

Week ②

PHY 402 Atomic and Molecular Physics

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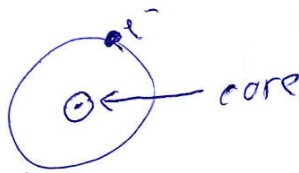
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2 Atoms

2.1 Single (active) electron Atoms

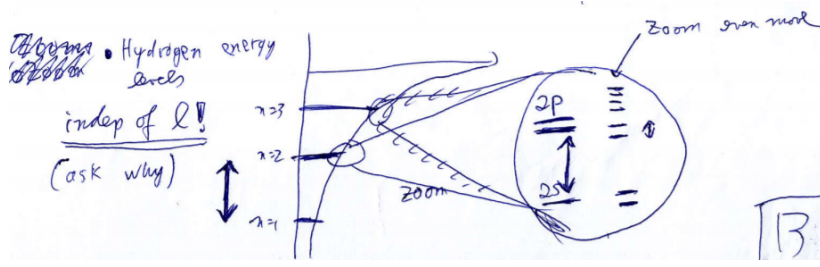
See section (1.2.3) for most basic : Hydrogen atoms

- Directly applies to Hydrogenic *atoms*:
 - deuterium ($pn+e^-$), tritium ($pnn+e^-$) (these are just heavier atoms due to nucleus, but the electron behaves the same).
- Next simplest are Hydrogenic *ions*
 He^+ , Li^{++} etc, here nuclear charge $Z>1$ in section 1.2.3
- Also almost applicable to Rydberg states of Alkali atoms,
Li, Na, K, Rb, Cs (mainly their single valence electron is important)



Rydberg States ($n \gg 10$)

- In this chapter, we first take a more detailed look at spins, E/ B fields and relativistic corrections. In section 1.2.3 we had just added m_s quantum number without consequences.



2.1.1 Relativistic corrections, effect of spins, fine structure

- Spins arise naturally in *relativistic* Quantum Mechanics, hence they are part of "relativistic corrections".
- Calculations in section 1.2.3 are however fully non-relativistic, i.e. we use $\hat{H} = \frac{p^2}{2m}$ not

$$\hat{H} = \sqrt{p^2 c^2 + m_0^2 c^4}. \quad (2.1)$$

Fine Structure:

Start from relativistic wave-equation (Dirac Equation), expand for $v \ll c$ (electron velocity much less than speed of light) and get,

$$\hat{H} = \hat{H}_0 + \hat{H}'_{FS}, \quad (2.2)$$

where \hat{H}_0 is same as in section 1.2.3 for Hydrogen and,

$$\hat{H}'_{FS} = \hat{H}'_1 + \hat{H}'_2 + \hat{H}'_3. \quad (2.3)$$

Relativistic Corrections, fine-structure Hamiltonians

$$\hat{H}_1^1 = -\frac{p^4}{8m^3 c^2} \quad \text{relativistic correction to Kinetic Energy} \quad (2.4)$$

$$\hat{H}_2^1 = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad \text{spin-orbit coupling} \quad (2.5)$$

$$\hat{H}_3^1 = -\frac{\pi \hbar^2}{2m^2 c^2} \frac{Ze^2}{4\pi \epsilon_0} \delta(\mathbf{r}) \quad \text{Darwin term} \quad (2.6)$$

Comment on relativistic correction: Rather than from Dirac equation, \hat{H}_1^1 can also be gotten directly by expanding Eq. (2.1) to $\mathcal{O}(p^4)$ and replacing kinetic energy $\hat{T} = \hat{p}^2/(2m)$ accordingly.

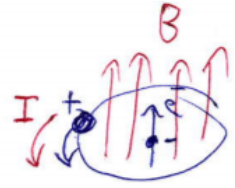
Comments on spin orbit coupling

Atom "cartoon":



Spin-energy?

Rest
frame
of e⁻



Comment on spin-orbit coupling:

- Let us work in the *rest-frame* of the electron, where the proton moves with velocity $-\mathbf{v}$ (where \mathbf{v} is the electron velocity in the lab-frame).
- The electron "sees" a positively charged proton orbiting itself and hence a magnetic field:

$$\mathbf{B} = -\frac{e\mu_0}{4\pi} \frac{\mathbf{v} \times \mathbf{r}}{r^3} \quad \left(\text{from } \mathbf{B} = \frac{\mu_0}{4\pi} \frac{q\mathbf{v} \times \hat{\mathbf{r}}}{r^2}, \text{ see E-dyn.} \right) \quad (2.7)$$

Now we use

$$\hat{H}_{mag} = -\hat{\mu} \cdot \mathbf{B} \quad \text{Energy of spin in magnetic field} \quad (2.8)$$

$$\hat{\mu} = -g_s \mu_b \hat{\mathbf{S}} / \hbar \quad \text{Electron magnetic moment} \quad (2.9)$$

$$\hat{H}_{mag} = +g_s \frac{\mu_b}{\hbar} \mathbf{B} \cdot \hat{\mathbf{S}} \quad \hat{\mu} \sim -\hat{\mathbf{S}} \text{ since } \mathbf{q} < \mathbf{0} \quad (2.10)$$

$$g_s \simeq 2 \quad \text{Gyromagnetic factor} \quad (2.11)$$

$$\mu_B = \frac{e\hbar}{2m_e} \quad \text{Bohr Magneton } e > 0 \text{ here} \quad (2.12)$$

and then get:

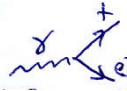
$$\hat{H}_{mag} = g_s \underbrace{\frac{\mu_b}{\hbar}}_{=\frac{e}{2m_e}} \underbrace{\left(-\frac{\mu_0 e}{4\pi m_e} \frac{\mathbf{p} \times \mathbf{r}}{r^3} \right)}_{=\mathbf{B}} \cdot \hat{\mathbf{S}} \quad (2.13)$$


$$\stackrel{\mathbf{L}=\mathbf{r} \times \mathbf{p}}{=} \frac{g_s \mu_0 \epsilon_0}{2m_e^2} \underbrace{\frac{e^2}{4\pi \epsilon_0 r^3}}_{\frac{1}{r} \frac{dV(r)}{dr}} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = 2\hat{H}'_2. \quad (2.14)$$

This is (2.5) up to a factor of two, which is due to the e^- rest frame not being inertial, see Shankar.

Comments on Darwin term:

- Further consequence of relativistic QM is the existence of anti-particles (positrons, e^+). Can

have  for time $\Delta E \Delta t \sim \hbar$. Vacuum fluctuations interact with e^- and cause

Zitterbewegung  (Amplitude $\frac{\hbar}{2m_e c} = \frac{\lambda_c}{2}$, freq = $\frac{2m_e c^2}{\hbar}$, where λ_c is the Compton wavelength, 2.4×10^{-12} m).

- Effectively smears out nuclear position, $\mathbf{r} \rightarrow \mathcal{O}$.
- This is the origin of Darwin term

Calculation of Energy Shift in Perturbation Theory, sketch:

- **term 1:** Relativistic correction: $\Delta E_1 = \langle \phi_{nlm} | \hat{H}'_1 | \phi_{nlm} \rangle$. See B&J book, we can use non-degenerate PT because \hat{H}'_1 is diagonal in l, m .
- **term 2:** We have to rewrite the second term (since \hat{H}'_2 , does not commute with $\hat{\mathbf{L}}, \hat{\mathbf{S}}$).

Define Total angular momentum of electron (see section 1.2.2)

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (2.15)$$

New Eigenfunctions $|\phi_{n,l,j,m_j}\rangle$

$$\hat{\mathbf{J}}^2 |\phi\rangle = \hbar^2 j(j+1) |\phi\rangle, \quad (2.16)$$

$$\hat{J}_z |\phi\rangle = \hbar m_j |\phi\rangle. \quad (2.17)$$

With eigenvalues

$$j = \frac{1}{2} \quad (l = 0, s = \frac{1}{2}), \quad (2.18)$$

$$j = l \pm \frac{1}{2} \quad (l > 0, s = \frac{1}{2}). \quad (2.19)$$

For non-relativistic Hydrogen (without (2.4)-(2.6)), the states $|\phi_{nljm_j}\rangle$ are still degenerate in l, j, m_j , energy only depends on n .

Now write:

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (2.20)$$

Now we can again use non-degenerate Perturbation Theory (in coupled basis)

$$\Delta E_2 = \langle \phi_{nljm_j} | \hat{H}'_2 | \phi_{nljm_j} \rangle \quad (2.21)$$

$$= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - l(l+1) - \frac{3}{4} \right]. \quad (2.22)$$

Where $\frac{\hbar^2}{2}$ comes from $\frac{\mathbf{J}^2}{2}$ and we used the short hand $\hat{H}'_2 = \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and,

$$\langle \xi(r) \rangle = \int d^3r \phi_{nljm_j}^*(\mathbf{r}) \xi(\mathbf{r}) \phi_{nljm_j}(\mathbf{r}). \quad (2.23)$$

See B&J for detailed integration and result.

- **term 3:** Darwin term:

$$\Delta E_3 = \langle \phi_{nljm_j} | \hat{H}'_3 | \phi_{nljm_j} \rangle = \frac{\pi \hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} |\phi_{nljm_j}(0)|^2. \quad (2.24)$$

From Eq. (1.36) we see that this shifts $l = 0$ states only (others have $|\phi(0)|^2 = 0$).

Fine structure Energy Shifts: All terms together:

$$E_{n_j} = E_n \left(1 + \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right) \quad (2.25)$$

with E_n from Eq. (1.43).

- Here $\alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} \simeq \frac{1}{137}$ is again the fine structure constant.
- Now degeneracy of energy in j is lifted.
- Note $E_n < 0$, the sign of shift depends on n, j but is mostly towards lower energies.

2.1.2 Lamb-Shift

So far, even when discussing interactions of spins, we always used classical formulae for electric / magnetic fields and interaction potentials.

Fundamentally, electromagnetic-fields and their interactions are due to discrete quanta (photons), as described by *quantum electro-dynamics* (QED).

The resulting vacuum fluctuations of γ , e^+ , e^- cause a further,

Lamb Shift:

$$\Delta E_{\text{Lamb}} = \alpha^5 m_e c^2 \begin{cases} \frac{1}{4n^3} \left[k(n, l) \pm \frac{1}{\pi(j+\frac{1}{2})(l+\frac{1}{2})} \right] & \text{when } l \neq 0, j = l \pm \frac{1}{2} \\ \frac{1}{4n^3} k(n, 0) & \text{when } l = 0 \end{cases} \quad (2.26)$$

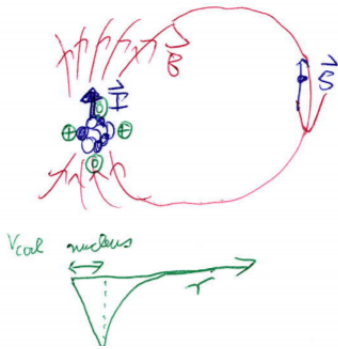
Here $k(n, l) < 0.05$ are small numerical constants.

- This lifts the degeneracy between s and p states (so might cause splitting not only shift)
- The Lamb-Shift or splitting is much *smaller* than the fine-structure splitting, see also section 2.1.4 later.

2.1.3 Hyperfine-structure

Some more details neglected so far that we will consider now:

- Nuclear spin, operator \hat{I} , quantum numbers I, m_I .
- Finite nuclear extension, hence correction to Coulomb potential at very short r (inside the nucleus).
- Due to finite nuclear extension, the nucleus can also have an electric quadrupole moment. However we will not discuss that case here and assume it vanishes, which is true for some nuclei. See Bransden/ Joachain for non-vanishing case.



left: Sketches of nuclear Quadrupole-moment, potential in the nucleus.

Let us write the Hamiltonian now as

$$\hat{H} = \hat{H}'_0 + \hat{H}'_{HFS}, \quad (2.27)$$

where \hat{H}'_0 already includes fine-structure effects ($\hat{H}'_0 = \hat{H}_0 + \hat{H}'_{FS}$, see Eq. (2.3)).

Hamiltonian of Hyperfine Interactions

$$\hat{H}'_{HFS} = \frac{\mu}{4\pi} \frac{2}{\hbar} g_I \mu_B \mu_N \frac{1}{r^3} \left[\hat{\mathbf{L}} \cdot \hat{\mathbf{I}} - \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} + 3 \frac{(\hat{\mathbf{S}} \cdot \hat{\mathbf{r}})(\hat{\mathbf{I}} \cdot \hat{\mathbf{r}})}{r^3} \right] \quad (2.28)$$

- Here g_I is the nuclear g-factor ($g_I = -2 \dots 6$), that means:
- Nuclear magnetic moment $\hat{\mu}_N = g_I \mu_N \hat{\mathbf{I}}/\hbar$, c.f. Eq. (2.9)

- $\mu_N = 5 \times 10^{-27}$ J/T is the nuclear magneton, $\mu_N = (m_e/M_p)\mu_B \sim 5 \times 10^{-4}\mu_B$.
- $\hat{\mathbf{I}}$ is the nuclear angular momentum operator (contains proton and neutron spins and possibly orbital angular momentum of these).
- $\hat{r} = \mathbf{r}/r$.

We can again use perturbation theory. As for fine-structure, it will be useful to change to a coupled spin basis, using

Total Angular Momentum of the atom Is given as the sum of electron- and nuclear angular momenta.

$$\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}} \quad (2.29)$$

As for the other angular momentum operators, eigenstates and eigenvalues are given by

$$\hat{\mathbf{F}}^2|F, m_f\rangle = \hbar^2 F(F+1)|F, m_f\rangle, \quad (2.30)$$

$$\hat{F}_z|F, m_f\rangle = \hbar m_f|F, m_f\rangle, \quad (2.31)$$

with ranges

$$F = |I - J|, \dots, |I + J| \quad (2.32)$$

and

$$m_F = -F, \dots, F. \quad (2.33)$$

Treating Eq. (2.28) and corrections at $r = 0$ using perturbation theory (see book) we find the

Hyperfine energy-shift

$$\Delta E = \frac{\mu_0}{4\pi} 2g_I \mu_B \mu_N \frac{Z^3}{a_0^3 n^3} \left(\frac{m_{\text{red}}}{m_e}\right)^3 \frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} \quad (2.34)$$

$$= \frac{g_I}{2} [m_e c^2] \left(\frac{m_e}{M_p}\right) \frac{\alpha^4 Z^3}{n^3} \left(\frac{m_{\text{red}}}{m_e}\right)^3 \frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} \quad (2.35)$$

- After considering fine structure and Lamb shift, levels are already split according to their different values of j and l , and nuclear spin I is fixed for a given atom.
- Hence 2.34 now causes additional splitting into different allowed values of F in the range,

$$j + I \geq F \geq |j - I| \quad (2.36)$$

- Hyper-fine effects are, as the name suggests, again much smaller than the Lamb-shift, see also section 2.1.4

2.1.4 Hierarchy of level splittings

- Now that we have collected the most important corrections to atomic energy levels, let us estimate their relative strengths.
- We have (for $Z=1$).

$$E_{\text{base}} = -\frac{\alpha^2 [m_e c^2]}{2} \frac{1}{n^2} \sim \alpha^2 \quad (2.37)$$

$$\Delta E_{\text{fine}} = (\alpha)^2 E_{\text{base}} \mathcal{N}_{\text{fine}} \sim \alpha^4 [m_e c^2] \quad (2.38)$$

$$\Delta E_{\text{Lamb}} = \alpha^5 [m_e c^2] \mathcal{N}_{\text{Lamb}} \sim \alpha^5 [m_e c^2] \quad (2.39)$$

$$\Delta E_{\text{hyperfine}} \frac{g_I}{2} [m_e c^2] \underbrace{\left(\frac{m_e}{M_p} \right)}_{5 \times 10^{-4}} \frac{\alpha^4}{n^3} \mathcal{N}_{\text{HFS}} \sim (5 \times 10^{-4}) \alpha^4 [m_e c^2] \quad (2.40)$$

from Eq. (1.43), Eq. (2.25), Eq. (2.26), Eq. (2.34), where we have only re-expressed some energy scales in terms of α and $m_e c^2$, and written \mathcal{N} for expressions that depend on quantum numbers and are of $\mathcal{O}(1)$.

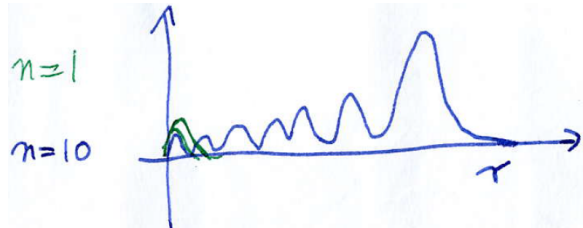
- Since $\alpha \ll 1$ and $5 \times 10^{-4} \ll \alpha$ we see the typical hierarchy already mentioned: Fine Structure > Lamb-Shift > Hyperfine Structure.

2.1.5 Alkali atoms/ Rydberg atoms

Alkali atoms: Li, Na, K, Rb, Cs have a single valence electron above fully-filled electron shells, as we shall see in section 2.4.

Valence electrons are responsible for chemistry and visible spectra.

Consider very highly excited states, e.g. $n \gg 10$. These are called Rydberg States.



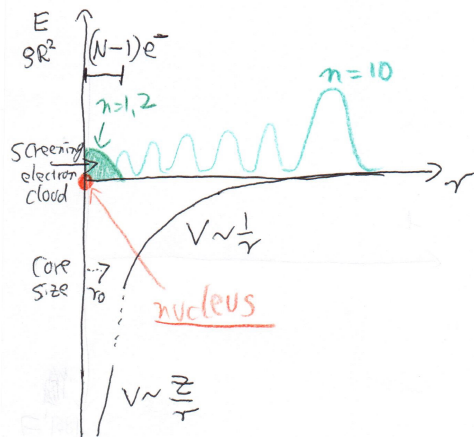
left: Sketch of $n = 1$ versus $n = 10$ radial probability density

Mean electron orbital radius

$$\langle \phi_{nlm} || \hat{r} || \phi_{nlm} \rangle = a_0 \frac{n^2}{Z} \left(1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right). \quad (2.41)$$

Orbital radius roughly scales like $a_0 n^2$ ($l = 0, Z = 1$).

For, e.g. Li-atom with 3 electrons, two in (1s) and the outer one in (n=60):
 → Valence e^- much further out than others (we call the others + nucleus the atomic core).
 Let N be the number of electrons and Z the nuclear charge. The potential "seen" by the valence electron is as follows:



We can phenomenologically describe this by a modified Coulomb potential

$$V_{\text{eff}} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + U_d(r), \quad (2.42)$$

with $U_d(r) = 0$ for $r > r_0$ (outside the tiny atomic core).

A possible choice is $U_d(r) = -e^2/(4\pi\epsilon_0)[(Z-1)e^{-a_1 r} - r(a_3 + a_4 r)e^{-a_2 r}]$.

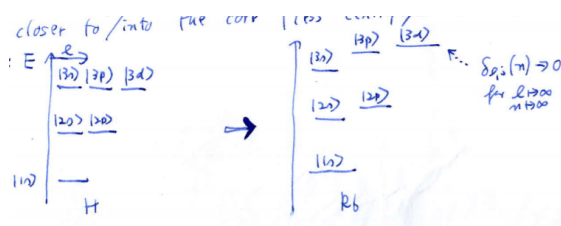
Using this effective potential $V(r) = V_{\text{eff}}$ we can again solve Eq. (1.34) radial SE \Rightarrow get slightly different energies compared to Hydrogen.

Energy levels for Alkali atoms ($Z=1$)

$$E = -\frac{R_y}{(n - \delta_{l,j}(n))^2} \quad (2.43)$$

Where $\delta_{l,j}$ includes fine-structure and, $\delta_{l,j} =$ quantum defect (due to $U_d(r)$)

- The lower the l the higher the quantum defect, since $\phi_{n,l,m}(r)$ reaches closer to/ into the core (less centrifugal barrier)



- We will see these features over and over again for multi-electron systems.

