

# Notes on estimating Coulomb repulsion integrals in multielectron atoms

In order to evaluate the “term” splittings of open shell atoms, we need to evaluate matrix elements of the Coulomb repulsion

$$\mathcal{H}^1 \equiv \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

For example, consider the  $2p^2$  configuration of carbon. The part of the 6-electron Slater determinant corresponding to the  $L=2$   $M=2$  state of the  ${}^1D$  term can be written:

$$|{}^1D; L = 2M = 2\rangle = R_p(r_1)R_p(r_2)Y_{11}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2).$$

In order to evaluate the expectation value  $\langle {}^1D; L = 2M = 2 | \mathcal{H}^1 | {}^1D; L = 2M = 2 \rangle$ , we need to make use of the expansion

$$\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = e^2 \sum_{\lambda\mu} \frac{\sqrt{4\pi}Y_{\lambda\mu}^*(\hat{\mathbf{r}}_1)\sqrt{4\pi}Y_{\lambda\mu}(\hat{\mathbf{r}}_2)}{2\lambda + 1} \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}}.$$

Here  $r_{<}$  ( $r_{>}$ ) denotes the smaller (larger) of  $r_1$  and  $r_2$ . It will also be useful to define the radial integral

$$\mathcal{R}_l^\lambda \equiv e^2 \int r_1^2 dr_1 \int r_2^2 dr_2 \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} (R_l(r_1))^2 (R_l(r_2))^2.$$

It will also be useful to define Gaunt coefficients in terms of the integral of 3 spherical harmonic functions:

$$G_{l_1 m_1 l_2 m_2}^{\lambda\mu} \equiv \sqrt{4\pi} \int d\Omega Y_{\lambda\mu}^*(\hat{\mathbf{r}}) Y_{l_1 m_1}^*(\hat{\mathbf{r}}) Y_{l_2 m_2}(\hat{\mathbf{r}}).$$

Then, we can evaluate

$$\langle {}^1D; L = 2M = 2 | \mathcal{H}^1 | {}^1D; L = 2M = 2 \rangle = \mathcal{R}_1^0 (G_{1111}^{00})^2 + \frac{1}{5} \mathcal{R}_1^2 (G_{1111}^{20})^2.$$

In this case,  $G_{1111}^{00} = 1$  and  $G_{1111}^{20} = -1/\sqrt{5}$ , so that

$$\langle {}^1D; L = 2M = 2 | \mathcal{H}^1 | {}^1D; L = 2M = 2 \rangle = \mathcal{R}_1^0 + \frac{1}{25} \mathcal{R}_1^2.$$

The evaluation of the term integrals for an example of the  ${}^3P$  term is a little more complicated. In this case, the spatial part is antisymmetric. A representative wavefunction in this term can be written:

$$|{}^3P; L = 1M = 1\rangle = \sqrt{\frac{1}{2}} R_p(r_1)R_p(r_2) (Y_{11}(\hat{\mathbf{r}}_1)Y_{10}(\hat{\mathbf{r}}_2) - Y_{10}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2)).$$

In this case we can evaluate the matrix element:

$$\langle {}^3P; L = 1M = 1 | \mathcal{H}^1 | {}^3P; L = 1M = 1 \rangle = \mathcal{R}_1^0 G_{1111}^{00} G_{1010}^{00} + \frac{1}{5} \mathcal{R}_1^2 (G_{1111}^{20} G_{1010}^{20} - (G_{1011}^{21})^2).$$

In this case,  $G_{1111}^{00} = G_{1010}^{00} = 1$ ,  $G_{1111}^{20} = -1/\sqrt{5}$ ,  $G_{1010}^{20} = 2/\sqrt{5}$ , and  $G_{1011}^{21} = \sqrt{3/5}$ , so that

$$\langle {}^3P; L = 1M = 1 | \mathcal{H}^1 | {}^3P; L = 1M = 1 \rangle = \mathcal{R}_1^0 - \frac{5}{25} \mathcal{R}_1^2.$$

The energy for the  ${}^1S$  term can be found in a similar (but more tedious) way. To summarize the energies of the 3  $2p^2$  terms of carbon:

$$E({}^3P) = \mathcal{R}_1^0 - \frac{5}{25} \mathcal{R}_1^2$$

$$E({}^1D) = \mathcal{R}_1^0 + \frac{1}{25} \mathcal{R}_1^2$$

$$E({}^1S) = \mathcal{R}_1^0 + \frac{10}{25} \mathcal{R}_1^2$$