Physic 531: Atomic Physics

Lecture 1: Overview

Structure of Matter? "Reductiveist 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: Fingerprints 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: Quantum mechanical 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 is 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 \( m_e = 9.11 \times 10^{-28} \text{ g} = 0.511 \text{ MeV} / c^2 \)
- charge \( e = 4.8 \times 10^{-10} \text{ esu} = 1.6 \times 10^{-19} \text{ Coul} \)

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

- action \( \hbar = 1.055 \times 10^{-27} \text{ erg} \cdot \text{s} \)
  \[= 1.055 \times 10^{-34} \text{ J} \cdot \text{s} \]
  \[= 1974 \text{ eV} \cdot \text{A} / \text{c} \]
Let \( a_c = \text{Characteristic length scale} \)

\[ p_c = \frac{\hbar}{a_c} \]

\[ E_c = \frac{p_c^2}{m_e} = \frac{\hbar^2}{m_e a_c^2} \]

Using Coulomb force \( \Rightarrow E_c = \left[ \frac{1}{9\pi\epsilon_0} \right] \frac{e^2}{a_c} \]

In cgs \( \Rightarrow 1 \)

\[ a_c = \frac{\hbar^2}{m_e e^2} = a_0 \approx 0.5 \AA \quad \text{Bohr radius} \]

\[ E_c = \frac{m_e e^4}{\hbar^2} = 2 \text{Rydberg} \approx 27.2 \text{eV} = 1 \text{hartree} \]

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

\[ \hat{H} = \frac{\hat{p}_N^2}{2M_N} + \frac{\hat{p}_e^2}{2m_e} - \frac{Ze^2}{r} \quad (\text{ignoring relativistic corrections}) \]
Separate in center-of-mass, relative coordinates

\[ \hat{H} = \hat{H}_{\text{cm}} + \hat{H}_{\text{free}} \]

\[ \hat{H}_{\text{cm}} = \frac{\hat{p}^2}{2M} \quad M = m_e + m_N \quad \text{(total mass)} \]

describing binding

\[ \hat{H}_{\text{rel}} = \frac{\hat{p}^2}{2\mu} - \frac{Ze^2}{r} \quad \mu = \frac{m_em_N}{m_e + m_N} \]

Typically ignore reduced mass correction \(\Rightarrow \quad q_c = \frac{\hbar^2}{2\mu e^2} = \frac{q_a}{Z} \quad (E_c = Ze^2(E_{\text{Hor}}) \}

Characteristic scale

\[ E_c = \frac{Ze^2}{a_c} \quad a_c = \frac{\hbar^2}{2\mu e^2} = \frac{q_a}{Z} \]

Bound State Solutions

\[ \hat{H}_{\text{rel}} | \Psi \rangle = -E_{\text{bind}} | \Psi \rangle \]

ignore total \( E_{\text{bind}} \) = binding energy \( \text{(positive #)} \)

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

Potential has rotational symmetry

\[ [\hat{H}, \hat{L}_z^2] = 0 \quad [\hat{H}, \hat{L}_z] = 0 \]

Complete set of commuting observables

\[ \{\hat{H}, \hat{L}_z^2, \hat{L}_z\} = 3 \]
Kinetic energy: Sum of radial and angular motion
\[ \hat{T} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{l}^2}{2\mu r^2} \]

\[ \hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{l}^2}{2\mu r^2} + \hat{V}(r) \]

Since \( \hat{H} \) has no explicit dependence on \( \hat{L}_z \),

**essential degeneracy** \( \Rightarrow \) At least \( 2l+1 \), for given \( l \)

Wave function representation
\[ \Psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi) \]
(Separate in spherical coords)

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

Define "reduced" radial wave function \( U(r) = r \ R(r) \)

\[ \left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} U(r) + V_{\text{eff}} U(r) = -E_{\text{bind}} \ U(r) \right\} \]

Radial equation = 1D Schrödinger eq on the half-line \( 0 \leq r < \infty \) with effective potential \( V_{\text{eff}} = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \) < center of barrier

Bound states \( \Rightarrow n_r \) nodes \( \Rightarrow U_{n_r, l}^m(r) \)
Because we are on the half line, we have an extra boundary condition at origin.

\[ U(r) \sim r^{l+1} \Rightarrow U(0) = 0 \]

(Like hard wall)

Note \( R_{\ell}(r) = \frac{U_{\ell}(r)}{r} \Rightarrow R_{\ell}(0) = 0 \ \forall \ell \) except \( \ell = 0 \Rightarrow s\)-state big at origin

Coulomb, one electron atom

\[
V_{\text{eff}}^{(l)} = V_{\text{central}} - \frac{Z e^2}{r}
\]

\[
-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} U_{n\ell}(r) + \left( \frac{k^2 l(l+1)}{2\mu r^2} - \frac{Z^2 e^2}{r} \right) U_{n\ell} = -E_{\text{bind}} U_{n\ell}(r)
\]

Make dimensionless in characteristic units

\[ x = \frac{r}{a_c}, \quad \epsilon = \frac{E_{\text{bind}}}{a_c} \]

\[
\Rightarrow -\frac{1}{2} \frac{d^2}{dx^2} U(x) + \left( \frac{1}{2x^2} - \frac{1}{x} \right) U(x) = -\epsilon U(x)
\]

Asymptotic: As \( x \to \infty \) \( U_e(x) \Rightarrow A e^{-\frac{Z^2 e}{\epsilon x}} \)

\[ x \to 0 \quad U_e(x) \to x^{l+1} \]
\[
\Rightarrow \text{Ansatz: } \psi_l(x) = x^{l+1} e^{-\sqrt{2}e^{-1} x} \frac{\Gamma(\ell)}{\Gamma(\ell+1)} f_\ell(x)
\]
\[
\Rightarrow x f''_\ell + 2(\ell + 1 - \sqrt{2}e^{-1} x) f'_\ell + 2(1 - \sqrt{2}e^{-1} (x+1)) f_\ell(x) = 0
\]

Hypergeometric diff eq \Rightarrow Discrete solutions

\[
\Rightarrow n_r = \frac{1}{2} - l - 1 \quad \text{(no nodes)}
\]

\[
\Rightarrow E_n = \frac{1}{n_r + \ell + 1} \quad \text{Dimensionless binding energy}
\]

"Accidental degeneracy"

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

\Rightarrow Define "principle \(q\)-\#"

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

\[
\Rightarrow E_n = \frac{1}{2n^2} \quad \text{with dimensions}
\]

\[
E = -\frac{\frac{\pi^2}{3}}{2n^2} E_0 = -\frac{\frac{\pi^2}{3}}{n^2} \frac{1}{R}
\]

Spectrum

\[
\begin{array}{c|c|c|c}
\ell \leq 0 & \ell = 1 & \ell = 2 & n = 3 \\
\hline
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{3}{2} \\
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{3}{2} \\
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{3}{2} \\
\end{array}
\]

\[
\Rightarrow \text{\# of bound state}
\]

\[
\Rightarrow \Delta E \text{ gets smaller near } E = 0
\]

\[
\Rightarrow \text{Large } n \Rightarrow \text{Rydberg series}
\]

\[
\Rightarrow \text{Given } n \Rightarrow \ell = 0, 1, \ldots, n-1
\]

\[
\Rightarrow \text{Degeneracy } \ell = 0, 1, \ldots, n-1
\]

\[
\Rightarrow G_n = \sum_{\ell=0}^{n-1} n^2 = n^2
\]
Eigenfunction:
\[ f_{nlm}(\chi) = A_{nl} F_l \left(-n_r, 2l+2, \frac{2}{n} \chi\right) \]
\[ = C_{nl} L^{2l+1} \left(\frac{2}{n} \chi\right) \]
\[ \text{normalization} \quad \text{Associate Laguerre Polynomial} \]

Putting it all together:
\[ \Psi_{n,r,m}(r, \theta, \phi) = \frac{U_{nlm}(r)}{r} Y_{l,m}(\theta, \phi) \]
\[ = C_{nl} \left(\frac{2r}{a_0}\right)^l e^{-\frac{2r}{a_0}} L^{2l+1}_{n-l-1} \left(\frac{2z}{n a_0}\right) Y_{l,m}(\theta, \phi) \]

Probability distribution:
\[ |\Psi|^2 d^3x = |\Psi(r, \theta, \phi)|^2 r^2 dr d\Omega \]
\[ = r^2 |R_{nlm}(r)|^2 dr \quad |Y_{l,m}(\theta, \phi)|^2 d\Omega \]

Radial density: \[ |U_{n}^2| \]
Angular densities: \[ |Y_{l,m}^2| \]
Accidental degeneracy = NO!

The fact the energy levels depend only on \( n \) and not \( n' \) and \( l \) independently is no accident, but a result of another symmetry, unique for potentials \( V(r) = -\frac{k}{r} \).

This is well known from classical mechanics. Typically for central potential trajectory "processes",

\[
V(r) = -\frac{k}{r}
\]

New conserved quantity (originally introduced by Lopud)

\[
\vec{A} = \frac{1}{m} (\vec{L} \times \vec{p}) + \frac{k\vec{r}}{r}
\]

Quantum mechanical \( \Rightarrow \) Operator

\[
\frac{\hat{A}}{\hat{A}} = \frac{1}{m} \left( \frac{\hat{L} \times \hat{p}}{2} - \frac{\hat{p} \times \hat{L}}{2} \right) + \frac{\hat{r}}{r}
\]

\[\uparrow \text{Commuted with Hamiltonian} \]

\[\Rightarrow \text{New conserved quantities} \]

\[\Rightarrow \text{New symmetries} \]

Related to rotation in 4D

\[\Rightarrow SO(4) \text{ symmetry (see homework)} \]
The existence of another symmetry due to potential

⇒ Another complete set of commuting operators
to specify eigenstates of Hamiltonian

\[ \hat{H}, \hat{r}z, \hat{L}_z \]

Note: \([\hat{r}z, \hat{L}_z] \neq 0 \quad \Rightarrow \quad l \text{ no longer a good quantum number}

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

⇒ Parabolic coordinates

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

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

In this coordinate system:

\[ \frac{d^2}{(\xi + \eta)} \frac{d}{d\xi} \frac{d}{d\eta} \frac{d^2}{d\phi^2} \]

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

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

T.I.S.E.

\[ \left( -\frac{1}{2} \frac{\nabla^2}{\xi + \eta} + \frac{1}{2} \right) \psi(\xi, \eta, \phi) = \frac{-E_\ell}{\xi + \eta} \psi(\xi, \eta, \phi) = -E_\ell \psi(\xi, \eta, \phi) \]
Separation Ansatz: \( \Psi(\xi, \eta, \phi) = f(\xi) g(\eta) e^{im\phi} \)

\[ \frac{\partial ^2}{\partial \eta^2} \left( \eta \frac{\partial}{\partial \eta} \right) g(\eta) + \frac{\partial ^2}{\partial \xi^2} f(\xi) \right] = \frac{\hbar^2}{2m} \left( \frac{\partial ^2}{\partial \xi^2} f(\xi) + \frac{\partial ^2}{\partial \eta^2} g(\eta) \right) \]

\[ - \frac{2 \alpha}{\eta + \xi} f(\xi) g(\eta) = -E_\eta f(\xi) g(\eta) \]

\[ \frac{d^2}{d\xi^2} \left( \xi \frac{d}{d\xi} \right) - \left( \frac{1}{2} E_\xi \xi + \frac{m^2}{4\xi} \right) + \frac{1}{2} \frac{d}{d\eta} \left( \eta \frac{d}{d\eta} \right) = - (\frac{1}{2} E_\eta + \frac{m^2}{4\eta} ) \]

only depends on \( \xi \)

only depends on \( \eta \)

\[ = - \Omega \] (constant independent of \( \xi \) or \( \eta \))

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

(\( \xi \) term) \( \equiv - \Omega_1 \)

(\( \eta \) term) \( \equiv - \Omega_2 \)

so that \( \Omega_1 + \Omega_2 = \Omega \)

The equations for the \( \xi \) and \( \eta \) wave equation thus have exactly the same form

\[ \frac{d}{d\xi} \left( \xi \frac{df}{d\xi} \right) - \left( \frac{1}{2} E_\xi \xi + \frac{m^2}{4\xi} \right) f(\xi) + \Omega_1 f = 0 \]

And same for \( g \) with \( \xi \rightarrow \eta \), \( \Omega_1 \rightarrow \Omega_2 \)

Solution: As for the radial eq. in spherical coordinates, we make an ansatz that takes into account the short range and asymptotic behavior.
Solution: \( f(\xi) = e^{-\beta \xi} (\beta \xi)^{1m/2} \sum_{n,1m}^{1m} \left( \beta \xi \right) \)

\( g(\eta) = e^{-\beta \eta} (\beta \eta)^{1m/2} \sum_{n,1m}^{1m} \left( \beta \eta \right) \)

where \( \beta = \sqrt{2E_b} \), \( n = \frac{\nu_s}{\beta} - \frac{1}{2} \left( 1m + 1 \right) = 0,1,2, \ldots \)

Constraint \( \nu_1 + \nu_2 = 1 \)

\[ \Rightarrow n_1 + n_2 = \frac{1}{\sqrt{2E_b}} - 1m - 1 \]

\[ \Rightarrow E_b = \frac{1}{2} \frac{\nu_s^2}{2(n_1 + n_2 + 1m + 1)^2} \]

Degeneracy: Binding energy depends only on sum \( n = \sum_{i=1}^{n} \frac{\nu_s}{\beta} - \frac{1}{2} \left( 1m + 1 \right) \)

Principal quantum number \( n = n_1 + n_2 + 1m + 1 \)

For a given \( n \), and fixed \( 1m < n \),

- There are \( n - 1m \) different pairs of parabolic quantum \( n_1, n_2 \),
- Two choices \( \delta m = \pm 1m \neq 0 \),
- There are \( n \) different choices \( 1m = 0 \).

\[ \Rightarrow \text{Total \# of state} = \sum_{1m=1}^{n} \left( n - 1m \right) \sum_{m=0}^{n-1} 2 \]

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

\[ = n^2 \quad \text{as expected} \]