho} \quad \text{not acceptable}\]

\[\psi(\rho) \to A e^{-\rho} \quad \rho \to \infty\]

Near the origin, (6) becomes

\[\frac{d\psi}{d\rho} = \frac{\ell (\ell + 1)}{\rho} \psi \]

\[\psi(\rho) = C \rho^\ell + D \rho^{-(\ell + 1)} \quad \text{to avoid divergence}\]

Seek solution

\[\psi(\rho) = \rho^\ell e^{-\rho} v(\rho) \quad (7)\]

In terms of \(v(\rho)\)

\[r \frac{d^2v}{dr^2} + 2(\ell + 1 - r) \frac{dv}{dr} + \left[ \rho_0 - 2(\ell + 1) \right] v = 0 \quad (8)\]
The solution of eq. (8) is called Laguerre polynomial

\[ \psi_{n\ell m}(r, \theta, \phi) = L^{2\ell+1}_{n-\ell-1} \left(2\ell+1\right) e^{-\sigma/na} \sum_{\ell m} \left(2\ell+1\right)_{n-\ell-1} Y_{\ell m}(\theta, \phi) \]

See eq. [4.89]

The eigenvalues

\[ E_n = -\frac{E_1}{2n^2} \quad n = 1, 2, 3, \ldots \]

\[ E_1 = 29.21 \text{ eV} \]

How to designate an eigenstate?

\[ \psi_{n\ell m}(r, \theta, \phi) = |n\ell m\rangle \]

\[ n = 1, 2, \ldots \]

For a given \( n \), \( \ell = 0, 1, 2, \ldots (n-1) \)

For a given \( \ell \), \( m = -\ell, -\ell + 1, \ldots, \ell \)

\[ \begin{cases} \ell = 0 & \text{s} \\ \ell = 1 & \text{p} \\ \ell = 2 & \text{d} \\ \ell = 3 & \text{f} \end{cases} \]

Typical energy levels

--- 3s  --- 3p  --- 3d

--- 2s  --- 2p

--- 1s  
\[ \ell = 0 \quad \ell = 1 \quad \ell = 2 \]
5.4 Getting comfortable with atomic hydrogen

(1) Take a look at the wavefunction $R_n e(r)$ and density $r^2 R_n^2 e(r)$ next on a page.

(2) It can be shown

$$\langle r \rangle_{n\ell m} = a_0 \frac{n^2}{\varepsilon} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{\varepsilon_{n\ell m}}{n^2} \right] \right\}$$

roughly $\langle r \rangle \sim n^2$

Thus the orbital radius goes like $n^2$.

(3) Some rough estimate

$$H = T + V = \frac{p^2}{2m} + V$$

$$\langle H \rangle = \frac{1}{2m} \langle p^2 \rangle_{n\ell m} + \langle -\frac{1}{4\pi\varepsilon_0} \frac{1}{r} \rangle_{n\ell m}$$

$$\approx \frac{1}{n^2}$$

Thus $\langle V \rangle_{n\ell m} \sim \frac{1}{n}$

Classical estimate:

$$\frac{T}{V} = \frac{2\pi v}{\nu} \sim \frac{n^2}{\nu_n} = n^3$$

For 1s orbital

$$T = \frac{2\pi a_0}{\nu a c} \approx 150 \times 10^{-18} \text{ sec}$$

$$= 150 \text{ as}$$

For $n = 100$

$$T = 150 \text{ (as)} \times 10^6 = 150 \text{ ps}$$
Figure 3.3  Radial functions $R_n\phi$ and radial distribution functions $r^2 R_n^2(r)$ for atomic hydrogen.