1.) Introduction

A) Short overview + historical review

i) Spectrum of atomic Hydrogen

- elements (e.g. H) have spectral "fingerprint" → test by eye, prism, spectrophotometer

- 1888: Rydberg found for H

\[ \bar{v} = \frac{1}{\lambda} = \frac{1}{R} \left( \frac{1}{n^2} - \frac{1}{n'^2} \right) \]

with integer numbers \( n, n' \), \( R \) constant

(\( \bar{v} \) : "wavenumber")

"Rydberg constant"

- series with \( n = 2, n' \geq 3 \) "Balmer"

\( n = 3, n' \geq 4 \) "Paschen" (visible)

\( n = 1, n' \geq 2 \) "Lyman"

Why important?

→ discrete!

→ they add up (also good for deduction
of spectra)

i) Bohr's theory (1913)

- known: small nucleus with positive charge (Rutherford)
- negative "cloud"
  
  $\rightarrow$ bound by Coulomb force $(e^2 / r^2)$

- Bohr: assumed discrete energy levels!

- Idea of quantization:

  Orbits of $e^-$

  \[
  \frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r} \Rightarrow \omega^2 = \frac{e^2}{4\pi\varepsilon_0 m_e r^3}
  \]

  (like Kepler)

  $\Rightarrow E = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{2 \varepsilon_0} \frac{e^2}{4\pi\varepsilon_0 r} \rightarrow$ Virial theorem

- Assumption: certain allowed orbits for $e^-$ when it does not lose energy unless it moves between orbits

  They are given by quantized angular momentum:

  \[
  (2) \quad \sqrt{m_e v \cdot r} = n \pi \theta \quad \text{n: integer}
  \]

  $\rightarrow$ constant (Plank's)
\[ R_{\text{allowed}} = a_0 \, n^2 \]

with \( a_0 = \frac{k^2}{e^2/4\pi\epsilon_0 mc^2} \) \( \text{Bohr radius} \)

\[ R_n = R_\infty \frac{M_N}{M_N + mc^2} \]

(Note: In order to find (2), Bohr made a second assumption: With the correspondence principle, for large \( n \) the quantum system would have to behave the same as a classical one.)

iii) Relativistic effects

Circular orbits: once simplified =\( \rightarrow \) elliptic!

(Scannenfeld)

\[ (2) \rightarrow \left| \frac{1}{m_e} \mathbf{v} \times \mathbf{r} \right| = n \hbar \]

Elliptic orbits: for same \( n \) different velocities =\( \rightarrow \) relativity plays a role.

\[ E(v) = \gamma mc^2 \quad (\gamma = \sqrt{1 - \frac{v^2}{c^2}}) \]
\[ \Delta E = E(2) - E(0) = (8-1) m_e c^2 \]
\[ \Rightarrow \frac{\Delta E}{E} \propto \frac{2^2}{c^2} \frac{1}{n(1)} \frac{1}{n(2)} = \left( \frac{\alpha}{n} \right)^2 \]
\[ \alpha = \frac{e^2}{4\pi\varepsilon_0} \approx \frac{1}{137} \text{ "fine structure constant"} \]

10) Atomic number \( Z \)

Moseley (-1913): X-ray spectra

Found: \( \sqrt{\nu} \propto Z \) (cf. graphs on 1-5)

(\( \nu \): frequency)

Assume: "shells" with certain number of available spaces

\[ \begin{align*}
  n = 1 & \rightarrow 2 \quad \text{(K shell)} \\
  n = 2 & \rightarrow 8 \quad \text{(L : : :)} \\
  n = 3 & \rightarrow 18 \\
\end{align*} \]

Moseley bombarded samples with accelerated \( e^- \) to knock \( e^- \) out of shell, some other \( e^- \) falls down as radiation

\[ \text{Theory: 1e}^- + \text{nucleus of charge } Z \]

\[ \Rightarrow \text{replace } \frac{e^2}{4\pi\varepsilon_0} \text{ by } \frac{2e^2}{4\pi\varepsilon_0} \]
from C. Foot (book no 5.)

Wavelength $\times 10^8$ cm

Square root of frequency $\times 10^{-8}$

had elec vac high wav

Th of a ch in a of $\varepsilon$

for to $\varepsilon$

Bol one elec stra
\[ V = R \left( \frac{(2-\delta^2)}{m^2} - \frac{(2-\delta^2)}{m^2} \right) \]

\( \delta^2 \): screening

\[ V \propto Z^2 \]

But: Moreley's curves have strong substructure for same \( n \):

\[ \frac{e^2}{4\pi\varepsilon_0} \rightarrow \frac{2e^2}{4\pi\varepsilon_0} \]

\[ \Rightarrow \quad \alpha \rightarrow 2\alpha \]

\[ \Rightarrow \Delta E_{\text{rel}} \propto (2\alpha)^2 \quad \text{Energetic} \]

\[ \alpha (2\alpha)^2 \quad \text{Energetic, } z=1, 2^2 \times 2^4 \]

\[ \Rightarrow \text{Very strong fine structure!} \]

v) Einstein A and B coefficients

S pertinent: 2-level atom:

- \( E_1, g_1, N_1 \) energy
- \( E_2, g_2, N_2 \) degeneracy

- Interaction with radiation with energy density \( g(\nu) \)
- Assumption: interaction only with radiation of \( \omega = \omega_{12} = \frac{E_2 - E_1}{h} \)

- Processes:

  - Transition \( 1 \rightarrow 2 \)
    \[ \alpha \propto g(\omega_{12}) \propto N_2 \]  
    proportionality constant \( B_{12} \)

  - Transition \( 2 \rightarrow 1 \) (stimulated)
    \[ \alpha \propto g(\omega_{12}) \propto N_2 \]  
    \( B_{21} \)

  - Spontaneous emission \( 2 \rightarrow 1 \)
    \[ \alpha \propto N_2 \]  
    \( A_{21} \)

- Rate equation:

  \[
  \frac{dN_2}{dt} = N_1 g(\omega_{12}) B_{12} - N_2 g(\omega_{21}) B_{21} - N_2 A_{21}
  \]

  \[
  \frac{dN_1}{dt} = - \frac{dN_2}{dt}
  \]

1) No light \( \Rightarrow g(\omega_{12}) = 0 \)

\[ \Rightarrow N_2(t) = N_2(0) e^{-A_{21}t} \]

\[ A_{21} = \frac{1}{\tau} \]

Lifetime
2) Black body radiation:

\[ S(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \quad \text{(Planck)} \]

Equilibrium: \[ \frac{dN_2}{dt} = 0 \]

\[ -i \partial S(\omega, t) = A_{21} \frac{1}{B_{12}} \frac{N_1/N_2}{B_{12}/B_{21}} - 1 \]

\[ \text{Boltzmann} = \frac{N_2}{N_1} = \frac{N_1}{N_2} e^{-\frac{\hbar \omega}{k_B T}} \]

3) A, B coefficients are assumed for any radiation (broadband, narrow band, no rad, black body...)

\[ A_{21} = \frac{5 \omega^3}{\pi^2 c^3} B_{21} \]

\[ B_{12} = \frac{5 \omega^2}{g_2} B_{21} \]
vi) 

Zeeman effect

- Add magnetic field

- Assume: \( \mathbf{e}^{-}(\mathbf{v} \pm \mathbf{B}) \) field like harmonic oscillator

\[ m_e \ddot{\mathbf{r}} = -m_e \omega^2 \mathbf{r} - e \mathbf{v} \times \mathbf{B} \]

Assume \( \mathbf{B} \parallel \mathbf{v} \) = 1

\[ \mathbf{r}'' + 2 \Omega \mathbf{L} \times \mathbf{r} + \omega^2 \mathbf{r} = 0 \]

\( \omega / \Omega = \frac{eB}{2mc} \) "Larmor frequency"

\( \omega / \text{ansatz} \quad \mathbf{r} = \mathbf{r}_0 \ e^{-i\omega t} \)

\( \Rightarrow \) eigenvectors

\[ \mathbf{r}_1 = \begin{pmatrix} \cos (\omega t - \Omega t) \\ -\sin (\omega t - \Omega t) \end{pmatrix}, \quad \mathbf{r}_2 = \begin{pmatrix} 0 \\ \cos \omega t \end{pmatrix}, \quad \mathbf{r}_3 = \begin{pmatrix} (\cos (\omega t + \Omega t)) \\ \sin (\omega t + \Omega t) \end{pmatrix} \]

left polarized, linear, right polarized

\( \Rightarrow \)

transverse

\( \Rightarrow \)

longitudinal
3) Units

Usually:

<table>
<thead>
<tr>
<th>m (mass)</th>
<th>l (length)</th>
<th>t (time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg</td>
<td>m</td>
<td>s</td>
</tr>
<tr>
<td>g</td>
<td>cm</td>
<td>s</td>
</tr>
</tbody>
</table>

are distinct units

- However, taking, e.g., the speed of light \( c = 299,792,458 \, \text{m/s} \) as given, either \( l \) or \( t \) becomes redundant as an independent unit.

- Numerical values \( 299,792,458 \, \text{m/s} \)
  of any natural/fundamental constant depend on our choice of units, and are therefore arbitrary.

\( \Rightarrow \) any value could be chosen as a reference.

Atomic units

Set \[ \hbar = e = m_c = 1 \] (see 1.11)
Atomic Units and Their SI Equivalents

We will for the most part use SI units in this course. However, be aware that many graduate texts still use the gaussian unit system, because the electromagnetic field equations are somewhat more symmetric than in SI units. A third system of units is also useful—from time to time, we will lapse into the “theorist’s units” appropriate to atomic physics, making many uninteresting constants disappear by setting them equal to unity.

The system of atomic units is defined by the following (dimensions given in square brackets):

\[
\begin{align*}
\hbar &= 1 \text{ [E \cdot t or m \cdot \ell^2 \cdot t^{-1}]} \\
\mu &= 1 \text{ [m]} \\
e &= 1 \text{ [m}^{-1/2} \cdot \ell^{3/2} \cdot t^{-1}]
\end{align*}
\]

The atomic units for other common physical quantities are given below:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit ((K=1/4\pi\varepsilon_0))</th>
<th>SI equivalent</th>
<th>Name or Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>(e = 1)</td>
<td>(1.602 \times 10^{-19} \text{ C})</td>
<td>electron charge</td>
</tr>
<tr>
<td>Angular Momentum</td>
<td>(\hbar = 1)</td>
<td>(1.05 \times 10^{-34} \text{ J\cdotsec})</td>
<td>“h-bar”</td>
</tr>
<tr>
<td>Mass</td>
<td>(m_e = 1)</td>
<td>(9.11 \times 10^{-31} \text{ kg})</td>
<td>electron mass</td>
</tr>
<tr>
<td>Length</td>
<td>(a_0 = \frac{\hbar^2}{m_eK^2} \approx 1)</td>
<td>(5.29 \times 10^{-11} \text{ m})</td>
<td>Bohr or “atomic unit”</td>
</tr>
<tr>
<td>Velocity</td>
<td>(K e^2/h \approx c \alpha = 1)</td>
<td>(2.188 \times 10^6 \text{ m/sec})</td>
<td>velocity in first Bohr orbit</td>
</tr>
<tr>
<td>Time</td>
<td>(\frac{\hbar^2}{m_eK^2e^4} \approx 1)</td>
<td>(2.419 \times 10^{-17} \text{ s})</td>
<td>(1/\omega) for first Bohr orbit</td>
</tr>
<tr>
<td>Energy</td>
<td>(m_eK^2e^4/h^2 \approx 1)</td>
<td>(4.36 \times 10^{-18} \text{ J}) or (219474 \text{ cm}^{-1})</td>
<td>Hartree (= 2 Rydbergs)</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>(\mu = \frac{eh}{2m_e} \approx 1/2)</td>
<td>(1.400 \times 10^{10} \text{ Hz\cdotTesla (times h)})</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>Electric field</td>
<td>(K e/a_0^2 \approx 1)</td>
<td>(5.142 \times 10^{11} \text{ V/m})</td>
<td>Internal field of H atom</td>
</tr>
</tbody>
</table>

The fine structure constant is given by \(\alpha = \frac{K e^2}{\hbar c} = 1/137.036\), so in atomic units, the speed of light is \(c = 1/\alpha\).

Also very useful: The wavenumber or “inverse centimeter” is very often used as an energy unit in spectroscopy; what one means by this is:

\[
1 \text{ cm}^{-1} = \frac{\hbar c}{\lambda} \text{ with } \lambda = 1 \text{ cm}
\]

\[
= 1.98658 \times 10^{23} \text{ J}
\]

\[
= 2.99792458 \times 10^{19} \text{ Hz (exactly)}
\]

\[
= 1/8065.02 \text{ eV}
\]

(by E. Eyler)
Gaussian units

use cgs, + Gaussian gauge

e.g. Coulomb force:

\[ F = \alpha_{\text{e.m.}} \frac{q_1 q_2}{r_{12}^2} \]

Ampère's law:

\[ \mathbf{B} = \frac{1}{2} \mathbf{A} \cdot \mathbf{\beta}_{\text{e.m.}} \]

SI:

\[ \lambda_{\text{e.m.}} = \frac{1}{4\pi\varepsilon_0} \quad \mathbf{\beta}_{\text{e.m.}} = \frac{\mu_0}{2\pi} = 2 \times 10^7 \frac{N}{A^2} \]

Gaussian:

\[ \lambda_{\text{e.m.}} = 1 \quad \Rightarrow \quad \mathbf{\beta}_{\text{e.m.}} = \frac{2}{c^2} \]

(for \( \frac{1}{\varepsilon_0 c^2} = c^2 \))

(cf. Back of Jackson)

C) RESIDUES OF QUANTUM MECHANICS

States: Complete knowledge of system resides in \( |\psi\rangle \in \mathcal{H} \) (Hilbert space)

\[ |\psi\rangle = \sum_{n} c_n |n\rangle \langle n | \psi \rangle \] \( \{ |n\rangle \} \) : orthogonal normal basis
Probability of finding system in \( |m\rangle \):
\[
P_m = |c_m|^2
\]

Superposition/interference

Assume:
\[
|14,\rangle = \sum_m |m\rangle c_m^{(1)}
\]
\[
|14_2\rangle = \sum_m |m\rangle c_m^{(2)}
\]

\[
P_m \propto \frac{1}{\sqrt{2}} \left( |14,\rangle + |14_2\rangle \right)
\]

\[
P_m = \frac{1}{2} |c_m^{(1)} + c_m^{(2)}|^2
\]

(rather than \( \frac{1}{2} (|c_m^{(1)}|^2 + |c_m^{(2)}|^2) \))

Observables

\(\hat{\sigma}\) is observable if

\[
\langle 4_1 \hat{\sigma} 4_2 \rangle = (\langle 4_2 \hat{\sigma} 4_1 \rangle)^* = \langle \hat{\sigma} \rangle = \langle 4 \hat{\sigma} 4 \rangle
\]

\(\hat{\sigma}\) diagonal in basis \( |m\rangle \),

\[
\hat{\sigma} |m\rangle = O_m |m\rangle
\]

\[
P_m = \sum_n O_m |c_n|^2 = \sum_n O_m p_m
\]
**Uncertainty Principle**

Assume \( [\hat{A}, \hat{B}] = i\hat{C} \)

\( \hat{A}, \hat{B} \) don't commute if \( \hat{C} \neq 0 \)

Heisenberg:

\[
\Delta \hat{A} \Delta \hat{B} = \frac{i}{2} \langle \hat{C} \rangle
\]

**Time Evolution**

- Schrödinger picture:
  \[ |\psi(t)\rangle = e^{\frac{it\hat{H}}{\hbar}} |\psi(0)\rangle \]

Stationary solutions:

\[ E_n |\psi_n\rangle = \hat{H} |\psi_n\rangle \]

\[ |\psi\rangle = \sum_n c_n |\psi_n\rangle \]

General:

\[ |\psi(t)\rangle = U(t) |\psi(0)\rangle \]

with 'evolution operator'

\[ U(t) = e^{\frac{it\hat{H}}{\hbar}} \]

- Heisenberg picture:
  \[ \hat{\psi}(t) = \text{const.} \]
  \[ \hat{\psi} = \hat{\psi}(t) \]
\[ i \hbar \frac{\partial}{\partial t} \tilde{\mathcal{O}}(t) = [\tilde{\mathcal{O}}, \hat{H}] \]

**Interaction picture**

\[ H = H_0 + \hat{\mathcal{H}}_I \]

\[ |4z\rangle = e^{\frac{i}{\hbar} \frac{\mathcal{N}_0}{k}} |4z\rangle \]

\[ = 0 \quad i \hbar \frac{\partial}{\partial t} |4z\rangle = -\hat{V}_I |4z\rangle \]

with

\[ \hat{V}_I = e^{\frac{i}{\hbar} \frac{\mathcal{N}_0}{k}} \hat{A}_I e^{-\frac{i}{\hbar} \frac{\mathcal{N}_0}{k}} \]

and

\[ i \hbar \frac{\partial}{\partial t} \tilde{\mathcal{O}} = [\tilde{\mathcal{O}}, \hat{H}_0] \]

always

\[ \langle \tilde{\mathcal{O}} \rangle = \langle y | \langle 0 | \hat{Y} | 0 \rangle | y \rangle \]