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PHY 741 – Notes on Multiplet splittings

Reference: E. U. Condon and G. H. Shortley, **The Theory of Atomic Spectra**, Cambridge University Press, 1967. (First printed in 1935.)

We are concerned with evaluating the "atomic terms" which approximate the possible states of a two-electron open shell system such as np^2, nd^2, nf^2, etc.

Suppose that the spatial part of the two-electron wavefunction can be written as an eigenstate of total $\mathbf{L^2}$ and L_z:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = R_{nl}(r_1)R_{nl}(r_2) \sum_{m_a m_b} \langle LM|lm_a lm_b\rangle Y_{lm_a}(\hat{\mathbf{r_1}})Y_{lm_b}(\hat{\mathbf{r_2}}), \tag{1}$$

where $\langle LM|lm_a lm_b\rangle$ denotes a Clebsch-Gordon coefficient. The multiplet energy will be determined by evaluating the expectation value of

$$\Delta E = \left\langle \Psi \left| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi \right\rangle . \tag{2}$$

We can define the radial integral

$$F^\lambda \equiv \int r_1^2 dr_1 \int r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} (R_{nl}(r_1))^2 (R_{nl}(r_2))^2. \tag{3}$$

We also need to use the Gaunt coefficients:

$$G^{LM}_{l_1m_1l_2m_2} \equiv \sqrt{4\pi} \int d\Omega Y^*_{l_1m_1}(\hat{\mathbf{r}})Y^*_{LM}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}}) = \sqrt{4\pi} \int d\Omega Y_{l_1m_1}(\hat{\mathbf{r}})Y_{LM}(\hat{\mathbf{r}})Y^*_{l_2m_2}(\hat{\mathbf{r}}) \tag{4}$$

As discussed in Cohen-Tannoudji's text, the Gaunt coefficent can be expressed in terms of a product of two Clebsch-Gordan coefficients:

$$G^{LM}_{l_1m_1l_2m_2} = (-1)^{m_2} \sqrt{\frac{(2l_1+1)(2l_2+1)}{(2L+1)}} \langle l_1\ 0\ l_2\ 0|L\ 0\rangle \langle l_1\ m_1\ l_2\ -m_2|L\ M\rangle. \tag{5}$$

In terms of these quantities, the multiplet energy can be calculated according to:

$$\Delta E = e^2 \sum_\lambda F^\lambda A^\lambda_L, \tag{6}$$

where the angular term is given by

$$A^\lambda_L = \frac{1}{2\lambda+1} \sum_{m_a m_b m_c m_d} \langle LM|lm_a lm_b\rangle \langle lm_c lm_d|LM\rangle G^{\lambda(m_c-m_a)}_{lm_a lm_c} G^{\lambda(m_b-m_d)}_{lm_d lm_b}. \tag{7}$$