06 - Time-Independent Perturbation Theory

- Aim of Section:
  - Introduce time-independent perturbation theory. Applications include Stark effect, Zeeman effect, fine structure of hydrogenic atoms, and hyperfine structure of hydrogen atom.

Introduction - I

- Consider following common problem. Hamiltonian of a quantum mechanical system is written

$$H = H_0 + H_1.$$

- Here, H_0 is a simple Hamiltonian whose eigenvalues and eigenstates are known exactly.
- H_1 introduces some interesting additional physics into problem, but is sufficiently complicated that when added to H_0 we can no longer find exact energy eigenvalues and eigenstates.
- However, H_1 can, in some sense (which we shall specify more precisely later on), be regarded as small compared to H_0.
- Can we find approximate eigenvalues and eigenstates of modified Hamiltonian, $H_0 + H_1$, by performing some sort of perturbation expansion about eigenvalues and eigenstates of original Hamiltonian, H_0?

Introduction - II

- In this section, we shall only discuss so-called time-independent perturbation theory, in which modification to Hamiltonian, H_1, has no explicit dependence on time.
- It is also assumed that unperturbed Hamiltonian, H_0, is time independent.

Improved Notation - I

- Let the ψ_i be a complete set of eigenstates of Hamiltonian, H, corresponding to eigenvalues E_i: i.e.,

$$H\,\psi_i = E_i\,\psi_i.$$

- Expect the ψ_i to be orthonormal.
- For spatial wavefunction, this implies that

$$\int \psi_i^*\,\psi_j\,d^3\mathbf{x} = \delta_{ij}. \tag{1}$$

- For spinor, this implies that

$$\psi_i^\dagger\,\psi_j = \delta_{ij}. \tag{2}$$

- Generalization to case where ψ is a product of a spatial wavefunction and a spinor is fairly obvious.

Improved Notation - II

- Can represent all of previous possibilities by writing

$$\langle \psi_i | \psi_j \rangle \equiv \langle i | j \rangle = \delta_{ij}.$$

- Term in angle brackets represents integral appearing in (1) in regular space, and spinor product appearing in (2) in spin-space.
- Advantage of our new notation is its great generality: i.e., it can deal with both spatial wavefunctions and spinors.

Improved Notation - III

- Expanding general wavefunction, ψ_a, in terms of energy eigenstates, ψ_i, we obtain

$$\psi_a = \sum_i c_i\,\psi_i. \tag{3}$$

- If ψ_a is a spatial wavefunction then

$$c_i = \int \psi_i^*\,\psi_a\,d^3\mathbf{x}.$$

- If ψ_a is a spinor then

$$c_i = \psi_i^\dagger\,\psi_a.$$

- Can represent both these possibilities by writing

$$c_i = \langle\psi_i|\psi_a\rangle \equiv \langle i|a\rangle.$$

- Expansion (3) thus becomes

$$\psi_a = \sum_i \langle\psi_i|\psi_a\rangle\,\psi_i \equiv \sum_i \langle i|a\rangle\,\psi_i. \tag{4}$$

Improved Notation - IV

- Incidentally, it follows that

$$\langle i|a\rangle^* = \langle a|i\rangle.$$

- Could further generalize (4) by writing

$$|a\rangle = \sum_i \langle i|a\rangle\, |i\rangle.$$

- Here, $|a\rangle$ represents ψ_a, etc.
- Likewise, $\langle i|$ represents ψ_i^* (or $\psi_i^\dagger$ if ψ_i is a spinor).

Improved Notation - V

- If A is a general operator, and wavefunction ψ_a is expanded in manner shown in (3), then expectation value of A is written

$$\langle A \rangle = \sum_{i,j} c_i^* \, c_j \, A_{ij}. \tag{5}$$

- Here, the A_{ij} are unsurprisingly known as matrix elements of A.
- If ψ_a is a spatial wavefunction then

$$A_{ij} = \int \psi_i^* \, A \, \psi_j \, d^3\mathbf{x}. \tag{6}$$

- If ψ is a spinor then

$$A_{ij} = \psi_i^\dagger \, A \, \psi_j. \tag{7}$$

Improved Notation - VI

- Can represent both possibilities by writing

$$A_{ij} = \langle \psi_i | A | \psi_j \rangle \equiv \langle i | A | j \rangle.$$

- Expansion (5) thus becomes

$$\langle A \rangle \equiv \langle a | A | a \rangle = \sum_{i,j} \langle a | i \rangle \langle i | A | j \rangle \langle j | a \rangle. \tag{8}$$

- Incidentally, follows that

$$\langle i | A | j \rangle^* = \langle j | A^\dagger | i \rangle.$$

- Finally, it is clear from (8) that

$$\sum_i |i\rangle\langle i| \equiv 1,$$

where the ψ_i are a complete set of eigenstates, and 1 is identity operator.

Two-State System - I

- Consider simplest possible non-trivial quantum mechanical system in which there are only two independent eigenstates of unperturbed Hamiltonian: i.e.,

$$H_0 \left|1\right\rangle = E_1 \left|1\right\rangle, \tag{9}$$

$$H_0 \left|2\right\rangle = E_2 \left|2\right\rangle. \tag{10}$$

- It is assumed that these states, and their associated eigenvalues, are known.
- We also expect states to be orthonormal, and to form a complete set.

Two-State System - II

- Let us now try to solve modified energy eigenvalue problem

$$(H_0 + H_1)\,|E\rangle = E\,|E\rangle. \tag{11}$$

- In fact, we can solve this problem exactly.
- Because eigenstates of H_0 form a complete set, we can write

$$|E\rangle = \langle 1|E\rangle\,|1\rangle + \langle 2|E\rangle\,|2\rangle. \tag{12}$$

- It follows from (11) that

$$\langle i|H_0 + H_1|E\rangle = E\,\langle i|E\rangle, \tag{13}$$

where $i = 1$ or 2.

Two-State System - III

- (9), (10), (12), (13), and orthonormality condition

$$\langle i|j\rangle = \delta_{ij}, \tag{14}$$

yield two coupled equations that can be written in matrix form:

$$\begin{pmatrix} E_1 - E + e_{11}, & e_{12} \\ e_{12}^*, & E_2 - E + e_{22} \end{pmatrix} \begin{pmatrix} \langle 1|E\rangle \\ \langle 2|E\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{15}$$

where

$$e_{11} = \langle 1|H_1|1\rangle, \tag{16}$$

$$e_{22} = \langle 2|H_1|2\rangle, \tag{17}$$

$$e_{12} = \langle 1|H_1|2\rangle = \langle 2|H_1|1\rangle^*. \tag{18}$$

- Here, use has been made of fact that H_1 is an Hermitian operator.

Two-State System - IV

- Consider special (but not uncommon) case of perturbing Hamiltonian whose diagonal matrix elements are zero, so that

$$e_{11} = e_{22} = 0.$$

- Solution of (15) (obtained by setting determinant of matrix to zero) is

$$E = \frac{(E_1 + E_2) \pm \sqrt{(E_1 - E_2)^2 + 4\,|e_{12}|^2}}{2}.$$

- Expand in supposedly small parameter

$$\epsilon = \frac{|e_{12}|}{E_1 - E_2}.$$

Two-State System - V

- We obtain

$$E \simeq \frac{1}{2}\,(E_1 + E_2) \pm \frac{1}{2}\,(E_1 - E_2)\,(1 + 2\,\epsilon^{\,2} + \cdots).$$

- Previous expression yields modification of energy eigenvalues due to perturbing Hamiltonian:

$$E_1' = E_1 + \frac{|e_{12}|^{\,2}}{E_1 - E_2} + \cdots,$$

$$E_2' = E_2 - \frac{|e_{12}|^{\,2}}{E_1 - E_2} + \cdots.$$

- Note that H_1 causes upper eigenvalue to rise, and lower to fall.

Two-State System - VI

- Easily demonstrated that modified eigenstates take form

$$|1\rangle' = |1\rangle + \frac{e_{12}^{*}}{E_1 - E_2}\,|2\rangle + \cdots,$$
$$|2\rangle' = |2\rangle - \frac{e_{12}}{E_1 - E_2}\,|1\rangle + \cdots.$$

- Thus, modified energy eigenstates consist of one of unperturbed eigenstates, plus a slight admixture of other.
- Expansion procedure is only valid when $|\epsilon| \ll 1$.
- This suggests that condition for validity of perturbation method is

$$|e_{12}| \ll |E_1 - E_2|.$$

- In other words, when we say that H_1 needs to be small compared to H_0, what we really mean is that previous inequality must be satisfied.

Non-Degenerate Perturbation Theory - I

- Let us generalize perturbation analysis to deal with systems possessing more than two energy eigenstates.
- Consider system in which energy eigenstates of unperturbed Hamiltonian, H_0, are denoted

  $$H_0 \left| n \right\rangle = E_n \left| n \right\rangle,$$

  where n runs from 1 to N.
- Eigenstates are assumed to be orthonormal, so that

  $$\langle m | n \rangle = \delta_{nm},$$

  and to form a complete set.
- Let us now try to solve energy eigenvalue problem for perturbed Hamiltonian:

  $$(H_0 + H_1) \left| E \right\rangle = E \left| E \right\rangle.$$

Non-Degenerate Perturbation Theory - II

- It follows that

  $$\langle m|H_0 + H_1|E\rangle = E\,\langle m|E\rangle,$$

  where m can take any value from 1 to N.
- We can express $|E\rangle$ as a linear superposition of unperturbed energy eigenstates:

  $$|E\rangle = \sum_k \langle k|E\rangle\,|k\rangle,$$

  where k runs from 1 to N.
- We can combine previous equations to give

  $$(E_m - E + e_{mm})\,\langle m|E\rangle + \sum_{k\neq m} e_{mk}\,\langle k|E\rangle = 0, \qquad (19)$$

  where

  $$e_{mk} = \langle m|H_1|k\rangle. \qquad (20)$$

Non-Degenerate Perturbation Theory - III

- Let us now develop our perturbation expansion.
- We assume that
  $$\frac{e_{mk}}{E_m - E_k} \sim \mathcal{O}(\epsilon)$$
  for all $m \neq k$, where $\epsilon \ll 1$ is our expansion parameter.
- We also assume that
  $$\frac{e_{mm}}{E_m} \sim \mathcal{O}(\epsilon)$$
  for all m.
- Search for a modified version of nth unperturbed energy eigenstate for which
  $$|E\rangle = |n\rangle + \mathcal{O}(\epsilon),$$
  and
  $$\langle n|E\rangle = 1,$$
  $$\langle m|E\rangle = \mathcal{O}(\epsilon)$$
  for $m \neq n$.

Non-Degenerate Perturbation Theory - IV

- Suppose that we write out (19) for $m \neq n$, neglecting terms that are $\mathcal{O}(\epsilon^2)$ according to our expansion scheme.
- We find that

  $$(E_m - E_n)\,\langle m|E\rangle + e_{mn} \simeq 0,$$

  giving

  $$\langle m|E\rangle \simeq -\frac{e_{mn}}{E_m - E_n}.$$
- Substituting previous expression into (19), evaluated for $m = n$, and neglecting $\mathcal{O}(\epsilon^3)$ terms, we obtain

  $$(E_n - E + e_{nn}) - \sum_{k\neq n} \frac{|e_{nk}|^2}{E_k - E_n} \simeq 0.$$

Non-Degenerate Perturbation Theory - V

- Thus, modified nth energy eigenstate possesses an eigenvalue

$$E_n' = E_n + e_{nn} + \sum_{k\neq n} \frac{|e_{nk}|^2}{E_n - E_k} + \mathcal{O}(\epsilon^3), \tag{21}$$

  and a wavefunction

$$|n\rangle' = |n\rangle + \sum_{k\neq n} \frac{e_{kn}}{E_n - E_k}\, |k\rangle + \mathcal{O}(\epsilon^2). \tag{22}$$

- Incidentally, it is easily demonstrated that modified eigenstates remain orthonormal to $\mathcal{O}(\epsilon^2)$.

Stark Effect - I

- Suppose that hydrogenic atom is subject to uniform external electric field, of magnitude $\mathcal{E}$, directed along z-axis.
- Hamiltonian of system can be split into two parts.
- First, unperturbed Hamiltonian,

$$H_0 = \frac{p^2}{2\,m_e} - \frac{Z\,e^2}{4\pi\epsilon_0\,r}.$$

- Second, perturbing Hamiltonian,

$$H_S = e\,\mathcal{E}\,z. \tag{23}$$

Stark Effect - II

- Electron spin is irrelevant to this problem (because spin operators all commute with H_S), so we can ignore spin degrees of freedom of system.
- Hence, energy eigenstates of unperturbed Hamiltonian are characterized by three quantum numbers—radial quantum number n, and two angular quantum numbers l and m.
- Let us denote energy eigenstates as the $|n, l, m\rangle$, and let their corresponding energy eigenvalues be the $E_{n,l,m}$.

Stark Effect - III

- According to (20), (21), and (23), change in energy of eigenstate characterized by quantum numbers n, l, m in presence of small electric field given by

$$\Delta E_{n,l,m} = e\,\mathcal{E}\,\langle n, l, m|z|n, l, m\rangle + e^2\,\mathcal{E}^2 \sum_{n',l',m' \neq n,l,m} \frac{|\langle n, l, m|z|n', l', m'\rangle|^2}{E_{n,l,m} - E_{n',l',m'}}. \quad (24)$$

- This energy-shift is known as Stark effect.

Selection Rules

- Sum on right-hand side of (24) seems very complicated.
- However, turns out that most of terms in sum are zero.
- Follows because matrix elements $\langle n, l, m|z|n', l', m'\rangle$ are zero for virtually all choices of two sets of quantum number, n, l, m and n', l', m'.
- Let us try to find a set of rules that determine when these matrix elements are non-zero.
- These rules are usually referred to as selection rules for problem in hand.

Selection Rules for m

- Recall that
$$L_z = x\,p_y - y\,p_x. \tag{25}$$
- It follows that
$$[L_z, z] = 0, \tag{26}$$
because z commutes with all operators on r.h.s. of (25).
- Thus,
$$\begin{aligned}\langle n, l, m|[L_z, z]|n', l', m'\rangle &= \langle n, l, m|L_z\,z - z\,L_z|n', l', m'\rangle \\ &= \hbar\,(m - m')\,\langle n, l, m|z|n', l', m'\rangle = 0,\end{aligned}$$
because $|n, l, m\rangle$ is eigenstate of L_z corresponding to eigenvalue $m\,\hbar$.
- Hence, matrix element $\langle n, l, m|z|n', l', m'\rangle$ is zero unless
$$m' = m. \tag{27}$$

Selection Rules for *l* - I

- Easily demonstrated that (Hw. 5, Q. 1)

$$[A\,B, C] = A\,[B, C] + [A, C]\,B, \tag{28}$$

$$[A, B\,C] = B\,[A, C] + [A, B]\,C. \tag{29}$$

- Definition of **L** combined with fundamental commutation relations for position and momentum yield (Hw. 5, Q. 2)

$$[L_i, x_j] = \mathrm{i}\,\hbar\,\epsilon_{ijk}\,x_k. \tag{30}$$

- Now,

$$[L^2, z] = [L_x^2, z] + [L_y^2, z],$$

  where use has been made of (26).

- So,

$$[L^2, z] = L_x\,[L_x, z] + [L_x, z]\,L_x + L_y\,[L_y, z] + [L_y, z]\,L_y,$$

  where use has been made of (28).

Selection Rules for l - II

- So,
$$[L^2, z] = \mathrm{i}\,\hbar\,(-L_x\,y - y\,L_x + L_y\,x + x\,L_y),$$
where use has been made of (30).
- So,
$$[L^2, z] = 2\,\mathrm{i}\,\hbar\,(L_y\,x - L_x\,y + \mathrm{i}\,\hbar\,z), \tag{31}$$
where use has again been made of (30).
- Finally,
$$[L^2, z] = 2\,\mathrm{i}\,\hbar\,(L_y\,x - y\,L_x) = 2\,\mathrm{i}\,\hbar\,(x\,L_y - L_x\,y), \tag{32}$$
because $-L_x\,y + \mathrm{i}\,\hbar\,z = -y\,L_x$ and $L_y\,x + \mathrm{i}\,\hbar\,z = x\,L_y$.

Selection Rules for l - III

- We can write

$$[L^2,[L^2,z]] = 2\,\mathrm{i}\,\hbar\,[L^2, L_y\,x - L_x\,y + \mathrm{i}\,\hbar\,z],$$

  where use has been made of (31).

- Hence,

$$\begin{aligned}[L^2,[L^2,z]] &= 2\,\mathrm{i}\,\hbar\left([L^2,L_y]\,x + L_y\,[L^2,x] - L_x\,[L^2,y] - [L^2,L_x]\,y\right.\\ &\qquad\left.+\,\mathrm{i}\,\hbar\,[L^2,z]\right)\\ &= 2\,\mathrm{i}\,\hbar\left(L_y\,[L^2,x] - L_x\,[L^2,y] + \mathrm{i}\,\hbar\,[L^2,z]\right),\end{aligned}$$

  where use has been made of (29) and fact that L^2 commutes with L_i.

Selection Rules for l - IV

- So we get

  $$[L^2,[L^2,z]] = -4\,\hbar^2\,L_y\,(y\,L_z - L_y\,z) + 4\,\hbar^2\,L_x\,(L_x\,z - x\,L_z) - 2\,\hbar^2\,(L^2\,z - z\,L^2),$$

  where use has been made of cyclic permutations of (32).
- Previous expression can be rearranged to give

  $$[L^2,[L^2,z]] = -\hbar^2\,\{4\,(L_x\,x + L_y\,y + L_z\,z)\,L_z - 4\,(L_x^2 + L_y^2 + L_z^2)\,z + 2\,(L^2\,z - z\,L^2)\},$$

  where use has been made of (26).

Selection Rules for *l* - V

- Hence, we obtain

$$[L^2,[L^2,z]] = -\hbar^2\,\left\{4\,(L_x\,x + L_y\,y + L_z\,z)\,L_z - 2\,(L^2\,z + z\,L^2)\right\}.$$

- It is easily demonstrated that (Hw. 5, Q. 3)

$$L_x\,x + L_y\,y + L_z\,z = 0.$$

- Hence, we get

$$[L^2,[L^2,z]] = 2\,\hbar^2\,(L^2\,z + z\,L^2).$$

- Finally, can expand previous equation to give

$$L^4\,z - 2\,L^2\,z\,L^2 + z\,L^4 - 2\,\hbar^2\,(L^2\,z + z\,L^2) = 0. \qquad (33)$$

Selection Rules for l - VI

- (33) yields

  $$\langle n, l, m| L^4 z - 2 L^2 z L^2 + z L^4 - 2 \hbar^2 (L^2 z + z L^2)|n', l', m\rangle = 0.$$

- Because $|n, l, m\rangle$ is eigenstate of L^2 corresponding to eigenvalue $l (l+1) \hbar^2$, previous expression yields

  $$\begin{aligned}\{ l^2 (l+1)^2 - 2 l (l+1) l' (l'+1) + l'^2 (l'+1)^2 \\ -2 l (l+1) - 2 l' (l'+1) \} \langle n, l, m|z|n', l', m\rangle = 0,\end{aligned}$$

  which reduces to

  $$(l + l' + 2) (l + l') (l - l' + 1) (l - l' - 1) \langle n, l, m|z|n', l', m\rangle = 0. \tag{34}$$

Selection Rules for l - VII

- According to (34), matrix element $\langle n, l, m|z|n', l', m\rangle$ vanishes unless $l = l' = 0$ or $l' = l \pm 1$. (Of course, factor $l + l' + 2$ can never be zero because l and l' can never be negative.)
- However, an $l = 0$ wavefunction is spherically symmetric. Follows, from symmetry, that matrix element $\langle n, l, m|z|n', l', m\rangle$ is zero when $l = l' = 0$.
- In conclusion, selection rule for l is that matrix element $\langle n, l, m|z|n', l', m\rangle$ is zero unless

$$l' = l \pm 1. \tag{35}$$

Quadratic Stark Effect

- Application of selection rules (27) and (35) to (24) yields

$$\Delta E_{n,l,m} = e^{2}\,\mathcal{E}^{2} \sum_{n',l'=l\pm 1} \frac{|\langle n,l,m|z|n',l',m\rangle|^{2}}{E_{n,l,m} - E_{n',l',m}}. \tag{36}$$

- Note that, according to selection rules, all of terms in (24) that vary linearly with electric field-strength vanish.
- Only those terms that vary quadratically with field-strength survive.
- Hence, this type of energy-shift of an atomic state in presence of a small electric field is known as quadratic Stark effect.

Electric Polarizability

- A neutral atom placed in a small electric field develops an induced electric dipole moment:

$$\mathbf{p} = \alpha\,\vec{\mathcal{E}}.$$

- Here, α is termed electric polarizability of atom.
- Energy change due to induced dipole moment is

$$\Delta E = -\int_0^{\vec{\mathcal{E}}} \mathbf{p}\cdot d\vec{\mathcal{E}}' = -\frac{1}{2}\,\alpha\,\mathcal{E}^{\,2}. \tag{37}$$

- Comparison between (36) and (37) yields following expression for polarizability of n, m, l state:

$$\alpha_{n,l,m} = 2\,e^{\,2} \sum_{n',l'=l\pm1} \frac{|\langle n,l,m|z|n',l',m\rangle|^{\,2}}{E_{n',l',m} - E_{n,l,m}}. \tag{38}$$

Non-Degenerate Perturbation Theory

- Unfortunately, (36) predicts infinite energy-shift if there exists some non-zero matrix element, $\langle n, l, m|z|n', l', m\rangle$, that couples two degenerate unperturbed energy eigenstates: i.e., if $\langle n, l, m|z|n', l', m\rangle \neq 0$ and $E_{n,l,m} = E_{n',l',m}$.
- Perturbation method breaks down completely in this situation.
- Conclude that (36) and (38) are only applicable to cases where coupled eigenstates are non-degenerate.
- For this reason, type of perturbation theory employed here is known as non-degenerate perturbation theory.
- Unperturbed eigenstates of hydrogenic atom have energies that only depend on radial quantum number, n.
- Follows that we can only apply previous results to $n = 1$ eigenstate (because for $n > 1$ there is coupling to degenerate eigenstates with same value of n but different values of l).

Polarizability of Hydrogenic Ground-State - I

- According to non-degenerate perturbation theory, polarizability of ground-state (i.e., $n = 1$) of a hydrogenic atom is given by

$$\alpha_{1,0,0} = 2\,e^{2} \sum_{n>1} \frac{|\langle 1,0,0|z|n,1,0\rangle|^{2}}{E_{n,0,0} - E_{1,0,0}}. \tag{39}$$

  Here, we have made use of fact that $E_{n,1,0} = E_{n,0,0}$.

- Sum in previous expression can be evaluated approximately by noting that

$$E_{n,0,0} = -\frac{Z^2\,e^{2}}{8\pi\epsilon_0\,a_0\,n^{2}},$$

  where a_0 is Bohr radius.

Polarizability of Hydrogenic Ground-State - II

- We can write

$$E_{n,0,0} - E_{1,0,0} \geq E_{2,0,0} - E_{1,0,0} = \frac{3}{4}\,\frac{Z^2\,e^2}{8\pi\epsilon_0\,a_0}.$$

- This implies that

$$\alpha_{1,0,0} < \frac{16}{3}\,4\pi\epsilon_0\,a_0 \sum_{n>1} |\langle 1,0,0|z|n,1,0\rangle|^2.$$

- However,

$$\begin{aligned}\sum_{n>1} |\langle 1,0,0|z|n,1,0\rangle|^2 &= \sum_{n>1}\langle 1,0,0|z|n,1,0\rangle\,\langle n,1,0|z|1,0,0\rangle\\ &= \sum_{n',l',m'}\langle 1,0,0|z|n',l',m'\rangle\,\langle n',l',m'|z|1,0,0\rangle\\ &= \langle 1,0,0|z^2|1,0,0\rangle = \frac{1}{3}\,\langle 1,0,0|r^2|1,0,0\rangle,\end{aligned}$$

where use has been made of selection rules, fact that $|n',l',m'\rangle$ form complete set, and fact that ground-state of hydrogenic atom is spherically symmetric.

Polarizability of Hydrogenic Ground-State - III

- In fact,

$$\langle 1,0,0|r^{2}|1,0,0\rangle = \frac{3\,a_0^2}{Z^2}.$$

- Hence, we conclude that

$$\alpha_{1,0,0} < \frac{16}{3}\,\frac{4\pi\epsilon_0\,a_0^3}{Z^4} \simeq 5.3\,\frac{4\pi\epsilon_0\,a_0^3}{Z^4}.$$

- Exact result (which can be obtained by solving Schrödinger's equation in parabolic coordinates) is

$$\alpha_{1,0,0} = \frac{9}{2}\,\frac{4\pi\,\epsilon_0\,a_0^3}{Z^4} = 4.5\,\frac{4\pi\epsilon_0\,a_0^3}{Z^4}. \tag{40}$$

Polarizability of Hydrogenic Ground-State - IV

- In principle, should be able to get result (40) by summing series (39) exactly.
- I find that

  $$\alpha_{1,0,0} = A_{1,0,0}\,\frac{4\pi\epsilon_0\,a_0^3}{Z^4},$$

  where

  $$A_{1,0,0} = \frac{1}{12}\sum_{n=2,\infty}\frac{n^5\,I_n^2}{(n^2-1)^2},$$

  and

  $$I_n = \int_0^\infty \rho^4\,\mathrm{e}^{-(1+n)\,\rho/2}\,L_{n-2}^3(\rho)\,d\rho.$$
- But numerical evaluation of $A_{1,0,0}$ gives 3.663 not 4.5! Extra credit opportunity!

Degenerate Perturbation Theory - I

- Let us investigate Stark effect in excited (i.e., $n > 1$) state of hydrogenic atom using non-degenerate perturbation theory.
- We can write
$$H_0 \left|n, l, m\right\rangle = E_n \left|n, l, m\right\rangle, \tag{41}$$
because energy eigenstates of unperturbed Hamiltonian only depend on quantum number n.
- Making use of selection rules (27) and (35), non-degenerate perturbation theory yields following expressions for perturbed energy levels and eigenstates [see (21) and (22)]:
$$E'_{n,l} = E_n + e_{n,l;n,l} + \sum_{n',l'=l\pm 1} \frac{\left|e_{n',l';n,l}\right|^2}{E_n - E_{n'}}, \tag{42}$$
$$\left|n, l, m\right\rangle = \left|n, l, m\right\rangle + \sum_{n',l'=l\pm 1} \frac{e_{n',l';n,l}}{E_n - E_{n'}} \left|n', l', m\right\rangle, \tag{43}$$
where
$$e_{n',l';n,l} = \langle n', l', m|H_S|n, l, m\rangle.$$

Degenerate Perturbation Theory - II

- Unfortunately, if $n > 1$ then summations in previous expressions are not well defined, because there exist non-zero matrix elements, $e_{n,l';n,l}$, that couple degenerate eigenstates: i.e., there exist non-zero matrix elements that couple states with same value of n, but different values of l.
- These particular matrix elements give rise to singular factors $1/(E_n - E_n)$ in summations.
- This does not occur if $n = 1$ because, in this case, selection rule $l' = l \pm 1$, and fact that $l = 0$ (because $0 \leq l < n$), only allow l' to take single value 1.
- Of course, there is no $n = 1$ state with $l' = 1$. Hence, there is only one coupled state corresponding to eigenvalue E_1.
- However, if $n > 1$ then there are multiple coupled states corresponding to eigenvalue E_n.

Degenerate Perturbation Theory - III

- Our problem would disappear if matrix elements of perturbed Hamiltonian corresponding to same value of n, but different values of l, were all zero: i.e.,

$$\langle n, l', m | H_S | n, l, m \rangle = \lambda_{n,l}\, \delta_{l,l'}. \tag{44}$$

- In this case, all of singular terms in (42) and (43) would reduce to zero.
- Unfortunately, previous equation is not satisfied in general.
- Fortunately, we can always redefine unperturbed eigenstates corresponding to eigenvalue E_n in such a manner that (44) is satisfied

Degenerate Perturbation Theory - IV

- Suppose that there are N_n coupled eigenstates belonging to eigenvalue E_n.
- Let us define N_n new states which are linear combinations of our N_n original degenerate eigenstates:

$$|n, l^{(1)}, m\rangle = \sum_{k=1,N_n} \langle n, k, m|n, l^{(1)}, m\rangle \, |n, k, m\rangle. \tag{45}$$

- Note that new states are also degenerate energy eigenstates of unperturbed Hamiltonian, H_0, corresponding to eigenvalue E_n.
- The $|n, l^{(1)}, m\rangle$ are chosen in such a manner that they are also eigenstates of perturbing Hamiltonian, H_S: i.e., they are simultaneous eigenstates of H_0 and H_S. Thus,

$$H_S \, |n, l^{(1)}, m\rangle = \lambda_{n,l} \, |n, l^{(1)}, m\rangle. \tag{46}$$

Degenerate Perturbation Theory - V

- The $|n, l^{(1)}, m\rangle$ are also chosen so as to be orthonormal: i.e.,

$$\langle n, l'^{(1)}, m | n, l^{(1)}, m\rangle = \delta_{l,l'}. \tag{47}$$

- It follows that

$$\langle n, l'^{(1)}, m | H_S | n, l^{(1)}, m\rangle = \lambda_{n,l}\, \delta_{l,l'}. \tag{48}$$

- Thus, if we use new eigenstates, instead of old ones, then we can employ (42) and (43) directly, because all of singular terms vanish.
- Only remaining difficulty is to determine new eigenstates in terms of original ones.

Degenerate Perturbation Theory - VI

- Now,

  $$\sum_{l=1,N_n} |n,l,m\rangle\langle n,l,m| \equiv 1,$$

  where 1 denotes identity operator in sub-space of all coupled unperturbed eigenstates corresponding to eigenvalue E_n.
- Using this completeness relation, eigenvalue equation (46) can be transformed into a straightforward matrix equation:

$$\sum_{l''=1,N_n} \langle n,l',m|H_S|n,l'',m\rangle\,\langle n,l'',m|n,l^{(1)},m\rangle$$

$$= \lambda_{n,l}\,\langle n,l',m|n,l^{(1)},m\rangle.$$

Degenerate Perturbation Theory - VII

- Matrix equation can be written more transparently as

  $$\mathbf{U}\,\mathbf{x} = \lambda\,\mathbf{x}, \tag{49}$$

  where elements of $N_n \times N_n$ Hermitian matrix $\mathbf{U}$ are

  $$U_{jk} = \langle n, j, m|H_S|n, k, m\rangle. \tag{50}$$

- (49) can be solved to give N_n eigenvalues $\lambda_{n,l}$ (for $l = 1$ to N_n), with N_n corresponding eigenvectors $\mathbf{x}_{n,l}$.
- Normalized eigenvectors specify weights of new eigenstates in terms of original eigenstates: i.e.,

  $$(\mathbf{x}_{n,l})_k = \langle n, k, m|n, l^{(1)}, m\rangle, \tag{51}$$

  for $k = 1$ to N_n.

Degenerate Perturbation Theory - VIII

- In our new scheme, (42) and (43) yield

$$E'_{n,l} = E_n + \lambda_{n,l} + \sum_{n' \neq n, l' = l \pm 1} \frac{\left| e_{n',l';n,l} \right|^2}{E_n - E_{n'}},$$

$$|n, l^{(1)\prime}, m\rangle = |n, l^{(1)}, m\rangle + \sum_{n' \neq n, l' = l \pm 1} \frac{e_{n',l';n,l}}{E_n - E_{n'}} \, |n, l^{(1)}, m\rangle.$$

- There are no singular terms in these expressions, because summations are over $n' \neq n$: i.e., they specifically exclude problematic, degenerate, unperturbed energy eigenstates corresponding to eigenvalue E_n.
- Note that first-order energy shifts are equivalent to eigenvalues of matrix equation (49).
- Type of perturbation theory just described is known as degenerate perturbation theory, for obvious reasons.

Linear Stark Effect - I

- Let us examine effect of an external electric field on energy levels of $n = 2$ states of a hydrogenic atom.
- There are four such states: an $l = 0$ state, usually referred to as $2S$, and three $l = 1$ states (with $m = -1, 0, 1$), usually referred to as $2\mathrm{P}$.
- All of these states possess same unperturbed energy,

$$E_{2,0,0} = -\frac{Z^2\, e^2}{32\pi\epsilon_0\, a_0}.$$

- As before, perturbing Hamiltonian is

$$H_S = e\,\mathcal{E}\,z.$$

Linear Stark Effect - II

- According to previously determined selection rules (i.e., $m' = m$, and $l' = l \pm 1$), perturbing Hamiltonian couples $|2,0,0\rangle$ and $|2,1,0\rangle$.
- Hence, non-degenerate perturbation theory breaks down when applied to these two states.
- On other hand, non-degenerate perturbation theory works fine for $|2,1,1\rangle$ and $|2,1,-1\rangle$ states, because these are not coupled to any other $n = 2$ states by perturbing Hamiltonian.

Linear Stark Effect - III

- In order to apply perturbation theory to $|2,0,0\rangle$ and $|2,1,0\rangle$ states, we have to solve matrix eigenvalue equation

$$\mathbf{U}\,\mathbf{x} = \lambda\,\mathbf{x},$$

where $\mathbf{U}$ is matrix of matrix elements of H_1 between states.

- Thus,

$$\mathbf{U} = e\,\mathcal{E}\begin{pmatrix} 0, & \langle 2,0,0|z|2,1,0\rangle \\ \langle 2,1,0|z|2,0,0\rangle, & 0 \end{pmatrix},$$

where rows and columns correspond to $|2,0,0\rangle$ and $|2,1,0\rangle$, respectively.

Linear Stark Effect - IV

- Here, have again made use of selection rules, which tell us that matrix element of z between two hydrogenic atom states is zero unless states possess l quantum numbers that differ by unity.
- It is easily demonstrated, from exact forms of 2S and 2P wavefunctions, that

$$\langle 2,0,0|z|2,1,0\rangle = \langle 2,1,0|z|2,0,0\rangle = -\frac{3\,a_0}{Z}.$$

Linear Stark Effect - V

- Can be seen, by inspection, that eigenvalues of **U** are $\lambda_1 = 3\, e\, a_0\, \mathcal{E}/Z$ and $\lambda_2 = -3\, e\, a_0\, \mathcal{E}/Z$.
- Corresponding normalized eigenvectors are

$$\mathbf{x}_1 = \begin{pmatrix} -1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix},$$

$$\mathbf{x}_2 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}.$$

Linear Stark Effect - VI

- Thus, simultaneous eigenstates of H_0 and H_S take form

$$|1\rangle = \frac{|2,0,0\rangle - |2,1,0\rangle}{\sqrt{2}},$$
$$|2\rangle = \frac{|2,0,0\rangle + |2,1,0\rangle}{\sqrt{2}}.$$

- In absence of an external electric field, both of these states possess same energy, $E_{2,0,0}$.
- First-order energy shifts induced by an external electric field are given by

$$\Delta E_1 = +\frac{3\,e\,a_0\,\mathcal{E}}{Z},$$
$$\Delta E_2 = -\frac{3\,e\,a_0\,\mathcal{E}}{Z}.$$

Linear Stark Effect - VII

- Thus, in presence of an electric field, energies of states 1 and 2 are shifted upwards and downwards, respectively, by an amount $3\,e\,a_0\,\mathcal{E}/Z$.
- These states are orthogonal linear combinations of original $|2,0,0\rangle$ and $|2,1,0\rangle$ states.
- Note that energy shifts are linear in electric field-strength, so this effect—which is known as linear Stark effect—is much larger than quadratic Stark effect.
- Note, also, that energies of $|2,1,1\rangle$ and $|2,1,-1\rangle$ states are not affected by electric field to first order.
- Of course, to second order energies of these states are shifted by an amount that depends on square of electric field-strength.

Relativistic Correction - I

- According to special relativity, kinetic energy (i.e., difference between total energy and rest mass energy) of a particle of rest mass m and momentum p is

$$K = \sqrt{p^2\,c^2 + m^2\,c^4} - m\,c^2.$$

- In non-relativistic limit $p \ll m\,c$, can expand square-root in previous expression to give

$$K = \frac{p^2}{2\,m}\left[1 - \frac{1}{4}\left(\frac{p}{m\,c}\right)^2 + \mathcal{O}\left(\frac{p}{m\,c}\right)^4\right].$$

- Hence,

$$K \simeq \frac{p^2}{2\,m} - \frac{p^4}{8\,m^3\,c^2}.$$

- Recognize first term on right-hand side of previous equation as standard non-relativistic expression for kinetic energy.
- Second term is lowest-order relativistic correction to kinetic energy.

Relativistic Correction - II

- Consider effect of relativistic correction on energy levels of a hydrogenic atom.
- Perturbing Hamiltonian takes form

$$H_R = -\frac{p^4}{8\, m_e^3\, c^2}.$$

- According to first-order perturbation theory, lowest-order relativistic correction to energy of a hydrogenic atom state characterized by standard quantum numbers n, l, and m is

$$\Delta E_{n,l,m} = \langle n, l, m | H_R | n, l, m\rangle = -\frac{1}{8\, m_e^3\, c^2}\, \langle n, l, m | p^4 | n, l, m\rangle$$

$$= -\frac{1}{8\, m_e^3\, c^2}\, \langle n, l, m | p^2\, p^2 | n, l, m\rangle.$$

Relativistic Correction - III

- However, Schrödinger's equation for a unperturbed hydrogenic atom can be written

$$p^2\,|n,l,m\rangle = 2\,m_e\,(E_n - V)\,|n,l,m\rangle,$$

  where $V = -Z\,e^2/(4\pi\epsilon_0\,r)$.
- Because p^2 is Hermitian operator, follows that

$$\begin{aligned}\Delta E_{n,l,m} &= -\frac{1}{2\,m_e\,c^2}\,\langle n,l,m|(E_n - V)^2|n,l,m\rangle\\ &= -\frac{1}{2\,m_e\,c^2}\left(E_n^2 - 2\,E_n\,\langle n,l,m|V|n,l,m\rangle + \langle n,l,m|V^2|n,l,m\rangle\right)\\ &= -\frac{1}{2\,m_e\,c^2}\left[E_n^2 + 2\,E_n\left(\frac{Z\,e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{Z\,e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right].\end{aligned}$$

Relativistic Correction - IV

- However,

$$E_n = -\frac{Z^2\, e^2}{8\pi\epsilon_0\, a_0\, n^2},$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{Z}{a_0\, n^2},$$

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{Z^2}{a_0^2\, n^3\,(l+1/2)}.$$

- Hence, we obtain

$$\Delta E_{n,l,m} = E_n\,\frac{Z^2\,\alpha^2}{n^2}\left(\frac{n}{l+1/2}-\frac{3}{4}\right), \tag{52}$$

where $\alpha = e^2/(4\pi\epsilon_0\,\hbar\,c) \simeq 1/137$ is dimensionless fine structure constant.

Darwin Term - I

- According to Dirac's relativistic electron theory, there is additional relativistic correction to Hamiltonian of electron in hydrogenic atom that takes form

$$H_D = \frac{Z\,e^2\,\hbar^2}{8\,\epsilon_0\,m_e^2\,c^2}\,\delta^3(\mathbf{x}).$$

- This correction known as Darwin term.
- According to first-order perturbation theory, correction to energy of a hydrogenic atom state characterized by standard quantum numbers n, l, and m due to Darwin term is

$$\Delta E_{n,l,m} = \langle n, l, m|H_D|n, l, m\rangle = \frac{Z\,e^2\,\hbar^2}{8\,\epsilon_0\,m_e^2\,c^2}\,|\psi_{n,l,m}(\mathbf{0})|^2.$$

Darwin Term - II

- However,

$$|\psi_{n,l,m}(\mathbf{0})| = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{n\, a_0} \right)^{3/2} \delta_{l,0}\, \delta_{m,0}.$$

- Hence, we obtain

$$\Delta E_{n,l,m} = -E_n \, \frac{Z^2 \, \alpha^2}{n} \, \delta_{l,0}. \qquad (53)$$

- Note that Darwin term only modifies energies of $l = 0$ states.

Spin-Orbit Coupling - I

- Electron in a hydrogenic atom experiences an electric field

$$\mathbf{E} = \frac{Z\,e\,\mathbf{x}}{4\pi\epsilon_0\, r^3}$$

  due to charge on nucleus.

- However, according to electromagnetic theory, a non-relativistic particle moving in an electric field $\mathbf{E}$ with velocity $\mathbf{v}$ also experiences an effective magnetic field

$$\mathbf{B} = -\frac{\mathbf{v}\times\mathbf{E}}{c^2}.$$

- Recall, that an electron possesses a magnetic moment

$$\boldsymbol{\mu} = -\frac{e}{m_e}\,\mathbf{S}$$

  due to its spin angular momentum, $\mathbf{S}$.

Spin-Orbit Coupling - II

- Expect additional contribution to Hamiltonian of a hydrogenic atom of form

$$\begin{aligned} H_{LS} &= -\boldsymbol{\mu}\cdot\mathbf{B} \\ &= -\frac{Z\,e^2}{4\pi\epsilon_0\,m_e\,c^2\,r^3}\,\mathbf{v}\times\mathbf{x}\cdot\mathbf{S} \\ &= \frac{Z\,e^2}{4\pi\epsilon_0\,m_e^2\,c^2\,r^3}\,\mathbf{L}\cdot\mathbf{S}, \end{aligned}$$

  where $\mathbf{L} = m_e\,\mathbf{x}\times\mathbf{v}$ is electron's orbital angular momentum.

- This effect known as spin-orbit coupling.
- Previous expression is too large, by a factor 2, due to obscure relativistic effect known as Thomas precession.
- Hence, true spin-orbit correction to Hamiltonian is

$$H_{LS} = \frac{Z\,e^2}{8\pi\epsilon_0\,m_e^2\,c^2\,r^3}\,\mathbf{L}\cdot\mathbf{S}. \tag{54}$$

Spin-Orbit Coupling - III

- Now
  $$\mathbf{J} = \mathbf{L} + \mathbf{S}$$
  is total angular momentum of electron.
- Hence,
  $$J^2 = L^2 + S^2 + 2\,\mathbf{L}\cdot\mathbf{S},$$
  giving
  $$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\,(J^2 - L^2 - S^2).$$

Spin-Orbit Coupling - IV

- Recall that while J^2 commutes with both L^2 and S^2, it does not commute with either L_z or S_z.
- Follows that perturbing Hamiltonian (54) also commutes with both L^2 and S^2, but does not commute with either L_z or S_z.
- Hence, simultaneous eigenstates of unperturbed and perturbing Hamiltonians are simultaneous eigenstates of L^2, S^2, and J^2.
- Important to know this because we can only safely apply perturbation theory to simultaneous eigenstates of unperturbed and perturbing Hamiltonians.

Spin-Orbit Coupling - V

- Let $|l, s; j, m_j\rangle$ be a simultaneous eigenstate of L^2, S^2, J^2, and J_z corresponding to eigenvalues

$$
\begin{aligned}
L^2\,|l, s; j, m_j\rangle &= l\,(l+1)\,\hbar^2\,|l, s; j, m_j\rangle,\\
S^2\,|l, s; j, m_j\rangle &= s\,(s+1)\,\hbar^2\,|l, s; j, m_j\rangle,\\
J^2\,|l, s; j, m_j\rangle &= j\,(j+1)\,\hbar^2\,|l, s; j, m_j\rangle,\\
J_z\,|l, s; j, m_j\rangle &= m_j\,\hbar\,|l, s; j, m_j\rangle.
\end{aligned}
$$

Spin-Orbit Coupling - V

- According to first-order perturbation theory, energy-shift induced in simultaneous eigenstate by spin-orbit coupling is

$$
\begin{aligned}
\Delta E_{l,1/2;j,m_j} &= \langle l, 1/2; j, m_j | H_{LS} | l, 1/2; j, m_j \rangle \\
&= \frac{Z\, e^2}{16\pi\, \epsilon_0\, m_e^2\, c^2} \left\langle 1, 1/2; j, m_j \left| \frac{J^2 - L^2 - S^2}{r^3} \right| l, 1/2; j, m_j \right\rangle \\
&= \frac{Z\, e^2\, \hbar^2}{16\pi\, \epsilon_0\, m_e^2\, c^2} \left[j\,(j+1) - l\,(l+1) - 3/4 \right] \left\langle \frac{1}{r^3} \right\rangle .
\end{aligned}
$$

- Here, we have made use of fact that $s = 1/2$ for an electron.
- Note that energy-shift is zero for $l = 0$ state (because $j = 1/2$). More directly, $\mathbf{L} = \mathbf{0}$ in an $l = 0$ state, and perturbing Hamiltonian is proportional to $\mathbf{L} \cdot \mathbf{S}$.

Spin-Orbit Coupling - VI

- For an $l > 0$ state,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3\, n^3\, l\,(l+1/2)\,(l+1)}.$$

- Hence,

$$\Delta E_{l,1/2;j,m_j} = E_n\, \frac{Z^2\,\alpha^2}{n^2} \left\{ \frac{n\,[3/4 + l\,(l+1) - j\,(j+1)]}{2\,l\,(l+1/2)\,(l+1)} \right\} (1-\delta_{l,0}). \tag{55}$$

- Note that $j = l \pm 1/2$ for an $l > 0$ state.

Fine Structure - I

- Have found three perturbing Hamiltonians that all give rise to energy-shifts of nth energy level of a hydrogenic atom that are similar in magnitude.
- Perturbing Hamiltonians are that due to relativistic correction, H_R, that due to Darwin term, H_D, and that due to spin-orbit coupling, H_{LS}.
- Corresponding energy-shifts are given in (52), (53), and (55), respectively.
- Let us sum energy-shifts. There are three cases to consider.
    1. $l = 0$ and $j = 1/2$.
    2. $l > 0$ and $j = l - 1/2$.
    3. $l > 0$ and $j = l + 1/2$.

Fine Structure - II

- For $l = 0$, $j = 1/2$ case, find

$$\begin{aligned} \Delta E_{n,j} &= E_n \frac{Z^2 \alpha^2}{n^2} \left[\left(2\,n - \frac{3}{4} \right) - n + 0 \right] \\ &= E_n \frac{Z^2 \alpha^2}{n^2} \left(n - \frac{3}{4} \right) \\ &= E_n \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{j + 1/2} - \frac{3}{4} \right). \end{aligned} \tag{56}$$

Fine Structure - III

- For $l > 0$, $j = l - 1/2$ case, find

$$
\begin{aligned}
\Delta E_{n,j} &= E_n \frac{Z^2\,\alpha^2}{n^2}\left[\left(\frac{n}{l+1/2}-\frac{3}{4}\right)+0+\left(\frac{n\,[3/4+l\,(l+1)-j\,(j+1)]}{2\,l\,(l+1/2)\,(l+1)}\right)\right. \\
&= E_n \frac{Z^2\,\alpha^2}{n^2}\left[\frac{n\,[3/4+3\,l\,(l+1)-j\,(j+1)]}{2\,l\,(l+1/2)\,(l+1)}-\frac{3}{4}\right] \\
&= E_n \frac{Z^2\,\alpha^2}{n^2}\left(\frac{n\,[2\,(j+1)\,(j+3/2)]}{2\,(j+1/2)\,(j+1)\,(j+3/2)}-\frac{3}{4}\right) \\
&= E_n \frac{Z^2\,\alpha^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right). \qquad (57)
\end{aligned}
$$

Fine Structure - IV

- For $l > 0$, $j = l + 1/2$ case, find

$$\begin{aligned}
\Delta E_{n,j} &= E_n \frac{Z^2 \alpha^2}{n^2}\left[\left(\frac{n}{l+1/2} - \frac{3}{4}\right) + 0 + \left(\frac{n\,[3/4 + l\,(l+1) - j\,(j+1)]}{2\,l\,(l+1/2)\,(l+1)}\right)\right. \\
&= E_n \frac{Z^2 \alpha^2}{n^2}\left[\frac{n\,[3/4 + 3\,l\,(l+1) - j\,(j+1)]}{2\,l\,(l+1/2)\,(l+1)} - \frac{3}{4}\right] \\
&= E_n \frac{Z^2 \alpha^2}{n^2}\left(\frac{n\,[2\,(j-1/2)\,j]}{2\,(j-1/2)\,j\,(j+1/2)} - \frac{3}{4}\right) \\
&= E_n \frac{Z^2 \alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right). \qquad (58)
\end{aligned}$$

Fine Structure - V

- In all three cases, (56), (57), and (58), we find that

$$\Delta E_{n,j} = E_n \frac{Z^2\,\alpha^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right). \tag{59}$$

- This modification of energy levels of a hydrogenic atom due to a combination of relativity and spin-orbit coupling is known as fine structure.

Fine Structure - VI

- Note that if we solve energy eigenstate problem for a hydrogenic atom using relativistic quantum mechanics (i.e., Dirac equation), we get exact result

$$\frac{E_{n,j}}{m_e\,c^2} = \left\{1 + \frac{Z^2\,\alpha^2}{(n - j - 1/2 + [(j+1/2)^2 - Z^2\,\alpha^2]^{1/2})^2}\right\}^{-1/2}.$$

- Expansion in small parameter $Z\,\alpha$ yields

$$\frac{E_{n,j}}{m_e\,c^2} = 1 - \frac{Z^2\,\alpha^2}{2\,n^2} - \frac{Z^4\,\alpha^4}{2\,n^4}\left(\frac{n}{j+1/2} - \frac{3}{4}\right) + \mathcal{O}(Z\,\alpha)^6.$$

- First term on r.h.s. of previous expression corresponds to electron rest mass energy.
- Second term is standard non-relativistic expression for energy levels of hydrogenic atom.
- Third term is fine-structure correction to these energy levels.

Fine Structure - VII

- Conventional to refer to energy eigenstates of a hydrogenic atom that are also simultaneous eigenstates of J^2 as nL_j states, where n is radial quantum number, $L = (S, P, D, F, \cdots)$ as $l = (0, 1, 2, 3, \cdots)$, and j is total angular momentum quantum number.
- Let us examine effect of fine structure energy-shift (59) on these eigenstates for $n = 1, 2$ and 3.

Fine Structure - VIII

- For $n = 1$, in absence of fine structure, there are two degenerate $1S_{1/2}$ states.
- According to (59), fine-structure induced energy-shifts of these two states are same.
- Hence, fine structure does not break degeneracy of two $1S_{1/2}$ states of hydrogenic atom.

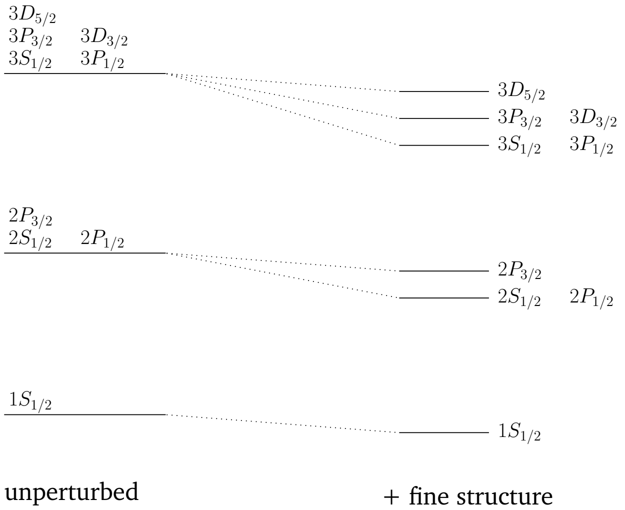
Fine Structure - IX

- For $n = 2$, in absence of fine structure, there are two $2S_{1/2}$ states, two $2P_{1/2}$ states, and four $2P_{3/2}$ states, all of which are degenerate.
- According to (59), fine-structure induced energy-shifts of $2S_{1/2}$ and $2P_{1/2}$ states are same as one another, but are different from induced energy-shift of $2P_{3/2}$ states.
- Hence, fine structure does not break degeneracy of $2S_{1/2}$ and $2P_{1/2}$ states of hydrogenic atom, but does break degeneracy of these states relative to $2P_{3/2}$ states.

Fine Structure - X

-
- For $n = 3$, in absence of fine structure, there are two $3S_{1/2}$ states, two $3P_{1/2}$ states, four $3P_{3/2}$ states, four $3D_{3/2}$ states, and six $3D_{5/2}$ states, all of which are degenerate.
- According to (59), fine structure breaks these states into three groups: $3S_{1/2}$ and $3P_{1/2}$ states, $3P_{3/2}$ and $3D_{3/2}$ states, and $3D_{5/2}$ states.
- Effect of fine-structure energy-shift on $n = 1$, 2, and 3 energy states of a hydrogenic atom is illustrated on next slide.

Fine Structure - XI



Zeeman Effect - I

- Consider a hydrogenic atom placed in a uniform z-directed external magnetic field of strength $\mathbf{B} = B\,\mathbf{e}_z$.
- Modification to Hamiltonian of system is

  $$H_Z = -\boldsymbol{\mu}\cdot\mathbf{B},$$

  where

  $$\boldsymbol{\mu} = -\frac{e}{2\,m_e}\,(\mathbf{L} + 2\,\mathbf{S})$$

  is total electron magnetic moment, including both orbital and spin contributions.
- Thus,

  $$H_Z = \frac{e\,B}{2\,m_e}\,(L_z + 2\,S_z). \tag{60}$$

Zeeman Effect - II

- Suppose that applied magnetic field is much weaker than atom's internal magnetic field.
- Internal magnetic field in hydrogen atom specified by

$$\mathbf{B}_{\rm int} = \frac{\mathbf{v}\times\mathbf{E}}{c^2},$$

$$\mathbf{E} = \frac{e\,\mathbf{x}}{4\pi\epsilon_0\,r^3}.$$

- But, $v \sim \alpha\,c$ and $r \sim a_0$, so we get

$$B_{\rm int} \sim \frac{1}{2}\,\alpha^4\,\frac{m_e\,c^2}{\mu_B} = 12.5\,{\rm T}.$$

- Here,

$$\mu_B = \frac{e\,\hbar}{2\,m_e} = 5.788\times 10^{-5}\,{\rm eV/T}$$

  is known as Bohr magnetron.
- Hence, weak field ordering valid as long as applied magnetic field strength is much less than 12.5 T.

Zeeman Effect - III

- In weak field limit, can treat H_Z as small perturbation acting on simultaneous eigenstates of unperturbed Hamiltonian and fine-structure Hamiltonian. (Because $|\mathbf{B}_{\rm int}| \gg |\mathbf{B}|$ implies that $H_{LS} \gg H_Z$.)
- These states are simultaneous eigenstates of L^2, S^2, J^2, and J_z. (Because energy depends on quantum number j, but is independent of l or m.)
- Hence, from standard perturbation theory, first-order energy-shift induced by a weak external magnetic field is

$$\begin{aligned}\Delta E_{l,1/2;j,m_j} &= \langle l, 1/2; j, m_j|H_Z|l, 1/2; j, m_j\rangle \\ &= \frac{e\,B}{2\,m_e}\,(m_j\,\hbar + \langle l, 1/2; j, m_j|S_z|l, 1/2; j, m_j\rangle),\end{aligned} \tag{61}$$

because $J_z = L_z + S_z$.

Zeeman Effect - IV

- However,

$$|j, m_j\rangle = \left(\frac{j+m_j}{2\,l+1}\right)^{1/2} |m_j - 1/2, 1/2\rangle' + \left(\frac{j-m_j}{2\,l+1}\right)^{1/2} |m_j + 1/2, -1/2\rangle' \qquad (62)$$

  when $j = l + 1/2$, and

$$|j, m_j\rangle = \left(\frac{j+1-m_j}{2\,l+1}\right)^{1/2} |m_j - 1/2, 1/2\rangle' - \left(\frac{j+1+m_j}{2\,l+1}\right)^{1/2} |m_j + 1/2, -1/2\rangle' \qquad (63)$$

  when $j = l - 1/2$.

- Here, the $|m, m_s\rangle'$ are simultaneous eigenstates of L^2, S^2, L_z, and S_z, whereas the $|j, m_j\rangle$ are simultaneous eigenstates of L^2, S^2, J^2, and J_z.

Zeeman Effect - V

- In particular,

$$S_z\,|m,\pm 1/2\rangle' = \pm\frac{\hbar}{2}\,|m,\pm 1/2\rangle'. \tag{64}$$

- Follows from (62) and (64) that

$$\begin{aligned}\langle l,1/2;j,m_j|S_z|l,1/2;j,m_j\rangle &= \langle j,m_j|S_z|j,m_j\rangle\\ &= \frac{\hbar}{2}\left(\frac{j+m_j}{2\,l+1}\right)-\frac{\hbar}{2}\left(\frac{j-m_j}{2\,l+1}\right)\\ &= \frac{m_j\,\hbar}{2\,l+1}, \end{aligned}\tag{65}$$

when $j = l + 1/2$.

Zeeman Effect - VI

- Likewise, follows from (63) and (64) that

$$\begin{aligned}\langle l, 1/2; j, m_j|S_z|l, 1/2; j, m_j\rangle &= \langle j, m_j|S_z|j, m_j\rangle \\ &= \frac{\hbar}{2}\left(\frac{j+1-m_j}{2\,l+1}\right) - \frac{\hbar}{2}\left(\frac{j+1+m_j}{2\,l+1}\right) \\ &= -\frac{m_j\,\hbar}{2\,l+1}, \qquad (66)\end{aligned}$$

when $j = l - 1/2$.

Zeeman Effect - VII

- Follows from (61), (65), and (66) that

$$\Delta E_{l,1/2;j,m_j} = \mu_B\, B\, m_j \left(1 \pm \frac{1}{2\,l+1}\right), \tag{67}$$

  where $\pm$ signs correspond to $j = l \pm 1/2$.
- Induced energy-shift when a hydrogenic atom is placed in an external magnetic field known as Zeeman effect.

Zeeman Effect - VIII

- Quantum number m_j takes values differing by unity in range $-j$ to j.
- Follows from (67) that Zeeman effect splits degenerate states characterized by $j = l + 1/2$ into $2\,j + 1$ equally spaced states of interstate spacing

$$\Delta E_{j=l+1/2} = \mu_B\,B\left(\frac{2\,l+2}{2\,l+1}\right). \tag{68}$$

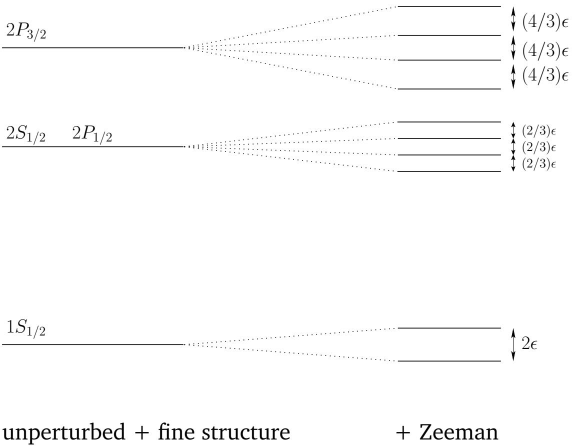
- Zeeman effect splits degenerate states characterized by $j = l - 1/2$ into $2\,j + 1$ equally spaced states of interstate spacing

$$\Delta E_{j=l-1/2} = \mu_B\,B\left(\frac{2\,l}{2\,l+1}\right). \tag{69}$$

Zeeman Effect - IX

- In presence of weak external magnetic field, two degenerate $1S_{1/2}$ states of hydrogenic atom are split by $2\,\mu_B\,B$.
- Four degenerate $2S_{1/2}$ and $2P_{1/2}$ states are split by $(2/3)\,\mu_B\,B$, whereas four degenerate $2P_{3/2}$ states are split by $(4/3)\,\mu_B\,B$.

Zeeman Effect - X



- Here, $\epsilon = \mu_B B$.

Zeeman Effect - XI

- We need to check that Zeeman Hamiltonian does not couple degenerate simultaneous eigenstates of unperturbed and fine-structure Hamiltonians, because, if it does, our perturbation expansion will break down at second order.
- Simultaneous eigenstates of unperturbed and fine-structure Hamiltonians are the $|l, 1/2; j, m_j\rangle$.
- $|l, 1/2; j, m_j\rangle$ and $|l', 1/2; j', m_j'\rangle$ are degenerate if $j = j'$.
- So we need to prove that all matrix elements of form

$$\langle l, 1/2; j, m_j | H_Z | l', 1/2; j, m_j' \rangle \tag{70}$$

are zero, unless $l = l'$ and $m_j = m_j'$.

Zeeman Effect - XII

- In fact, H_Z commutes with L^2 and J_z. Hence, H_Z, L^2, and J_z have simultaneous (orthonormal) eigenstates, which implies that matrix elements of form (70) are indeed zero if $l \neq l'$ or $m_j \neq m_j'$. (This is true even if $j \neq j'$.)
- Note that H_Z does not commute with J^2. Hence, matrix elements of form

  $$\langle l, 1/2; j, m_j | H_Z | l, 1/2; j', m_j \rangle$$

  can be non-zero when $j \neq j'$. However, this is not a problem because coupled states are non-degenerate.

Zeeman Effect - XIII

- Because the $|l, 1/2; j, m_j\rangle$ are not simultaneous eigenstates of unperturbed and perturbing Hamiltonians, (68) and (69) can only be regarded as expectation values of magnetic-field-induced energy-shifts.
- However, as long as external magnetic field is much weaker than internal magnetic field, these expectation values are almost identical to actual measured values of energy-shifts.

Hyperfine Structure - I

- Proton in a hydrogen atom is spin one-half charged particle, and therefore possesses a magnetic moment.
- In fact,

  $$\boldsymbol{\mu}_p = \frac{g_p\, e}{2\, m_p}\, \mathbf{S}_p,$$

  where $\boldsymbol{\mu}_p$ is proton magnetic moment, $\mathbf{S}_p$ is proton spin, and proton gyromagnetic ratio g_p is found experimentally to take value 5.59.
- Note that magnetic moment of proton is much smaller (by a factor of order m_e/m_p) than that of electron.

Hyperfine Structure - II

- According to classical electromagnetism, proton's magnetic moment generates a magnetic field of form

  $$\mathbf{B} = \frac{\mu_0}{4\pi\, r^3}\,\left[3\,(\boldsymbol{\mu}_p\cdot\mathbf{e}_r)\,\mathbf{e}_r - \boldsymbol{\mu}_p\right] + \frac{2\,\mu_0}{3}\,\boldsymbol{\mu}_p\,\delta^3(\mathbf{x}),$$

  where $\mathbf{e}_r = \mathbf{x}/r$.
- Can understand the origin of delta-function term in previous expression by thinking of proton as a tiny current loop centered on origin.
- All magnetic field-lines generated by loop must pass through loop.
- If size of loop goes to zero then field will be infinite at origin, and this contribution is represented by delta-function term.
- To be slightly more exact, delta-function ensures that divergence of field is zero everywhere, even at origin.

Hyperfine Structure - III

- Hamiltonian of electron in magnetic field generated by proton is
$$H_{hf} = -\boldsymbol{\mu}_e \cdot \mathbf{B},$$
where
$$\boldsymbol{\mu}_e = -\frac{e}{m_e}\,\mathbf{S}_e.$$
- Here, $\boldsymbol{\mu}_e$ is electron magnetic moment, and $\mathbf{S}_e$ is electron spin.
- Thus, perturbing Hamiltonian is written
$$H_{hf} = \frac{\mu_0\, g_p\, e^2}{8\pi\, m_p\, m_e}\,\frac{3\,(\mathbf{S}_p \cdot \mathbf{e}_r)\,(\mathbf{S}_e \cdot \mathbf{e}_r) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} + \frac{\mu_0\, g_p\, e^2}{3\, m_p\, m_e}\,\mathbf{S}_p \cdot \mathbf{S}_e\, \delta^3(\mathbf{x}).$$
- Note that, because we have neglected coupling between proton spin and magnetic field generated by electron's orbital motion, previous expression is only valid for $l = 0$ states.

Hyperfine Structure - IV

- According to first-order perturbation theory, energy-shift induced by spin-spin coupling between proton and electron is expectation value of perturbing Hamiltonian.
- Hence,

$$\Delta E = \frac{\mu_0\, g_p\, e^2}{8\pi\, m_p\, m_e}\left\langle\frac{3\,(\mathbf{S}_p\cdot\mathbf{e}_r)\,(\mathbf{S}_e\cdot\mathbf{e}_r)-\mathbf{S}_p\cdot\mathbf{S}_e}{r^3}\right\rangle + \frac{\mu_0\, g_p\, e^2}{3\, m_p\, m_e}\,\langle\mathbf{S}_p\cdot\mathbf{S}_e\rangle\,|\psi(\mathbf{0})|^2.$$

- For ground-state of hydrogen, which is spherically symmetric, first term in previous expression vanishes by symmetry.

Hyperfine Structure - V

- Easily demonstrated that $|\psi_{1,0,0}(\mathbf{0})|^2 = 1/(\pi\, a_0^3)$.
- Thus, we obtain

$$\Delta E = \frac{\mu_0\, g_p\, e^2}{3\pi\, m_p\, m_e\, a_0^3}\,\langle \mathbf{S}_p\cdot\mathbf{S}_e\rangle.$$

- Let

$$\mathbf{S} = \mathbf{S}_e + \mathbf{S}_p$$

  be total spin.
- We can show that

$$\mathbf{S}_p\cdot\mathbf{S}_e = \frac{1}{2}\,(S^2 - S_e^2 - S_p^2).$$

Hyperfine Structure - VI

- Thus, simultaneous eigenstates of perturbing Hamiltonian and main Hamiltonian are simultaneous eigenstates of S_e^2, S_p^2, and S^2.
- However, both proton and electron are spin one-half particles. When two spin one-half particles are combined (in absence of orbital angular momentum) net state has either spin 1 or spin 0.
- There are three spin 1 states, known as triplet states, and a single spin 0 state, known as singlet state.

Hyperfine Structure - VII

- For all states, eigenvalues of S_e^2 and S_p^2 are $(3/4)\,\hbar^2$.
- Eigenvalue of S^2 is 0 for singlet state, and $2\,\hbar^2$ for triplet states.
- Hence,

  $$\langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle = -\frac{3}{4}\,\hbar^2$$

  for singlet state, and

  $$\langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle = \frac{1}{4}\,\hbar^2$$

  for triplet states.

Hyperfine Structure - VIII

- Follows that spin-spin coupling breaks degeneracy of two $1S_{1/2}$ states in hydrogen, lifting energy of triplet configuration, and lowering that of singlet.
- This splitting is known as hyperfine structure.
- Net energy difference between singlet and triplet states is

$$\Delta E = \frac{8}{3}\, g_p\, \frac{m_e}{m_p}\, \alpha^2\, E_0 = 5.88 \times 10^{-6}\,\mathrm{eV},$$

where $E_0 = 13.6\,\mathrm{eV}$ is (magnitude of) ground-state energy.

Hyperfine Structure - IX

- If we convert previous energy into a wavelength then we obtain

$$\lambda = 21.1\,\mathrm{cm}.$$

- This is wavelength of radiation emitted by a hydrogen atom which is collisionally excited from singlet to triplet state, and then decays back to lower energy singlet state.
- 21 cm line is famous in radio astronomy because it was used to map out spiral structure of our galaxy in 1950's.