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

\[ e^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = e^2 \sum_{\lambda \mu} \frac{\sqrt{4\pi} Y^*_{\lambda\mu}(\hat{\mathbf{r}}_1) \sqrt{4\pi} Y_{\lambda\mu}(\hat{\mathbf{r}}_2)}{2\lambda + 1} \frac{r^\lambda_\prec}{r^\lambda_{\succ+1}}. \]

Here \( r_\prec (r_\succ) \) denotes the smaller (larger) of \( r_1 \) and \( r_2 \). It will also be useful to define the radial integral

\[ R^\lambda_i \equiv e^2 \int r_1^2 dr_1 \int r_2^2 dr_2 \frac{r^\lambda_\prec}{r^\lambda_{\succ+1}} (R_i(r_1))^2 (R_i(r_2))^2. \]

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

\[ G_{l_1m_1l_2m_2}^{\lambda\mu} \equiv \sqrt{4\pi} \int d\Omega \; Y^*_{\lambda\mu}(\hat{\mathbf{r}}) Y_{l_1m_1}(\hat{\mathbf{r}}) Y_{l_2m_2}(\hat{\mathbf{r}}). \]

Then, we can evaluate

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

In this case, \( G^{00}_{1111} = 1 \) and \( G^{20}_{1111} = -1/\sqrt{5} \), so that

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

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:

\[
\langle 3p; L = 1M = 1 | H^1 | 3p; L = 1M = 1 \rangle = R_1^0 G_{1111}^{00} G_{1010}^{00} + \frac{1}{5} R_1^2 \left( G_{1111}^{20} G_{1010}^{20} - (G_{1011}^{21})^2 \right).
\]

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

\[
\langle 3p; L = 1M = 1 | H^1 | 3p; L = 1M = 1 \rangle = R_1^0 - \frac{5}{25} R_1^2.
\]

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:

\[
E(3P) = R_1^0 - \frac{5}{25} R_1^2
\]

\[
E(1D) = R_1^0 + \frac{1}{25} R_1^2
\]

\[
E(1S) = R_1^0 + \frac{10}{25} R_1^2
\]