Physic 531: Atomic Physics

Lecture 1: Overview

Structure of Matter? "Reductionist atomistic viewpoint"

- Revolution of the 20th century
- Atomic and subatomic particles
- Physics of atoms ⇒ birth of quantum theory
  - Bohr - Atom
- Explanation of spectroscopy, chemistry
- Build up

  atoms → molecules → condensed matter

Why continue to study it today

- Spectroscopy: Finger prints of universe
- Applications:
  - Designing new materials
  - Biological studies
  - Lasers
  - * Quantum Control - information
  - * Quantum degenerate gases

Probes into the structure of matter

- Spectroscopy: Light emitted by matter (Dark matter?)
- Scattering: Quintessential example: Rutherford
  Particle accelerators
- Cooperative effects → condensed matter

Physics 531 - Lecture 1

Hydrogen and "Hydrogenic" Atoms

We now make our first foray into the study of atomic structure. The physical system involves the binding of electrons to the nucleus. The beauty of physics as that the same mathematical description applies to a wide variety of phenomena - the binding of arbitrary negative particles with positively charged ones. Examples: muonic atoms (the binding of muons to nuclei) and positronium (the binding of electrons to positrons).

Atomic Units

The first thing to do when analyzing any physics problem is to establish the characteristic scales. For "standard matter" (the periodic table) the key player is the electron characterized by

- mass $m_e = 9.11 \times 10^{-28}$ g $\hat{=} 0.511$ MeV/c^2
- charge $e = 4.8 \times 10^{-10}$ esu $= 1.6 \times 10^{-19}$ coul

To determine the characteristic atomic units in quantum mechanics we have one more player

- action $\hbar = 1.055 \times 10^{-27}$ erg-s
  $= 1.055 \times 10^{-34}$ J-s
  $= 1974$ eV·Å/c

Let a_c = Characteristic length scale

$\Rightarrow$ Momentum $p_c = \frac{\hbar}{a_c}$

Energy $E_c = \frac{p_c^2}{m_e} = \frac{\hbar^2}{m_e a_c^2}$

Using Coulomb force $\Rightarrow$ $E_c = \underbrace{\left[\frac{1}{4\pi\epsilon_0}\right]}_{\text{In cgs} \to 1} \frac{e^2}{a_c}$

$$\Rightarrow \boxed{a_c = \frac{\hbar^2}{m_e e^2} = a_0 \approx 0.5\,\text{Å} \quad \text{Bohr radius}}$$

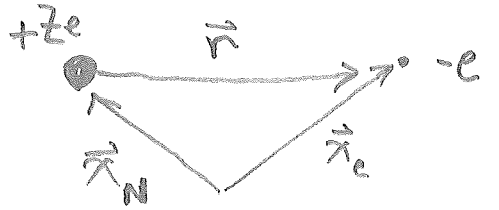
$$\boxed{E_c = \frac{m_e e^4}{\hbar^2} = 2\,\text{Rydberg} \cong 27.2\,\text{eV} = \text{Hartree}}$$

One electron atoms

The simplest "standard matter" is a one electron atom, i.e. an electron bound to a nucleus. Examples:

- Hydrogen : electron + proton
- He^+ : electron + alpha particle
- Li^{++} : electron + $Z=3$ nucleus

Two-body problem



$$\hat{H} = \frac{\hat{\vec{P}}_N^2}{2m_N} + \frac{\hat{\vec{P}}_e^2}{2m_e} - \frac{Ze^2}{r} \quad \left(\text{ignoring relativistic corrections}\right)$$

Separate in center-of-mass, relative coordinates

$$\hat{H} = \hat{H}_{cm} + \hat{H}_{rel}$$

free $\rightarrow \hat{H}_{cm} = \frac{\hat{p}^2}{2M}$ $\quad M = m_e + m_N$ (total mass)

describing binding $\left(\hat{H}_{rel} = \frac{\hat{p}^2}{2\mu} - \frac{Ze^2}{r}\right)$ $\quad \mu = \frac{m_e m_N}{m_e + m_N} \simeq m_e\left(1 - \frac{m_e}{m_N}\right)$

Characteristic scale $E_c = \frac{Ze^2}{a_c} = \frac{\hbar^2}{\mu a_c^2} \Rightarrow a_c = \frac{\hbar^2}{Z\mu e^2} = \frac{a_\mu}{Z}$

Typically ignore reduced mass correction $\rightarrow \begin{cases} a_c \cong \frac{a_0}{Z} \\ E_c = Z^2(E_{Ryd}) \end{cases}$

Bound State Solutions

$$\hat{H}_{rel}|\psi\rangle = -E_{bind}|\psi\rangle$$

($\hat{H}_{rel}$: ignore label)

E_{bind} = binding energy (positive #)

Central force problem $\hat{H} = \hat{T} + \hat{V}(r)$

Potential has rotational symmetry

$$\Rightarrow [\hat{H}, \hat{L}^2] = 0 \qquad [\hat{H}, \hat{L}_i] = 0$$

($\hat{L}_i$: any component; Pick $\hat{L}_z$)

$\Rightarrow$ Complete set of commuting observables

$$\{\hat{H}, \hat{L}^2, \hat{L}_z\}$$

Kinetic energy: Sum of radial and angular motion

$$\hat{T} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2}$$

$$\Rightarrow \hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + \hat{V}(r)$$

Since $\hat{H}$ has no explicit dependence on $\hat{L}_z \Rightarrow$

essential degeneracy $\Rightarrow$ At least $2\ell+1$, for given ℓ

Wave function representation $\psi(r,\theta,\phi) = R(r)\, Y_{\ell,m}(\theta,\phi)$
(separates in spherical coords)

$$\Rightarrow \text{Radial eq: } -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}(rR(r)) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right) R(r) = -E_{bind}\, R(r)$$

Define "reduced" radial wave function $u(r) = rR(r)$

$$\Rightarrow \boxed{-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u(r) + V_{eff}^{(\ell)}\, u(r) = -E_{bind}\, u(r)}$$

Radial equation = 1D Schrödinger eq on the half-line $0 \le r < \infty$ with effective potential $V_{eff}^{(\ell)} = V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}$ ← Centrifugal barrier

Bound states $\Rightarrow n_r$ nodes $\Rightarrow u_{n_r,\ell}(r)$

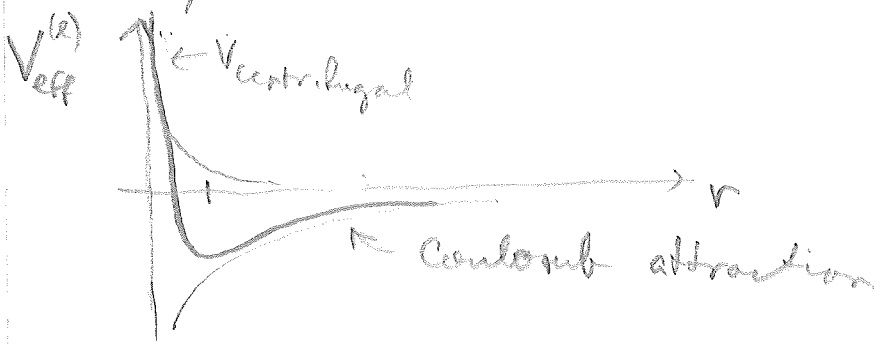
- Because we are on the half line, we have an extra boundary condition at origin.

$$\Rightarrow \underset{n_r,\ell}{u}(r) \sim r^{\ell+1} \Rightarrow u(0) = 0$$

(like hard wall)

Note $R_\ell(r) = \frac{u_\ell(r)}{r} \Rightarrow R_\ell(0) = 0 \quad \forall \ell$ except $\ell = 0 \Rightarrow$ s-state by at origin

- Coulomb, one electron atom



$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u_{n_r\ell}(r) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{zc^2}{r}\right)u_{n_r\ell} = -E_{bind}\,u_{n_r\ell}(r)$$

Make dimensionless in characteristic units

$$x \equiv \frac{r}{a_c} \qquad \epsilon \equiv \frac{E_{bind}}{a_c}$$

$$\Rightarrow -\frac{1}{2}\frac{d^2}{dx^2}u_\ell(x) + \left(\frac{1}{2x^2} - \frac{1}{x}\right)u(x) = -\epsilon\, u(x)$$

Asymptotic: As $x \to \infty \quad u_\ell(x) \Rightarrow A e^{-\sqrt{2\epsilon}\,x}$

$$x \to 0 \quad u_\ell(x) \Rightarrow x^{\ell+1}$$

$\Rightarrow$ Ansatz: $u_\ell(x) = x^{\ell+1} e^{-\sqrt{2\epsilon}\,x} f_\ell(x)$

$\Rightarrow x f_\ell'' + 2(\ell+1-\sqrt{2\epsilon}\,x) f_\ell' + 2(1-\sqrt{2\epsilon}\,(\ell+1)) f_\ell(x) = 0$

Hypergeometric diff'eq $\Rightarrow$ Discrete solutions

$\Rightarrow n_r = \frac{1}{\sqrt{2\epsilon}} - \ell - 1$ (# of radial nodes: 0, 1, 2, ...)

$\Rightarrow \boxed{\epsilon_{n_r,\ell} = \frac{1}{2(n_r+\ell+1)^2}}$ Dimensionless binding energy

"Accidental degeneracy"

For Coulomb interaction, binding energy eigenvalues depend only on $n_r+\ell$ and not n_r, ℓ independently

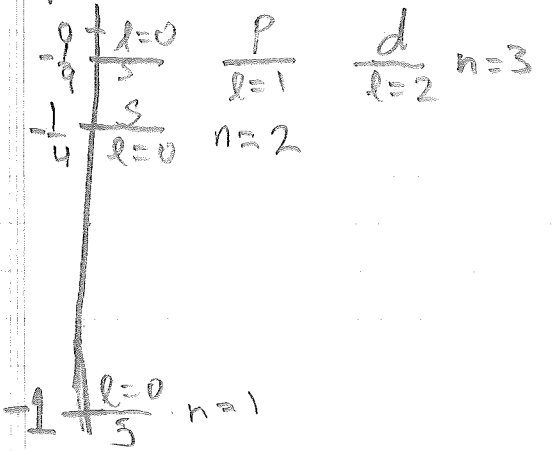
$\Rightarrow$ Define "principle q-#"

$$n \equiv n_r + \ell + 1 = 1, 2, 3, \ldots$$

$\Rightarrow \epsilon_n = \frac{1}{2n^2} \Rightarrow$ With dimensions

$$\boxed{E = -\frac{Z^2}{2n^2} E_0 = -\frac{Z^2}{n^2} \underbrace{13.6\,eV}_{R}}$$

Spectrum



- ∞ # of bound state
- ΔE gets smaller near $E=0$
- Large $n \Rightarrow$ Rydberg series
- Given n $\ell = 0, 1, \cdots, n-1$

Degeneracy

$$g_n = \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} = n^2$$

Eigenfunction:

$$f_{n_r,\ell}(x) = A_{n\ell}\, {}_1F_1\left(-n_r,\ 2\ell+2,\ \frac{2}{n}x\right)$$

$$= C_{n,\ell}\, \mathcal{L}^{2\ell+1}_{n_r}\left(\frac{2}{n}x\right)$$

$C_{n,\ell}$: normalization

$\mathcal{L}^{2\ell+1}_{n_r}\left(\frac{2}{n}x\right)$: Associate Laguerre Polynomial

Putting it all together

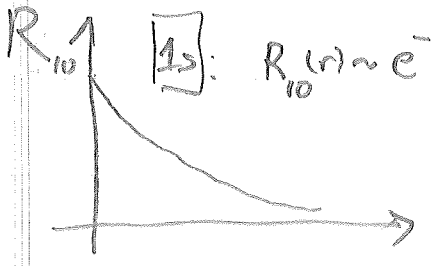
$$\psi_{n,\ell,m}(r,\theta,\phi) = \frac{u_{n,\ell}(r)}{r}\, Y_{\ell,m}(\theta,\phi)$$

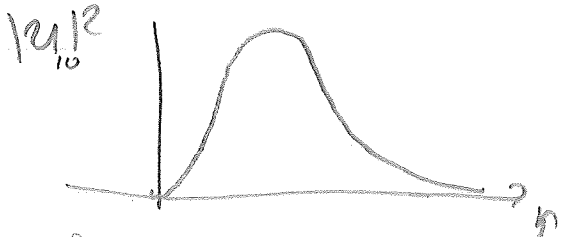
$$= C_{n,\ell}\left(\frac{2r}{a_0}\right)^{\ell} e^{-\left(\frac{2r}{n a_0}\right)}\, \mathcal{L}^{2\ell+1}_{n-\ell-1}\left(\frac{2Z}{n}\frac{r}{a_0}\right) Y_{\ell,m}(\theta,\phi)$$

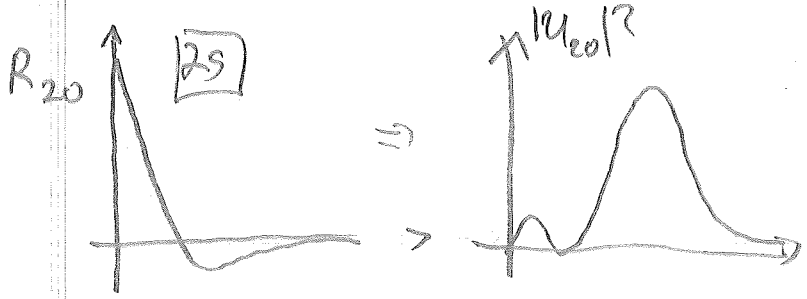
Probability distribution $|\psi|^2 d^3x = |\psi(r,\theta,\phi)|^2 r^2 dr\, d\Omega$

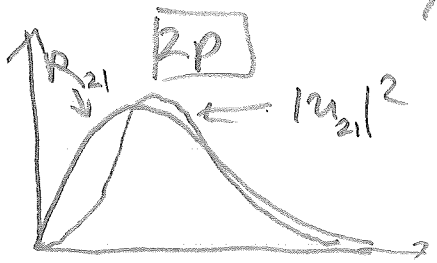
$$= \underbrace{r^2 |R_{n,\ell}(r)|}\, dr \quad |Y_{\ell,m}(\theta,\phi)|^2 d\Omega$$

radial density $= |u_{n,\ell}(r)|^2$ ← Angular





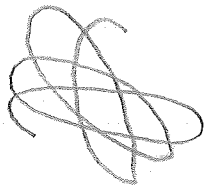




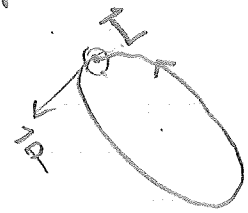
Accidental degeneracy - NO!

The fact the energy levels depend only on $n_r + l$ and not n_r and l independently is no accident, but a result of another symmetry, unique for potentials $\sim \frac{-1}{r}$

This is well know from classical mechanics.
Typically for central potential trajectory "precess"



$V(r) \neq -\frac{k}{r}$



Perfect ellipse

$V(r) = -\frac{k}{r}$

New conserved Quantity (originally introduced by Laplace)

$$\vec{A} \equiv \frac{1}{m}(\vec{L} \times \vec{p}) + k\frac{\vec{r}}{r}$$

Quantum mechanical $\Rightarrow$ Operator

$$\hat{\vec{A}} \equiv \frac{1}{m}\left(\frac{\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}}{2}\right) + \frac{\vec{r}}{r}$$

↑ Commutes with Hamiltonian

$\Rightarrow$ New conserved quantities
$\Rightarrow$ New symmetries

Related to rotation in 4D

$\Rightarrow$ SO(4) symmetry (see homework)

The existence of another symmetry for $\frac{1}{r}$ potential
$\Rightarrow$ Another complete set of commuting operators to specify eigenstates of Hamiltonian

$$\{\hat{H}, \hat{K}_z, \hat{L}_z\}$$

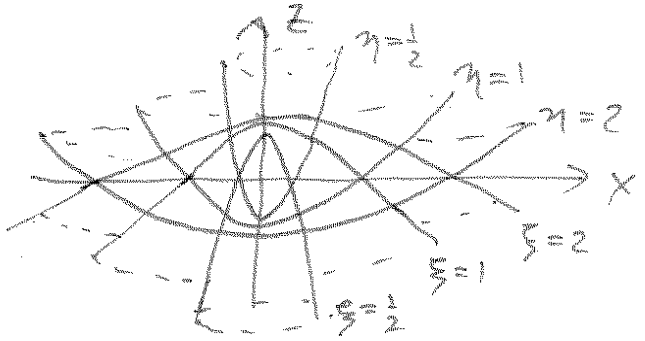
Note: $[\hat{K}_z, \hat{L}^2] \neq 0 \Rightarrow \ell$ no longer a good quantum #

For these operators, there is a new way of separating the 3D Schrödinger Eq. in curvilinear coordinates.

$\Rightarrow$ <u>Parabolic coordinates</u> (ξ, η, ϕ)

$\phi = \tan^{-1}\left(\frac{y}{x}\right)$ (the usual azimuthal angle)

$\xi = r + z$, $\eta = r - z$ (paraboloids of revolution about z-axis)



Confocal paraboloids

In this coordinate system: $d^3x = \frac{1}{4}(\xi + \eta)\, d\xi\, d\eta\, d\phi$

$$\nabla^2 = \frac{4}{\xi + \eta}\left[\frac{\partial}{\partial \xi}\left(\xi \frac{\partial}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\eta \frac{\partial}{\partial \eta}\right)\right] + \frac{1}{\xi \eta}\frac{\partial^2}{\partial \phi^2}$$

Coulomb potential $V(r) = -\frac{Ze^2}{r} \Rightarrow -\frac{Z}{r}$ (in a.u.)

$$= \frac{2Z}{\eta + \xi}$$

T.I.S.E. $\left(-\frac{1}{2}\nabla^2 - \frac{2Z}{\xi + \eta}\right)\psi(\xi, \eta, \phi)$

$$= -E_b \psi(\xi, \eta, \phi)$$

Separation Ansatz: $\psi(\xi,\eta,\phi) = f(\xi)\,g(\eta)\,\underbrace{e^{im\phi}}_{\uparrow \text{usual } L_z \text{ eigenfunction}}$

$$-\frac{2}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial f}{\partial\xi}\right)g(\eta) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial g}{\partial\eta}\right)f(\xi)\right] \pm \frac{m^2}{2\xi\eta} f(\xi)g(\xi)$$

$$-\frac{2Z}{\eta+\xi} f(\xi)g(\eta) \quad = \quad -E_b f(\xi) g(\eta)$$

$$\underbrace{\frac{1}{f(\xi)}\frac{d}{d\xi}\left(\xi\frac{df}{d\xi}\right) - \left(\frac{1}{2}E_b\xi + \frac{m^2}{4\xi}\right)}_{\text{only depends on } \xi} + \underbrace{\frac{1}{g(\eta)}\frac{d}{d\eta}\left(\eta\frac{dg}{d\eta}\right) - \left(\frac{1}{2}E_b\eta + \frac{m^2}{4\eta}\right)}_{\text{only depends on } \eta} = -Z$$

(constant independent of ξ or η)

In the usual way, the two terms must each be set equal to a "separation constant".

(ξ term) $\equiv -\nu_1$, (η term) $\equiv -\nu_2$

so that $\nu_1 + \nu_2 = Z$

The equations for the ξ and η wave equation thus have exactly the same form

$$\boxed{\frac{d}{d\xi}\left(\xi\frac{df}{d\xi}\right) - \left(\frac{1}{2}E_b\xi + \frac{m^2}{4\xi}\right)f(\xi) + \nu_1 f = 0}$$

And same for g with $\xi \to \eta$, $\nu_1 \to \nu_2$

Solution: As for the radial eq. in spherical coordinates, we make an ansatz that takes into account the short range and asymptotic behavior.

Solution: $f(\xi) = e^{-\beta\xi}(\beta\xi)^{|m|/2} L^{|m|}_{n_1+|m|}(\beta\xi)$

$g(\eta) = e^{-\beta\eta}(\beta\eta)^{|m|/2} L^{|m|}_{n_2+|m|}(\beta\eta)$

↑ associated Laguerre poly.

where $\beta = \sqrt{2E_b}$, $n_i = \frac{\nu_i}{\beta} - \frac{1}{2}(|m|+1) = 0, 1, 2, \ldots$

Constraint $\nu_1 + \nu_2 = Z$

$\Rightarrow n_1 + n_2 = \frac{Z}{\sqrt{2E_b}} - |m| - 1$

$\Rightarrow \boxed{E_b = \frac{Z^2}{2(n_1+n_2+|m|+1)^2}}$

Degeneracy: Binding energy depends only on sum

$\Rightarrow$ Principle quantum number $n \Rightarrow E_b = \frac{Z^2}{2n^2}$

$\boxed{n = n_1 + n_2 + |m| + 1}$

For a given n, and fixed $|m| < n$:

there are $n - |m|$ different pairs of parabolic quantum #s n_1, n_2. Two choices $m = \pm|m| \neq 0$

there are n different choices when $|m| = 0$.

$\Rightarrow$ Total # of state = $\underbrace{n}_{\text{states with } m=0} + \underbrace{2\sum_{|m|=1}^{n-1}(n-|m|)}_{\text{states with } m\neq 0}$

$= n + 2\left[n(n-1) - \frac{n(n-1)}{2}\right]$

$= n^2$ as expected