Problems Chapter 14

Quantum Mechanics
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Problem 1

Compute in dipole approximation the lifetime of the excited state 2p of hydrogen atom. Why does spin not affect the computation?

Solution

In the first part of the problem we neglect spin.

A 2p state has angular momentum 1 and parity -1, the ground state 1s has angular momentum 0 and parity +1, the transition 2p→1s is allowed (electric dipole transition).

In the text (see also the complements to chap.14) it is shown that the amplitude for a transition b→a+γ is, in dipole approximation

$$\mathcal{M} = -\frac{e}{c}\langle a;\, f \mid \mathbf{p}\cdot\mathbf{A}[x] \mid b;\, i\rangle \simeq -i\,\frac{\omega_{ba}}{c}\,\mathbf{d}_{ab}\,\langle f \mid \mathbf{A}[0] \mid i\rangle . \tag{1.1}$$

i, f are the initial and final states of the radiation field. b,a the initial and final states of the atom. In the process 2p→1s+γ the relevant radiation matrix element is the one for the creation of a photon, with momentum **k** and polarization λ, starting from the vacuum:

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$$\langle \mathbf{k},\, \lambda \mid A[0] \mid 0\rangle = \sqrt{\frac{4\,\pi\,c^2\,\hbar}{2\,\omega}}\;\epsilon^*_\lambda\ . \tag{1.2}$$

The factors in (2) takes care of our normalization convention for the photon states:

$$\left\langle \mathbf{k},\, \lambda \,\middle|\, \mathbf{k}',\, \lambda' \right\rangle = (2\,\pi)^3\,\delta^3\left(\mathbf{k}-\mathbf{k}'\right)\,\delta_{\lambda,\lambda'}\ ; \tag{1.3}$$

and of the CGS units.

The Fermi golden rule gives directly the probability of the decay per unit time:

$$d\Gamma = \frac{2\,\pi}{\hbar}\,\frac{\omega_{ba}^2}{c^2}\mid \mathbf{d}_{ab}\cdot\boldsymbol{\epsilon}^*_\lambda \mid^2 \frac{2\,\pi\,c^2\,\hbar}{\omega}\,\delta\left(E_b - E_a - \hbar\,\omega\right)\,\frac{d^3\,k}{(2\,\pi)^3}\ . \tag{1.4}$$

With k = ω/c we can easily integrate the δ factor and obtain the probability of decay per second and solid angle of the γ:

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$$d\Gamma = \frac{\omega_{ba}^3}{2\,\pi\,\hbar\,c^3}\mid \mathbf{d}_{ab}\cdot\boldsymbol{\epsilon}^*_\lambda \mid^2 d\Omega . \tag{1.5}$$

In (5) we have the product

$$\mid D_j\,\epsilon^*_j \mid^2 = D_j\,D^*_i\,\epsilon_i\,\epsilon^*_j\ ;\quad D_i \equiv \langle a \mid d_i \mid b\rangle .$$

In the general case the matrix $\epsilon_i\,\epsilon^*_j$ is the density matrix for the photon

$$\epsilon_i\,\epsilon^*_j \to \rho^{(\gamma)}_{ij}\ . \tag{1.6}$$

To compute the width of the state we have to sum over the final photon's polarizations, or equivalently take the average and multiply by a factor 2 (the number of independent polarizations). The matrix element for the unpolarized photons is

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$$\rho^{(\gamma)}_{ij} = \frac{1}{2}\left(\delta_{ij} - n_i\,n_j\right);\quad n_i \equiv \frac{k_i}{\mid \mathbf{k}\mid}\,. \tag{1.7}$$

In fact the matrix (7) is a multiple of the identity matrix in a plane orthogonal to the direction **n** of the photon, describing a mixed state with probability 1/2 on two orthogonal directions perpendicular to **n**. By substitution and summing on final polarizations:

$$d\Gamma = \frac{\omega_{ba}^3}{2\pi\hbar c^3} 2\rho_{ij}^{(\gamma)} D_j D_i^* d\Omega = \frac{\omega_{ba}^3}{2\pi\hbar c^3} \left(\delta_{ij} - n_i n_j\right) D_j D_i^* d\Omega .$$

The angular integral on the photon' s direction is easily done by using

$$\int d\Omega\, \delta_{ij} = 4\pi\delta_{ij}; \quad \int d\Omega\, n_i n_j = 4\pi \frac{1}{3}\delta_{ij} .$$

The resulting width is

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$$\Gamma = \int d\Gamma = \frac{2}{3} 4\pi \frac{\omega_{ba}^3}{2\pi\hbar c^3} D_i D_i^* = \frac{4}{3}\frac{\omega_{ba}^3}{\hbar c^3} D_i D_i^* . \tag{1.8}$$

The formula (8) verify the important property: *the width is equal for all states in the 2p level*. The simplest check is to write explicitly

$$D_i D_i^* = \langle b \mid (d_i \mid a\rangle\langle a \mid d_i) \mid b\rangle .$$

The operator enclosed in parenthesis, $(d_i \mid a\rangle\langle a \mid d_i)$ is clearly invariant under rotations, as such its matrix elements do not depend on the particular 2p state considered. The reader can easily check that the same proof works for every decay, once the summation on the final state $\mid a\rangle$ is performed.

Due to invariance we can choose an arbitrary 2p state to compute Γ, for instance $\mid 2p,\ L_z = 0\rangle$. From the Wigner-Eckart theorem (selection rules on the dipole operator) in the matrix element

$$D_i = \langle 1s \mid d_i\rangle \mid 2p,\ L_z = 0\rangle,$$

only the z component of the dipole is different from zero. With the known wave functions

$$\psi_{1s} = \frac{1}{\sqrt{a^3}} 2 e^{-r/a} Y_{00} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}; \quad \psi_{2p,L_z=0} = \frac{1}{\sqrt{a^3}} \frac{1}{2\sqrt{6}} \frac{r}{a} e^{-r/2a} Y_{10} = \frac{1}{\sqrt{a^3}} \frac{1}{4\sqrt{2\pi}} \frac{r}{a} e^{-r/2a} \mathrm{Cos}[\theta];$$

we get, with $d_z = e\,z = e\,r\,\mathrm{Cos}[\theta]$

$$D_z = e \int r^2 dr\, d\Omega \frac{1}{a^3} \frac{1}{4\pi\sqrt{2}} \frac{r^2}{a} e^{-3r/2a} \mathrm{Cos}[\theta]^2 = \frac{2^8}{3^5\sqrt{2}} e\,a ;$$

and finally

$$\Gamma = \frac{2^{17}}{3^{11}} \frac{\omega_{ba}^3}{\hbar c^3} e^2 a^2 = \frac{2^{17}}{3^{11}} \alpha a^2 \frac{\omega_{ba}^3}{c^3}; \quad \alpha \equiv \frac{e^2}{\hbar c} . \tag{1.9}$$

Using the explicit value for the transition frequency

$$E_b - E_a = \hbar\omega_{ba} = \frac{1}{2}\frac{3}{4}\frac{e^2}{a}; \quad a = \frac{\hbar^2}{m e^2};$$

we have

$$\Gamma = \left(\frac{2}{3}\right)^8 \alpha^5 \frac{m c^2}{\hbar} \simeq 0.63\,\mathrm{GHz}; \quad \tau = \frac{1}{\Gamma} \simeq 1.59\,10^{-9}\,\mathrm{sec.} \quad ; \quad \tau_{exp} = (1.60 \pm 0.01)\,10^{-9}\,\mathrm{sec.}$$

Spin

In the dipole approximation the interaction hamiltonian commutes with the spin. Thus if α, β denote the spin states

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$$\mathcal{M}_{\beta\alpha} = \langle 1s,\ \beta \mid H_I \mid 2p,\ \alpha\rangle = \mathcal{M}\delta_{\alpha\beta}. \tag{1.10}$$

In the definition of Γ we have to sum over the final states

$$d\Gamma = \sum_\beta \mid \mathcal{M}_{\beta\alpha} \mid^2 d\Phi.$$

The spin independence (10) imply that only the term $\alpha = \beta$ is different from zero and one recovers the previous result.

This property works for all quantum numbers commuting with H_I, for instance the nuclear spin.

If we include the spin in the definition of eigenstates of unperturbed Hamiltonian, i.e. we take into account the spin-orbit interaction, the property (10) continues to hold but the states now will be written as a superpositions of different spin states, as

$$|\psi\rangle = \sum_{\alpha} c_\alpha \, |\, 2p, \alpha\,\rangle .$$

This is true both for the decaying state and final states. For instance we have to specify if the 2p state is $2p_{1/2}$ or $2p_{3/2}$. For example, the total transition probability for 3s→2p transition is

$$\Gamma_{3s\to 2p} = \Gamma[3s \to 2p_{1/2}] + \Gamma[3s \to 2p_{3/2}] .$$

Problem 2

Let us consider an ensemble of hydrogen atoms in a 2p state, polarized along an axis, let us say the z axis. Compute the angular distribution of emitted photons in the transition 2p→2s and their polarizations.

Solution

In previous problem it has been shown that the decay probability per second, per sterad and for a given photon polarization is

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$$d\Gamma = \frac{\omega_{ba}^3}{2\pi\hbar c^3} \, |\, \mathbf{d}_{ab}\cdot\boldsymbol{\epsilon}_\lambda^* \,|^2 \, d\Omega . \tag{2.1}$$

If we *do not measure* the final polarizations we have (see previous problem)

$$d\Gamma = \frac{\omega_{ba}^3}{2\pi\hbar c^3} \, 2\,\rho_{ij}^{(\gamma)} \, D_j \, D_i^* \, d\Omega = \frac{\omega_{ba}^3}{2\pi\hbar c^3} \left(\delta_{ij} - n_i\, n_j\right) D_j \, D_i^* \, d\Omega .$$

$$\Gamma = \frac{4}{3}\,\frac{\omega_{ba}^3}{\hbar c^3}\, D^2 .$$

Let us now take into account the polarizations. Let us suppose that some z axis has been defined and choose a (x,y) plane to fix our reference frame. With the polar and azimuthal angles θ, φ the photon direction is

$$n = (\text{Sin}[\theta]\,\text{Cos}[\varphi],\ \text{Sin}[\theta]\,\text{Sin}[\varphi],\ \text{Cos}[\theta]) .$$

The following computations can be done or by decomposing the dipole operator in spherical components and applying the Wigner Eckart theorem or by parametrizing the 2p states as follows. The three possible 2p states have a wave function (m is the eigenvalue of L_z):

$$m = 0 :\ z\, f[r] \ ;\quad m = \pm 1 :\ \frac{x \pm i\, y}{\sqrt{2}}\, f[r] .$$

This is easily checked using the spherical harmonics. We have immediately:

$$\begin{aligned} &D = \langle 2s \,|\, d_z \,|\, 2p,\, 0\rangle \ ;\quad \langle 2s \,|\, d_x \,|\, 2p,\, 0\rangle = \left\langle 2s \,\middle|\, d_y \,\middle|\, 2p,\, 0\right\rangle = 0 ; \\ &\langle 2s \,|\, d_z \,|\, 2p,\, 1\rangle = 0 ;\quad \langle 2s \,|\, d_x \,|\, 2p,\, 1\rangle = \frac{1}{\sqrt{2}}\, D \ ;\quad \left\langle 2s \,\middle|\, d_y \,\middle|\, 2p,\, 1\right\rangle = i\,\frac{1}{\sqrt{2}}\, D \ . \end{aligned} \tag{2.2}$$

Let us note that

$$\left\langle 2s \,\middle|\, d_x + i\, d_y \,\middle|\, 2p,\, 1\right\rangle = 0 \ ;\quad \left\langle 2s \,\middle|\, d_x - i\, d_y \,\middle|\, 2p,\, 1\right\rangle = \sqrt{2}\, D \neq 0 ;$$

in agreement with selections rules on angular momentum. If we call $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ the unit vectors along the three axes, the previous relations can be also written as

c14prob2eq3

$$\langle 2s \,|\, \mathbf{d} \,|\, 2p,\, 0\rangle = D\,\mathbf{e}_z \ ;\qquad \langle 2s \,|\, \mathbf{d} \,|\, 2p,\, 1\rangle = \frac{D}{\sqrt{2}}\left(\mathbf{e}_x + i\,\mathbf{e}_y\right) . \tag{2.3}$$

The angular distribution of photons for decay of polarized states take now the form

$$d\Gamma[(2p,\, 0) \to 1s] = \frac{\omega_{ba}^3}{2\pi\hbar c^3}\left(\,|\,\mathbf{d}\,|^2 - \,|\,\mathbf{d}\cdot\mathbf{n}\,|^2\right) d\Omega = \frac{\omega_{ba}^3}{2\pi\hbar c^3}\, D^2\left(1 - \text{Cos}[\theta]^2\right) d\Omega = \Gamma\,\frac{3}{2}\,\frac{d\Omega}{4\pi}\,\text{Sin}[\theta]^2 ; \tag{2.4}$$

$$d\Gamma[(2p,\, 1) \to 1s] = \frac{\omega_{ba}^3}{2\pi\hbar c^3}\, D^2\left(1 - \frac{1}{2}\left(n_x^2 + n_y^2\right)\right) d\Omega = \Gamma\,\frac{3}{2}\,\frac{d\Omega}{4\pi}\,\frac{\left(1 + \text{Cos}[\theta]^2\right)}{2} . \tag{2.5}$$

Integrating both expressions gives Γ as result, confirming the independence of the total width from the decaying state.

Photon polarization

To study the photon polarization let us consider a reference system (ξ, η, ζ) where ζ is directed along **n**, and the ξ axis is on the plane z-**n**. One get easily the three associated unit vectors:

$$\mathbf{e}_\zeta = \mathbf{n} = (\text{Sin}[\theta]\,\text{Cos}[\varphi],\ \text{Sin}[\theta]\,\text{Sin}[\varphi],\ \text{Cos}[\theta]);$$
$$\mathbf{e}_\eta = \frac{\mathbf{e}_\zeta \wedge \mathbf{e}_z}{|\,\mathbf{e}_\zeta \wedge \mathbf{e}_z\,|} = (\text{Sin}[\varphi],\ -\text{Cos}[\varphi],\ 0); \tag{2.6}$$
$$\mathbf{e}_\xi = \mathbf{e}_\eta \wedge \mathbf{e}_\zeta = (-\text{Cos}[\theta]\,\text{Cos}[\varphi],\ -\text{Cos}[\theta]\,\text{Sin}[\varphi],\ \text{Sin}[\theta]);$$

One can consider as an instance rectilinear polarizations, like $\boldsymbol{\epsilon}_\xi = \mathbf{e}_\xi$, $\boldsymbol{\epsilon}_\eta = \mathbf{e}_\eta$ or circular polarizations, as

$$\boldsymbol{\epsilon}_+ = \frac{1}{\sqrt{2}}\left(\mathbf{e}_\zeta + \mathbb{i}\,\mathbf{e}_\eta\right); \quad \boldsymbol{\epsilon}_- = \frac{1}{\sqrt{2}}\left(\mathbf{e}_\zeta - \mathbb{i}\,\mathbf{e}_\eta\right).$$

1. In the decay (2p,0) → 1s we have seen that **d** = D $\mathbf{e}_z$ then for the amplitudes

$$\boldsymbol{\epsilon}_\xi^* \cdot \mathbf{d} = \text{D}\,\text{Sin}[\theta]\ ; \quad \boldsymbol{\epsilon}_\eta^* \cdot \mathbf{d} = 0\ .$$

The photon has a rectilinear polarization in the z-**n** plane and the probability of the decay is proportional to the square of the amplitude, i.e. $\text{D}^2\,\text{Sin}[\theta]^2$ in agreement with our previous results.
This decay corresponds classically to an oscillation along z axis.

2. In the decay (2p,1) → 1s the dipole matrix element is given by (3) and we have the two amplitudes

$$A_+ = (\boldsymbol{\epsilon}_+)^*\,\mathbf{d} = \frac{\text{D}}{2}\left(\mathbf{e}_\zeta - \mathbb{i}\,\mathbf{e}_\eta\right)\left(\mathbf{e}_x + \mathbb{i}\,\mathbf{e}_y\right) = -\frac{\text{D}}{2}\,(1+\text{Cos}[\theta])\,e^{\mathbb{i}\,\varphi};$$
$$A_- = (\boldsymbol{\epsilon}_-)^*\,\mathbf{d} = \frac{\text{D}}{2}\left(\mathbf{e}_\zeta + \mathbb{i}\,\mathbf{e}_\eta\right)\left(\mathbf{e}_x - \mathbb{i}\,\mathbf{e}_y\right) = \frac{\text{D}}{2}\,(1-\text{Cos}[\theta])\,e^{-\mathbb{i}\,\varphi}\ . \tag{2.7}$$

The probabilities, with C a common factor, are

$$P_+ = C\,\frac{\text{D}^2}{4}\,(1+\text{Cos}[\theta])^2; \quad P_- = C\,\frac{\text{D}^2}{4}\,(1-\text{Cos}[\theta])^2;$$

The angular distribution, summing over the final photon polarizations, is

$$P = P_+ + P_- \propto 1 + \text{Cos}[\theta]^2\ ;$$

in agreement with the previous results. The probabilities $P_\pm$ give, for a given measure, the probability to detect a + or - polarization. We can define a mean polarization degree by

$$\xi = \frac{P_+ - P_-}{P_+ + P_-} = \frac{2\,\text{Cos}[\theta]}{1+\text{Cos}[\theta]^2}.$$

Classically ξ gives the degree of elliptic polarization, in quantum mechanics we measure **or** +1 **or** -1 for the polarization, ξ is recovered as a statistical average.
Let us note that for the particular angle θ=0 the photon has a fixed polarization +1, this is in agreement with conservation of angular momentum: the $+\hbar$ component of the atom in 2p state has been taken by the photon.
Classically this kind of decay corresponds to a dipole rotating anticlockwise in the (x,y) plane, the reader can compare this process with the description of the light polarization in the Zeeman effect.

Problem 3

Use the Wigner-Eckart theorem to write the hyperfine spitting structure for a level with arbitrary L, S. The nucleus has spin I.

● Solution

In the text the hyperfine interaction Hamiltonian is computed:

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$$V = A\left(\frac{8\,\pi}{3}\,\mathbf{I}\cdot\mathbf{S}\,\delta[\mathbf{r}] - (\mathbf{I}\cdot\mathbf{S} - 3\,(\mathbf{I}\cdot\mathbf{n})\,\mathbf{n}\cdot\mathbf{S})\,\frac{1}{r^3} + \frac{1}{r^3}\,\mathbf{I}\cdot\mathbf{L}\right) \equiv V_S + V_L\,. \tag{3.1}$$

Here **n** = **r** / r . The first term, V_S contributes only to the s-levels shifts, as $\psi[0]\neq 0$ only in this cases. The last two terms, V_L, give contribution only for L≠0. In fact, the last term being proportional to **L** is zero on s-states. The second term is proportional to the rank 2 symmetric and traceless tensor

$$T = \delta_{ij} - 3\,\frac{x_i\,x_j}{r^2}\,.$$

This tensor transforms as an L = 2 spherical tensor, therefore on s states the selections rule on the angular momentum implies $\langle L{=}0|T|L{=}0\rangle = 0$.

The hyperfine interaction is small even with respect to the fine structure interaction. The typical scale involved is the atomic radius ~ a_B. Using

$$A \sim \mu_p \mu_B ; \quad \mu_B = \frac{|e|\hbar}{2 m_e c} ; \quad \mu_p = \frac{|e|\hbar}{2 m_p c} ; \quad (\text{Bohr's magneton and the nuclear Bohr magneton}), \quad m_p = \text{proton mass}.$$

one easily estimates

$$\delta E \sim \frac{A}{a_B^3} = \frac{m_e}{m_p} \alpha^2 \frac{e^2}{a_B},$$

The hyperfine splitting is depressed by a factor $m_e / m_p \sim 10^{-3}$with respect to the fine structure energies. In this situation the unperturbed states on which V acts can be taken as the eigenstates of $J, J_z,$ L,S, diagonalizing the fine structure interaction. The degeneracy of such levels is (2J+1)(2-I+1), taking into account the nuclear spin orientation.

The Hamiltonian (1) does not commute with J,L,S, but being a scalar commutes with the total angular momentum (the electron angular momentum plus the nuclear angular momentum):

$$\mathbf{F} = \mathbf{I} + \mathbf{J}. \tag{3.2}$$

For fixed L,S,J, I we will have a series of states with quantum numbers F, F_z. Each of these level will have a degeneracy (2F+1) and as usual the numbers of terms will be, be the rule of addition of angular momentum

$$|J - I| \le F \le I + J; \qquad \text{numb. terms} = (2J+1) \text{ if } J \ge I; \quad 2I+1 \text{ if } I \ge J.$$

Let us now compute the eigenvalues as a function of F.

■ **L=0**

The first term is easy to compute by using the identity (valid within a multiplet)

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$$\mathbf{I} \cdot \mathbf{S} = \frac{1}{2}\left(\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{S}^2\right) = \frac{1}{2}\left(F(F+1) - I(I+1) - S(S+1)\right). \tag{3.3}$$

Then for S - states

$$\Delta E = B \frac{1}{2}\left(F(F+1) - I(I+1) - S(S+1)\right),$$

where

$$B = A \frac{8\pi}{3} \psi[0]^2 ; \quad A = g_e g_N \mu_p \mu_B.$$

The g' s are the gyromagnetic factors of the electron and nucleon.

■ **L > 0**

For these states let us start by considering the second term in (1):

$$\frac{1}{r^3} I_i S_j \left(3 n_i n_j - \delta_{ij}\right).$$

To angular variables only the symmetric tensor gives a contribution. By the Wigner-Eckart theorem this contribution must be proportional to the symmetric traceless tensor constructed with L, i.e. (in a matrix sense within a given multiplet):

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$$\left(3 n_i n_j - \delta_{ij}\right) = c_Q \left(3 L_i L_j + 3 L_j L_i - 2 \mathbf{L}^2 \delta_{ij}\right). \tag{3.4}$$

We note that, both classically and as an operator :

$$n_i L_i = \frac{1}{r} x_i L_i = \frac{1}{r} x_i \epsilon_{ijk} x_j p_k = 0;$$

thus by left and right multiplication by $L_i$and L_j eq.(4) takes the form

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$$-\mathbf{L}^2 = c_Q \left(3\mathbf{L}^2\mathbf{L}^2 + 3 L_i L_j L_i L_j - 2\mathbf{L}^2\mathbf{L}^2\right) = c_Q \left(\mathbf{L}^2\mathbf{L}^2 + 3 L_i L_j L_i L_j\right). \tag{3.5}$$

Using the commutation relations for angular momentum one has

$$L_i L_j L_i L_j = \mathbf{L}^2\mathbf{L}^2 + i \epsilon_{ijk} L_k L_i L_j = \mathbf{L}^2\mathbf{L}^2 + \frac{i}{2} \epsilon_{ijk} L_k \left[L_i, L_j\right] = \mathbf{L}^2\mathbf{L}^2 + \frac{i^2}{2} \epsilon_{ijk} \epsilon_{ijm} L_k L_m = \mathbf{L}^2\mathbf{L}^2 - \mathbf{L}^2.$$

We used the identity

$$\epsilon_{ijk}\,\epsilon_{ijm} = 2\,\delta_{km}\,.$$

For c_Q then we have, from (5):

$$c_Q = -\frac{1}{4\,L\,(L+1)-3} = -\frac{1}{(2\,L-1)\,(2\,L+3)}\,.$$

The effective interaction V_L in (1) thus takes the form

$$V_L = \frac{A}{r^3}\left(\frac{2\,\mathbf{L}^2\,\mathbf{I}\cdot\mathbf{S} - 3\,(\mathbf{I}\cdot\mathbf{L})\,(\mathbf{I}\cdot\mathbf{S}) - 3\,(\mathbf{S}\cdot\mathbf{L})\,(\mathbf{I}\cdot\mathbf{L})}{(2\,L-1)\,(2\,L+3)} + \mathbf{I}\cdot\mathbf{L}\right)\,. \tag{3.6}$$

The Wigner-Eckart theorem implies that within a multiplet, in matrix sense, we can assume

$$\mathbf{L} = c_L\,\mathbf{J};\quad \mathbf{S} = c_S\,\mathbf{J}. \tag{3.7}$$

Multiplication by J gives immediately (expressing **L**·**J** etc. as in (3)):

$$c_L = \frac{J\,(J+1) + L\,(L+1) - S\,(S+1)}{2\,J\,(J+1)};\quad C_S = \frac{J\,(J+1) + S\,(S+1) - L\,(L+1)}{2\,J\,(J+1)}\,. \tag{3.8}$$

Also

$$c_{LS} \equiv \mathbf{L}\cdot\mathbf{S} = \frac{J\,(J+1) - S\,(S+1) - L\,(L+1)}{2}\,.$$

and finally we have for V_L

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$$V_L = \frac{A}{r^3}\,\mathbf{I}\cdot\mathbf{J}\left(\frac{2\,L\,(L+1)\,c_S - 6\,c_{LS}\,c_L}{(2\,L-1)\,(2\,L+3)} + c_L\right). \tag{3.9}$$

With

$$\mathbf{I}\cdot\mathbf{J} = \frac{F\,(F+1) - J\,(J+1) - I\,(I+1)}{2},$$

we can write the energy splitting in each multiplet.

For S = 1/2 the previous formulas can be simplified. For each l we can have J = L ± 1/2. By direct substitution the reader can easily verify that in both cases the parenthesis in (9) has the value:

$$() = 2\,L\,(L+1)\,\frac{1}{2\,J\,(J+1)} = \frac{L\,(L+1)}{J\,(J+1)},$$

therefore we can write

$$V_L = \frac{A}{r^3}\,\frac{L\,(L+1)}{J\,(J+1)}\,\mathbf{I}\cdot\mathbf{J} = \frac{A}{r^3}\,\frac{L\,(L+1)}{J\,(J+1)}\,\frac{F\,(F+1) - J\,(J+1) - I\,(I+1)}{2}$$

The actual values of the splitting depends on the integral of $1/r^3$ with the radial part of the wave functions.