Evaluating matrix elements of Coulomb repulsion

We calculate matrix element of Coulomb interaction

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

when the electrons are in states $\phi_a(\vec{r}_1)$, $\phi_b(\vec{r}_2)$,

$$\langle \phi_a \phi_b \left| V_{12} \right| \phi_a \phi_b \rangle = \int \int \phi_a^\star(\vec{r}_1) \phi_b^\star(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_a(\vec{r}_1) \phi_b(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \tag{1}$$

with

$$\phi_a(\vec{r}_1) = R_a(r_1) Y_{l_a m_a}(\hat{r}_1) \tag{2}$$

and

$$\phi_b(\vec{r}_2) = R_b(r_2) Y_{l_b m_b}(\hat{r}_2) \tag{3}$$

using the multipole expansion

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y_{LM}^\star(\hat{r}_1) Y_{LM}(\hat{r}_2) \tag{4}$$

where

$$\begin{aligned} r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\vec{r}_1| < |\vec{r}_2| \\ r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\vec{r}_2| < |\vec{r}_1| \end{aligned}$$

Then this can be separated in several integrals

$$\begin{aligned} &\langle \phi_a \phi_b \left| V_{12} \right| \phi_a \phi_b \rangle = \sum_{LM} \frac{4\pi}{2L+1} \\ &\int r_1^2 dr_1 \int r_2^2 dr_2 R_a^*(r_1) R_b^*(r_2) \frac{r_<^L}{r_>^{L+1}} R_a(r_1) R_b(r_2) \\ &\int Y_{l_a m_a}^\star(\hat{r}_1) Y_{LM}^\star(\hat{r}_1) Y_{l_a m_a}(\hat{r}_1) d\hat{r}_1 \quad \int Y_{l_b m_b}^\star(\hat{r}_2) Y_{LM}(\hat{r}_2) Y_{l_b m_b}(\hat{r}_2) d\hat{r}_2 \end{aligned} \tag{5}$$

with the notation

$$\hat{r}_1 \longrightarrow \left(\theta_1 \quad \phi_1 \right) \tag{6}$$

and the integrations

$$\int d\hat{r}_1 \longrightarrow \int_0^\pi \sin\theta_1 \; d\theta_1 \int_0^{2\pi} \; d\phi \tag{7}$$

For s-states, when $l_a = 0$, $m_a = 0$ each of the angular integrals simply give $\sqrt{4\pi}$ and cancel that factor in the first term.

What remains to be evaluated is the double integral

$$\int r_1^2 dr_1 \int r_2^2 dr_2 R_a^*(r_1) R_b^*(r_2) \frac{r_<^L}{r_>^{L+1}} R_a(r_1) R_b(r_2) \tag{8}$$

which for hydrogen-like states reduces to elementary integrations.

EXERCISE: by expanding the inequalities, write out the two double integrals to be evaluated.

Substitutions:

$$\int_0^\infty \quad x^n \quad dx e^{-\alpha x} = \frac{1}{\alpha^{n+1}} \int_0^\infty \quad y^n \quad dy e^{-y}$$