VI. Atomic Structure

A. Hamiltonian

- Charge in an EM field
- Semi-classical theory of radiation
  - ◇ Relativistic theory
    - ▲ Need annihlation and creation operators for photons
    - ▲ Virtual particles, etc.
- Lagrangian (ansatz)

$$L = -mc^2\sqrt{1 - v^2/c^2} + \frac{e}{c}\vec{v}\cdot\vec{A} - e\phi \tag{1}$$

  - ◇ Non-relativistic limit ($v \ll c$)
  - ◇ $L \to \frac{1}{2}m|\dot{\vec{r}}|^2 - e\phi + \frac{e}{c}\dot{\vec{r}}\cdot\vec{A}$
- Verify this ansatz by considering Lagrange's Equation

$$\frac{d}{dt}\frac{\partial L}{\partial\dot{\vec{r}}} = \frac{\partial L}{\partial\vec{r}} \tag{2}$$

$$\begin{aligned}
\left(\frac{\partial L}{\partial\vec{r}}\right)_{t,\dot{\vec{r}}} &= -e\nabla\phi + \frac{e}{c}\nabla(\dot{\vec{r}}\cdot\vec{A}) \\
&= -e\nabla\phi + \frac{e}{c}\left[\dot{\vec{r}}\times(\nabla\times\vec{A}) + (\vec{r}\cdot\nabla)\vec{A}\right] \\
\left(\frac{\partial L}{\partial\dot{\vec{r}}}\right)_{\vec{r},t} &= m\dot{\vec{r}} + \frac{e}{c}\vec{A} \\
\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{\vec{r}}}\right) &= m\ddot{\vec{r}} + \frac{e}{c}\left[\frac{\partial\vec{A}}{\partial t} + \dot{\vec{r}}\cdot\nabla\vec{A}\right]
\end{aligned}$$

  - ◇ Equating and cancelling terms

$$m\ddot{\vec{r}} = e\left(\vec{E} + \frac{\dot{\vec{r}}}{c}\times\vec{B}\right) \tag{3}$$

    - ▲ $\vec{E} = -\nabla\phi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}$
    - ▲ Lorentzian force
    - ▲ This ansatz is correct! (of course)
- Gauge

- $\diamond$ Recall, $\vec{E}, \vec{B}$ are unmodified if

$$\vec{A}' = \vec{A} + \nabla\Lambda(\vec{r}, t)$$
$$\phi' = \phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t}$$

- $\diamond$ Relativistic problems: Impose the Lorentz condition

$$\nabla \cdot \vec{A} + \frac{1}{c}\frac{\partial \phi}{\partial t} = 0 \tag{4}$$

  - ▲ Simplify Maxwell's equations
  - ▲ 4-vector formalism of relativity is satisfied
- $\diamond$ Coulomb gauge (our case)
  - ▲ Non-relativistic motions
  - ▲ Radiation field
  - ▲ Static charge distribution $\rho_c(\vec{r})$

$$\nabla \cdot \vec{A} = 0 \tag{5}$$

- What if $\vec{A}$ does not satisfy our condition?
  - $\diamond$ Let $A' = A + \nabla\Lambda$ where $\nabla^2\Lambda = -\nabla \cdot \vec{A}$ (i.e. $\nabla \cdot \vec{A}' = 0$)
  - $\diamond$ Consider $\nabla^2\phi'$

$$\nabla^2\phi' = \nabla^2\phi - \frac{1}{c}\frac{\partial}{\partial t}\left(-\nabla \cdot \vec{A}\right) \tag{6}$$
$$= -\nabla \cdot \vec{E} \tag{7}$$
$$= 4\pi\rho_c \tag{8}$$

$$\Rightarrow \ \phi'(\vec{r}) = \int d^3\vec{r}\,'\,\frac{\rho_c(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \tag{9}$$

- Implications of $\nabla \cdot \vec{A}' = 0$

$$\nabla^2\vec{A}' = -\nabla \times (\nabla \times \vec{A}')$$
$$= -\nabla \times \vec{B}$$
$$= -\frac{1}{c}\frac{\partial \vec{E}}{\partial t} \quad \text{(static charge)}$$

  - $\diamond$ Since $\vec{E} = -\nabla\phi' - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$ and ϕ is static

$$\nabla^2\vec{A} = \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} \tag{10}$$

- ◇ $\vec{A}'$ satisfies a wave equation
- ◇ Identify it with a vacuum radiation field

- Hamiltonian Equation

$$H = \sum \vec{P} \cdot \vec{v} - L \quad \text{where} \quad \vec{P} \equiv \frac{\partial L}{\partial \vec{v}} \tag{11}$$

- ◇ Recall $L = -mc^2\sqrt{1 - v^2/c^2} + \frac{e}{c}\vec{v} \cdot \vec{A} - e\phi$

$$\Rightarrow \ \vec{P} = \gamma m v + \frac{e}{c}\vec{A} \tag{12}$$

- ◇ Hamiltonian

$$H = e\phi + \gamma m c^2 \tag{13}$$

$$= e\phi + \sqrt{\left(\vec{P} - \frac{e\vec{A}}{c}\right)^2 c^2 + m^2c^4} \tag{14}$$

- ▲ Non-relativistic

$$H = \frac{1}{2}mv^2 + e\phi \tag{15}$$

$$= \frac{1}{2m}\left(\vec{P} - \frac{e}{c}\vec{A}\right)^2 + e\phi \tag{16}$$

$$= \frac{P^2}{2m} - \frac{e}{2mc}\left(\vec{P} \cdot \vec{A} + \vec{A} \cdot \vec{P}\right) + \frac{e^2}{2mc^2}A^2 + e\phi \tag{17}$$

- ▲ Valid only for non-rel particles without spin
- ◇ Identify $\vec{P}$ with $-i\hbar\nabla$ and impose the Coloumb gauge

$$\text{Expect} \quad [\vec{P}, \vec{A}] = 0 \tag{18}$$

$$H = \frac{P^2}{2m} - \frac{e}{mc}\vec{P} \cdot \vec{A} + \frac{e^2A^2}{2mc^2} + e\phi \tag{19}$$

B. Hydrogenic Ions

- Potentials
  - ◇ $\phi = -Ze/r$
  - ◇ $\vec{A} = 0$
- Hamiltonian

$$H = \frac{-\hbar\nabla^2}{2m} - \frac{Ze^2}{r} \tag{20}$$

- ◇ Note: ∇^2 and $1/r$ are rotational invariant
- ◇ $\Rightarrow$ $[H, L_i] = [H, L^2] = 0$
- ◇ In spherical coordinates, we have

$$P^2 = \frac{-\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}L^2 \tag{21}$$

- Seek Energy eigenstates of the form (separation of variables)

$$|a\rangle = R_{n\ell}(r)\mathcal{Y}_{\ell m}(\phi, \theta) \equiv |n\ell m\rangle \tag{22}$$

$$H|n\ell m\rangle = E_{n\ell m}|n\ell m\rangle \tag{23}$$

- Introduce Spherical Harmonics (See the Aside on Angular Momentum; A.1)
- Radial Equation
  - ◇ E will be degenerate in ℓ, m (at first)
  - ◇ Therefore

$$\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)R_{n\ell}(r) + \left[E_n - \frac{Ze^2}{r} - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]R_{n\ell}(r) = 0 \tag{24}$$

  - ◇ For a given ℓ, $\quad n = \ell+1, \ell+2, \ell+3, \ldots$
  - ◇ Of course

$$\int_0^\infty dr R^*_{\ell' n'}(r)R_{\ell n}(r) = \delta_{n,n';\ell,\ell'} = \langle n'\ell'|n\ell\rangle$$

  - ◇ Solutions

$$R_{n\ell}(r) = \left[\frac{Z(n-\ell-1)!}{n^2\{(n+\ell)!\}^3}\right]^{\frac{1}{2}} \mathrm{e}^{-\rho/2}\,\rho^{\ell+1}\,\mathcal{L}^{2\ell+1}_{n+1} \tag{25}$$

    - ▲ $\mathcal{L}$: Legendre polynomials
    - ▲ $\rho \equiv 2Zr/n$
    - ▲ Figs
  - ◇ There are also continuous radial eignefucntions corresponding to *unbound* states
- Energies

$$E_n = -\frac{1}{2}\mu c^2\frac{(Z\alpha)^2}{n^2} \tag{26}$$

  - ◇ μ: Reduced mass
  - ◇ $\mu \approx 0.999 m_e$ for H, closer to m_e for higher Z
  - ◇ Hydrogen

- ▲ Ground State: $E_1 = -13.6$ eV
- ▲ 1st Excited State: $E_2 = -3.4$ eV

Lyman Series

Transition	n	$E_n - E_1$ (eV)	λ_{rest} (Å)	λ_{exp} (Å)
Lyα	2	10.200000	1215.6845	1215.6701
Lyβ	3	12.088889	1025.7338	1025.7223
Lyγ	4	12.750000	972.54759	972.5368
Lyδ	5	13.056000	949.75351	949.7431
Lyϵ	6	13.222223	937.81375	937.8035
Ly6	7	13.322449	930.75844	930.7483
Ly7	8	13.387500	926.23580	926.2257
Ly8	9	13.432099	923.16041	923.1504
Ly9	10	13.464000	920.97310	920.9631
Ly10	11	13.487604	919.36139	919.3514
Ly11	12	13.505556	918.13933	918.1294
Ly12	13	13.519527	917.19053	917.1806
Ly13	14	13.530613	916.43908	916.429
Ly14	15	13.539556	915.83374	915.824
Ly15	16	13.546875	915.33891	915.329
Ly16	17	13.552942	914.92921	914.919
Ly17	18	13.558025	914.58616	914.576
Ly18	19	13.562327	914.29604	914.286
Ly19	20	13.566000	914.04849	914.039
Ly∞	∞	13.6	912.6	

- ▲ Difference between λ_{rest} and λ_{exp} is mainly due to spin-orbit coupling (coming soon)
- ▲ Fig (Lyman series at $z = 3$)

- Spin
  - ◇ Electron has angular momentum $s = \hbar/2$
  - ◇ Introduce eigenkets of the S_z operator

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

  - ◇ Quantum number: m_s
  - ◇ Complete state? $|n\ell m m_s\rangle$

C. Many Electrons

- Hamiltonian

$$H = \sum_j \frac{p_j^2}{2m} - Ze^2 \sum_j \frac{1}{r_j} + e^2 \sum_{i>j} \frac{1}{r_{ij}} \tag{27}$$

  - ◇ Single electron feels a complicated potential

$$V(r) = \begin{cases} -Ze^2/r & r \to 0 \\ -(Z-N+1)e^2/r & r \to \infty \end{cases} \tag{28}$$

  - ◇ H is a function of r only $\Rightarrow$ Separation of variables
    - ▲ Angular momentum and spin treated the same as Hydrogenic case
    - ▲ Spherical Harmonics, $|\pm>$, radial eigenfunctions
- System's wave function
  - ◇ Define orbital of 1 electron

$$a \equiv |n\ell m m_s> = u_a$$

  - ◇ For many electrons, guess

$$\Psi = u_a(1)u_b(2)\ldots u_k(N)$$

  - ◇ Electrons are identical (indistinguishable)
    - ▲ Cannot 'tag' particle 1,2,..
    - ▲ Solution: Consider a linear combination of all permutations of the u_a product
  - ◇ Pauli's Exclusion Principle:
    - ▲ No two electrons can occupy the same orbital
    - ▲ Require a linear combination such that Ψ vanishes if two electrons occupy the same orbital
  - ◇ Fermions $\Rightarrow$ Ψ anti-symmetric under interchange of two particles
  - ◇ Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_a(1) & u_a(2) & \ldots & u_a(N) \\ u_b(1) & u_b(2) & & \\ \vdots & \vdots & & \\ u_k(1) & u_k(2) & \ldots & u_k(N) \end{vmatrix} \tag{29}$$

    - ▲ If two electrons occupy the same orbital (e.g. a=b), then Ψ vanishes
    - ▲ Ψ is anti-symmetric under the interchange of two particles (fermions)
- Hartree-Fock Approximation (Energy States)
  - ◇ Exact states: Extremize the energy

$$\delta E = \delta(<\Psi|H|\Psi>) = 0 \tag{30}$$

- ◇ Approximation: Consider extremizing over a restricted set of orbitals
- ◇ Result: Schrodinger equation with two terms in the potential
  - (a) An electrostatic term due to the nucleus and averaged electron distribution
  - (b) An 'exchange potential' with no classical analog giving an effective repulsion of electrons with the same spin
- ◇ Averaging over angles gives a radial potential with a good approximation to the shell structure of atoms

- Atomic Configurations
  - ◇ Standard notation

$$n\ell^x \qquad \text{with x = number of electrons} \tag{31}$$

  - ▲ Express $\ell = 0, 1, 2, 3, \ldots$ as s,p,d,f,...
  - ▲ Each ℓ corresponds to $2(2\ell+1)$ degenerate m, m_s states
  - ◇ Shells generally fill up in order, but there are exceptions (e.g. K)
  - ◇ Table

D. Perturbations

- Electrostatic Interactions: Russel-Saunders Coupling
  - ◇ Multiple electrons only
  - ◇ Recall our central field Hamiltonian for the hydrogenic ions

$$H = \sum_j \frac{p_j^2}{2m} - \frac{Ze^2}{r}$$

  - ▲ Degenerate in ℓ, m, m_s
  - ▲ Additional terms for multiple electrons break some of this degeneracy
  - ◇ Express the multi-electron Hamiltonian as

$$H = \sum_j \frac{p_j^2}{2m} - Ze^2 \sum_j \frac{1}{r_j} + \sum_i V(r_i) + H_1 \equiv H_0 + H_1 \tag{32}$$

  - ▲ Identify $\sum V(r_i)$ as the central field potential due to the 'smeared out' electrons
  - ▲ H_1 is a perturbation to our spherically symmetric Hamiltonian (H_0)
  - ◇ Explicitly

$$H_1 = e^2 \sum_{i>j} \frac{1}{r_{ij}} - \sum_i V(r_i) + H_{SO} + \ldots \tag{33}$$

  - ▲ Electrostatic Interaction: H_{es}

$$H_{es} = e^2 \sum_{i>j} \frac{1}{r_{ij}} - \sum_i V(r_i) \tag{34}$$

- ▲ H_{SO} = Spin-orbit term
- ▲ ... = Higher order terms

◇ Note ℓ_i is not a constant of the motion: $[H_{es}, \ell_i] \neq 0$

◇ But, H_{es} does commute with the total angular momentum and spin

$$[H_{es}, \vec{L}] = 0 \qquad [H_{es}, \vec{S}] = 0$$

- ▲ $\vec{L} = \sum_i \vec{\ell}_i; \quad \vec{S} = \sum_i \vec{s}_i$
- ▲ So, the total angular momentum and spin are constants of the motion

◇ Qualitatively assessing the H_{es} perturbation

- ▲ Electrons repel each other
- ▲ $\Rightarrow$ Lower energy if they are farther apart

◇ Hund's Rules

(a) Large Spin $\Rightarrow$ Lower Energy

- ▲ Large spin $\Rightarrow$ individual $\vec{s}_i$ are aligned $\Rightarrow$ $s_1 = s_2 = s_3 = \cdots = \pm\frac{1}{2}$
- ▲ Pauli's exclusion $\Rightarrow$ electrons with same spin will be farther apart
- ▲ This is tyipcally the dominant RS Coupling effect

(b) For a given spin, larger angular momentum $\Rightarrow$ Lower Energy

- ▲ Large L $\Rightarrow$ individual $\vec{l}_i$ are aligned
- ▲ Pauli $\Rightarrow$ electrons with similar orbits will be farther apart

• Equivalent and Non-equivalent Electrons

◇ Closed shells

- ▲ Spherically symmetric

$$\sum_m |\mathcal{Y}_{\ell m}|^2 = \frac{2\ell+1}{4\pi} \tag{35}$$

- ▲ These electrons interact minimally with outer electrons
- ▲ Ignore them altogether

◇ Definition

- ▲ Equivalent electrons have the same n, ℓ
- ▲ Non-Equivalent electrons have different n, ℓ

◇ Spectroscopic labeling

$$^{(2S+1)}L_J$$

- ▲ L: Total orbital angular momentum
- ▲ S: Total spin
- ▲ J: Total angular momentum

◇ Example 1: Two 's' electrons

(a) Non-equivalent, e.g. 1s2s

$$\vec{L} = \sum_i \vec{\ell}_i = 0$$
$$\vec{S} = \sum_i \vec{s}_i = 0, 1$$

- ▲ Two terms allowed
- ▲ ^{1}S (singlet) and ^{3}S (triplet)
- ▲ By Hund's rule, ^{3}S should have lower energy

(b) Equivalent (e.g. $2s^2$)

- ▲ $\vec{L} = 0$ again
- ▲ Pauli $\Rightarrow$ $\vec{S} = 0$ only

◇ Example 2: Two 'p' electrons

(a) Non-equivalent

$$\vec{L} = \sum_i \vec{\ell}_i = 0, 1, 2$$
$$\vec{S} = \sum_i \vec{s}_i = 0, 1$$

- ▲ States:

Term	^{1}S	^{1}P	^{1}D	^{3}S	^{3}P	^{3}D
Number	1	3	5	3	9	15

- ▲ Each electron had 2 spin x $(2\ \ell + 1) = 6$ states
- ▲ Total had to be $6 \times 6 = 36$

(b) Equivalent

- ▲ Some states are excluded by Pauli
- ▲ Some states are indistinguishable
- ▲ $\Rightarrow$ Less than 36 states total (15)

m_1	m_2	m_{s_1}	m_{s_2}	Label	State
+1	+1	+	+	^{3}D	Pauli
+1	+1	+	-	^{1}D	1
+1	+1	-	+	^{1}D	1
+1	+1	-	-	^{3}D	Pauli
+1	0	+	+	^{3}P	2
+1	0	+	-		3
+1	0	-	+		4
+1	0	-	-	^{3}P	5
+1	–1	+	+		6
+1	–1	+	-		7
+1	–1	-	+		8
+1	–1	-	-		9
0	+1	+	+		2
0	+1	+	-		3
0	+1	-	+		4
0	+1	-	-		5
0	0	+	+	^{3}S	Pauli
0	0	+	-	^{1}S	10
0	0	-	+		10
0	0	-	-	^{3}S	Pauli
0	–1	+	+	^{3}P	11
0	–1	+	-		12
0	–1	-	+		13
0	–1	-	-	^{3}P	14
–1	+1	+	+		6
–1	+1	+	-		7
–1	+1	-	+		8
–1	+1	-	-		9
–1	–1	+	+	^{3}D	Pauli
–1	–1	+	-	^{1}D	15
–1	–1	-	+	^{1}D	15
–1	–1	-	-	^{3}D	Pauli

◇ Useful shortcut

- ▲ Holes in a closed shell give same results as corresponding electrons
- ▲ e.g. Terms corresponding to p^5 are the same as p^1

- Spin-Orbit Coupling
  - ◇ Classical motivation
    - ▲ e^- rest frame → Observes a magnetic field due to the current driven by the nucleus

$$\vec{B} = -\frac{1}{c}\vec{v} \times \vec{E} = \frac{1}{m_e c r}\ \vec{\ell}\ \frac{d\phi}{dr}$$

    - ▲ ϕ is the electrostatic potential
    - ▲ Energy

$$E = -\vec{\mu}_s \cdot \vec{B} \qquad \text{with} \quad \vec{\mu}_s = -\frac{eg\vec{s}}{2m_e c}$$

      - ○ $g \approx 2$ for an electron
      - ○ This energy is $2\times$ the relativsitic (correct) value
      - ○ Our 'classical' treatment failed to properly account for the transformations between non-interial frames
  - ◇ Proper Hamiltonian

$$H_{SO} = \frac{1}{2m_e^2c^2}\ \vec{s} \cdot \vec{\ell}\ \frac{1}{r}\ \frac{d\phi}{dr} \tag{36}$$

    - ▲ For many electrons

$$H_{SO} = \sum_i \xi_i(r_i)\ \vec{s}_i \cdot \vec{\ell}_i \tag{37}$$

$$\xi_i(r_i) = \frac{1}{2m_e^2c^2 r}\frac{d\phi(r_i)}{dr} \tag{38}$$

    - ▲ Taking an appropriate radial average of $\xi_i(r_i)$

$$H_{SO} = \xi \vec{S} \cdot \vec{L}$$

  - ◇ Degenerate Perturbation theory
    - ▲ Our unperturbed states $|n\ell m m_s\!>$ (ignoring R-S Coupling) are highly degenerate
    - ▲ Brute force: Find the linear combination of $|n\ell m m_s\!>$ which diaganolize $H_{SO} \equiv V^{(1)}$
    - ▲ Shortcut: Identify an operator which commutes with $H^{(0)}$ and H_{SO} and uniquely identifies the degenerate states → $\vec{J}$

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left(|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2 \right)$$

◇ Energies

$$E_{SO} =< H_{SO} >= \frac{1}{2}C\,[\,j(j+1) - \ell(\ell+1) - s(s+1)\,] \tag{39}$$

▲ C is a constant related to ξ

▲ For fixed $\vec{L}$ and $\vec{S}$,

$$\Delta E_{SO} = E_{J+1} - E_J = C(j+1)$$

∘ Lande interval rule

∘ Useful empirically

◇ Example: Hydrogenic ion

▲ $\phi = Ze^2/r \;\Rightarrow\; d\phi/dr = -Ze^2/r^2$

$$H_{SO} = \frac{Ze^2}{2m_e^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}$$

▲ Perturbation theory

$$\begin{aligned} < H_{SO} > &= <nj'm'\ell's'|H_{SO}|njm\ell s> \\ &= \frac{Ze^2}{2m^2c^2}\Big\langle\frac{1}{r^3}\Big\rangle_{n\ell\ell'}<nj'm'\ell's'|\frac{1}{2}(J^2 - L^2 - S^2)|njm\ell s> \\ &= \frac{Ze^2}{2m^2c^2}\frac{\hbar^2}{2}\Big\langle\frac{1}{r^3}\Big\rangle_{n\ell}\;[\,j(j+1) - \ell(\ell+1) - s(s+1)\,]\,\delta_{j'j}\delta_{m'm}\delta_{\ell'\ell}\delta_{s's} \end{aligned}$$

▲ As expected, $< H_{SO} >$ is diagonal

▲ For explicit calculation

$$\left\langle\frac{1}{r^3}\right\rangle_{n\ell} = \frac{Z^3}{a_0^3}\frac{1}{n^3\ell(\ell+\frac{1}{2})(\ell+1)} \tag{40}$$

▲ Hydrogen 2p level (Z=1; n=2; $\ell = 0, 1; j = 1/2, 3/2$)

$$< H_{SO} >= \begin{cases} 0 & 2^2\mathrm{S}_{\frac{1}{2}} \qquad (\ell = 0) \\ \frac{mc^2\alpha^4}{96} & 2^2\mathrm{P}_{3/2} \qquad (\ell = 1; j = 3/2) \\ \frac{-mc^2\alpha^4}{48} & 2^2\mathrm{P}_{1/2} \qquad (\ell = 1; j = 1/2) \end{cases}$$

▲ $2P_{3/2}$ - $2P_{1/2}$ splitting $= 4.5 \times 10^{-5}$ eV ≈ 1 km/s

▲ Note, relativisitic effects are of order α^4 and <u>cannot</u> be ignored!!

◇ One can also invert the problem to examine α

▲ Measure $< H_{SO} >$ in the lab

▲ Measure $< H_{SO} >$ at $z = 2$

▲ If there is a change, α is varying!

• Relativistic Correction

◇ Non-relativistic: K.E. $= p^2/2m$

◇ Expanding to the next term in v^2/c^2 from the Lagrangian

$$\text{K.E.} = \frac{p^2}{2m}\left(1 - \frac{1}{4}\frac{v^2}{c^2}\right) \tag{41}$$

◇ Relativstic perturbation: $H = H^{(0)} + H_{rel}$

$$H_{rel} = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 \tag{42}$$

▲ No spin dependence, spherically symmetric

▲ $[H_{rel}, L^2] = [H_{rel}, L] = 0$

▲ Standard $|n\ell m m_s>$ diagonalize H_{rel}

◇ Trick

$$H_{rel} = -\frac{1}{2mc^2}(H^{(0)} - V^{(0)})^2$$

◇ Computing the energies

$$< H_{rel} > = -\frac{1}{2mc^2}\left[(E_n^{(0)})^2 + 2E_n^{(0)} Ze^2\left\langle\frac{1}{r}\right\rangle_{n\ell} + Z^2e^4\left\langle\frac{1}{r^2}\right\rangle_{n\ell}\right] \tag{43}$$

$$= \frac{-Z^4\alpha^4 mc^2}{2n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{3}{4n}\right) \tag{44}$$

◇ Combine with spin-orbit

$$< H_{SO} > + < H_{rel} > = \frac{-Z^4\alpha^4 mc^2}{2n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right] \tag{45}$$

▲ No explicit ℓ dependence!

▲ Higher j $\Rightarrow$ Higher energy (3rd Hund's rule)

◇ Example: Hydrogen

$$\Delta E = -7.25 \times 10^{-4}\text{eV}\ \frac{1}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

State	n	j	$< H_{SO} > + < H_{rel} >$
$1\,^2\mathrm{S}_{\frac{1}{2}}$	1	$\frac{1}{2}$	-1.8×10^{-4} eV
$2\,^2\mathrm{S}_{\frac{1}{2}}$, $2\,^2\mathrm{P}_{\frac{1}{2}}$	2	$\frac{1}{2}$	-5.7×10^{-5} eV
$2\,^2\mathrm{P}_{\frac{3}{2}}$	2	$\frac{3}{2}$	-1.1×10^{-5} eV

▲ Does this explain our difference between λ_{theory} and λ_{exp} from before?

- ▲ Wavelength shift

$$\frac{\Delta\lambda}{\lambda} = -\frac{\Delta E}{E}$$

- ▲ Calculating ΔE from the above table and accounting for the relative degeneracy of the $2\,^2\mathrm{P}_{\frac{1}{2}}$, $2\,^2\mathrm{P}_{\frac{3}{2}}$ states

$$\begin{aligned}\Delta E &= \frac{1}{3}\left[2\Delta E_{1S\to 2P_{\frac{3}{2}}} + \Delta E_{1S\to 2P_{\frac{1}{2}}}\right] \\ &= 1.55\times 10^{-4}\ \mathrm{eV}\end{aligned}$$

- ▲ Therefore

$$\Delta\lambda = \frac{\Delta E}{E}\times 1215.68\text{Å} = -0.0138\text{Å}$$

- ▲ Success!

- • Zeeman Effect
  - ◇ External magnetic field: $\vec{B} = B\hat{z}$
  - ◇ Expect a perturbation to the Hamiltonian

$$H_Z = -\vec{\mu}\cdot\vec{B} \tag{46}$$

  - ◇ In this case, the magnetic moment includes both spin and angular momentum

$$\vec{\mu} = -\frac{e}{2mc}\sum_i\left[\vec{\ell}_i + 2\vec{s}_i\right] \tag{47}$$

  - ◇ Assume B is small enough that $H_Z \ll H_{LS}$
    - ▲ $B \ll \alpha e/a_0^2 \sim 10^5$ Gauss
    - ▲ Applies for most astrophysical problems
    - ▲ Key: In this case, $\vec{L}$ and $\vec{S}$ are still good quantum numbers

$$\begin{aligned}\vec{\mu} &= -\frac{1}{2}\frac{e}{mc}\left[\vec{L} + 2\vec{S}\right] \\ &= -\frac{1}{2}\frac{e}{mc}\left[\vec{J} + \vec{S}\right]\end{aligned}$$

  - ◇ Precession (Heuristic argument)
    - ▲ $\vec{\mu}$ precesses about $\vec{B}$
    - ▲ $\vec{L}, \vec{S}$ precess about $\vec{J}$ because of LS coupling
    - ▲ To obtain the average H_Z value, project μ onto the $\vec{J}$ direction and consider the projection of $\vec{J}$ with $\vec{B}$

- ▲ Fig

$$H_z \approx \frac{1}{2}\frac{e}{mc}\left[\,(\vec{J}+\vec{S})\cdot\vec{J}\,\right]\frac{\vec{J}\cdot\vec{B}}{|\vec{J}|^2}$$
$$= \frac{1}{2}\left(\frac{e\hbar B}{mc}\right) g J_z$$

- ▲ where

$$g(J,L,S) \equiv 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{48}$$

- ◇ Frequency of transition

$$\omega_{12} = \frac{1}{2}\frac{eB}{mc}\,(\,g_1 m_1 - g_2 m_2\,) \tag{49}$$

- ◇ Classical theory

$$\omega = \omega_0, \omega_0 \pm \frac{eB}{2mc}$$

  - ▲ Corresponds to $\Delta m = 0, \pm 1$ and $g_1 = g_2$
  - ▲ The above relations do not hold in general
  - ▲ Describe the QM Zeeman effect as the "Anomolous" Zeeman effect
- ◇ (Aside) – The above heuristic result can be derived formally using the Wigner-Eckart Theorem

- Nucleus and Hyperfine Structure
  - ◇ Thus far, we have assumed that the nucleus
    - (a) Has infinite mass
    - (b) Is a point-like particle
    - (c) Interacts through the Coulomb field only
  - ◇ Level splitting due to nuclear effects are called 'hyperfine' structure
  - ◇ Isotopic effect
    - (a) Different nuclear mass $\Rightarrow$ different reduced mass μ
    - (b) Also, different nuclear extent
    - (c) In a given atom, this leads to <u>no</u> new transitions
    - (d) Example: D and H
      - ▲ Reduced masses

$$\mu_H = \frac{m_p m_e}{m_p + m_e} \approx 0.51072 \text{ MeV}$$
$$\mu_D = \frac{2m_p m_e}{2m_p + m_e} \approx 0.51086 \text{ MeV}$$

- ▲ Energies

$$\Delta E = \frac{\Delta\mu}{\mu}\ E$$
$$\Delta v = \frac{\Delta\mu}{\mu}\ c \approx -82\ \ \mathrm{km\,s}^{-1}$$

- ◇ Nuclear spin
  - ▲ Nucleus has angular momentum $\vec{I}$
  - ▲ Nuclear magnetic moment

$$\vec{\mu}_N = g\frac{e}{2Mc}\vec{I} \tag{50}$$

    - ○ $g_{proton} = 5.5855$
    - ○ $M/m_e \approx 2000$
    - ○ $\Rightarrow\ |\vec{\mu}_N| \approx (10^{-3}\mathrm{to}10^{-4})|\vec{\mu}_e|$
  - ▲ Define another total angular momentum

$$\vec{F} = \vec{I} + \vec{J} \tag{51}$$

  - ▲ Splittings are similar to spin-orbit coupling
  - ▲ Example: H Ground state ($1^2\mathrm{S}_{\frac{1}{2}}$)
    - ○ Nucleus (proton) has spin $\frac{1}{2}$
    - ○ $F = 0, 1$
    - ○ $\Delta E = 1420$ MHz (21 cm)