Problem 1: Perturbation calculation

We consider a configuration \((1s)(2p)\) of a helium-like atom of nuclear charge \(Z\) e, approximating each orbital as hydrogenic \((1s)\) with nucleus \(Z\) e; \((2p)\) with nucleus \((2-1)\) e.

(a) We consider the matrix element

\[
\left\langle \phi_A^{(1)} \phi_B^{(2)} \right| \frac{1}{r_{12}} \left| \phi_C^{(1)} \phi_D^{(2)} \right\rangle
\]

where the \(\phi\)'s are:

\[
\phi_n^{(r)} = \frac{Un(r)}{r} Y_{lm}^{r}(\theta, \phi)
\]

with \(Un(r)\) the (reduced) radial wave function of a hydrogenic state with some nuclear charge.

We use the "addition theorem"

\[
\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{(-1)^{l}}{(r_{12}^{2+l})} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{l}^{*}(\theta_1, \phi_1) Y_{l}^{m}(\theta_2, \phi_2)
\]

where \(r_{12}(r_{12})\) is the lesser (greater) of \(r_1\) or \(r_2\).
\[ \langle \phi_A(\alpha) \phi_B(\beta) \mid \frac{1}{r_{AB}} \mid \phi_C(\gamma) \phi_D(\delta) \rangle \]

\[ \sum_{\ell} \int_{\tilde{\mathbb{R}}} \int_{\tilde{\mathbb{R}}} \int_{\tilde{\mathbb{R}}} \int_{\tilde{\mathbb{R}}} \frac{1}{r_{AB}} \ u_1(\alpha) u_2(\beta) u_3(\gamma) u_4(\delta) \]

\[ \sum_{\ell} \int \frac{1}{r_{AB}} \ Y^*_\ell^m(\alpha, \phi_\alpha) Y^*_\ell^m(\beta, \phi_\beta) Y_{\ell_m^m}^m(\gamma, \phi_\gamma) Y_{\ell_m^m}^m(\delta, \phi_\delta) \]

By the rules of the integrals of \( \mathbb{R}^4 \) two integral vanish, unless

\[ m_B = m + m_D \]
\[ m_C = m + m_A \]

\[ \Rightarrow m_B - m_D = m_C - m_A \Rightarrow m_A + m_B = m_C + m_D \]

Thus

\[ \langle \phi_A(\alpha) \phi_B(\beta) \mid \frac{1}{r_{AB}} \mid \phi_C(\gamma) \phi_D(\delta) \rangle \]

\[ \sum_{\ell} \sum_{m} \int \frac{1}{r_{AB}} \ Y^*_\ell^m(\alpha, \phi_\alpha) Y^*_\ell^m(\beta, \phi_\beta) Y_{\ell_m^m}^m(\gamma, \phi_\gamma) Y_{\ell_m^m}^m(\delta, \phi_\delta) \]

\[ F^{(m)}(AB, CD) \]
where \( C_{k^m, l^m}^{(n)} = \) \( \int d\Omega \ Y_{k^m}^*(\theta, \phi) \ Y_{l^m}^*(\theta, \phi) \ Y_{l^m}^*(\theta, \phi) \ Y_{k^m}^{(m)} \)

\( = \sum_{m^*} C_{k^m, l^m}^{(n)} \) (real)

\( F(\omega) = \) \( (a b, c d) = \int d\Omega \ d\varphi \ R_{k^m} \frac{r^{1/2}}{r^{k^m}} \ \rho_a(r) \rho_b(r) \rho_c(r) \rho_d(r) \)

(b) The two terms arising from the \((a b, c d)\) only

\[ 1 \ P(m_m) = \frac{1}{\sqrt{2}} \left\{ \phi_{15}(1) \phi_{2p,m_z}^{(2-1)} + \phi_{2p,m_z}^{(2)} \phi_{15}(1) \phi_{2p,m_z}^{(2)} \right\} \chi_{m_m} \]

\[ 3 \ P(m_m) = \frac{1}{\sqrt{2}} \left\{ \phi_{15}(1) \phi_{2p,m_z}^{(2-1)} - \phi_{2p,m_z}^{(2-1)} \phi_{15}(1) \phi_{2p,m_z}^{(2)} \right\} \chi_{m_m} \]

Note: I have denoted these states with \( m_3, m_x \) quantum numbers, though if the absence of external fields, the energy does not depend on them, and they may be chosen arbitrarily. I will pick \( m_3 = 0 \).

\[ \phi_{15}^{(2-1)} (r) = 2 \frac{2^{3/2}}{\sqrt{5\pi}} e^{-2z} \]

\[ \phi_{2p}^{(2-1)} (r, \theta) = \frac{(2-1)^{3/2}}{2\sqrt{6}} \left\{ e^{-2z} \frac{r e^{i(2-1)\frac{\pi}{2}}}{\sqrt{3} \sqrt{4\pi} \cos \theta} \right\} Y_{1o}^{(2-1)}(\theta) \]

\[ R_{2p}^{(2-1)}(r) \]

\[ Y_{1o}^{(2-1)}(\theta) \]
The total Hamiltonian is (in atomic units)

\[ H = -\frac{\hbar^2}{2} \nabla^2 + \frac{Z}{r_1} - \frac{1}{2} \nabla^2 + \frac{Z}{r_2} + \frac{1}{r_{12}} \]

The energy to first order is the expectation value

\[ E = \langle \psi_{\pm} | H | \psi_{\pm} \rangle = \langle \psi_{\pm} | H_0^{(2)} | \psi_{\pm} \rangle + \langle \psi_{\pm} | H_0^{(2)}(2p) | \psi_{\pm} \rangle \]

where

\[ | H_0^{(2)} \rangle = \frac{1}{2} \left( \psi_{1s}^{(2)} \right) \phi_{1s}^{(2)} + \phi_{2p_0}^{(2)} \phi_{2s}^{(2)} \]

\[ | H_0^{(2)}(2p) \rangle = \frac{1}{2} \nabla^2 + \frac{Z}{r} \]

is the Hydrogenic Hamiltonian

Following Lect. 11 notes

\[ \langle \psi_{\pm} | H_0 | \psi_{\pm} \rangle = \frac{1}{2} \left( \langle \phi_{1s}^{(2)} | H_0^{(2)}(1) | \phi_{1s}^{(2)} \rangle + \langle \phi_{2p_0}^{(2)} | H_0^{(2)}(1) | \phi_{1s}^{(2)} \rangle \right) \]

\[ + \frac{1}{2} \left( \langle \phi_{1s}^{(2)} | H_0^{(2)}(1) | \phi_{1s}^{(2)} \rangle + \langle \phi_{2p_0}^{(2)} | H_0^{(2)}(1) | \phi_{1s}^{(2)} \rangle \right) \]

\[ + \frac{1}{2} \left( \langle \phi_{2p_0}^{(2)} | H_0^{(2)}(1) | \phi_{2p_0}^{(2)} \rangle + \langle \phi_{2p_0}^{(2)} | H_0^{(2)}(1) | \phi_{2p_0}^{(2)} \rangle \right) \]

\[ = \langle \phi_{1s}^{(2)} | H_0^{(2)} | \phi_{1s}^{(2)} \rangle \]

\[ E_0^{(2)}(1s,1s) \]

The first term is just the Hydrogenic energy for one electron in a nucleus of charge 2

\[ E_0^{(2)}(1s,1s) = -\frac{Z^2}{2} \]
To calculate $E_{\text{coul}}^{(2s)}(2p, 1s)$ we use the virial theorem as in Lecture 11:

$$\langle \phi_{2p}^{(2s)} | H_{\text{coul}}^{(2s)} | \phi_{2p}^{(2s)} \rangle = \langle \phi_{2p}^{(2s)} | \frac{1}{2} \nabla^2 | \phi_{2p}^{(2s)} \rangle + \langle \phi_{2p}^{(2s)} | \frac{2}{r} | \phi_{2p}^{(2s)} \rangle$$

By virial

$$\langle \text{KE} \rangle = -E_{2p}^{(2s)} = \frac{(Z-1)^2}{8}$$

$$\langle \text{PE} \rangle = \frac{Z^2}{2} \langle \phi_{2p}^{(2s)} | \frac{(Z-1)}{r} | \phi_{2p}^{(2s)} \rangle = -\frac{Z(Z-1)}{4}$$

$$2E_{2p}^{(2s)} = 2 \frac{(Z-1)^2}{2(Z)^2}$$

Thus,

$$\langle H \rangle_{\pm} = -\frac{Z^2}{2} + \frac{(Z-1)^2}{8} - \frac{Z(Z-1)}{4} + \langle \frac{1}{r_{12}} \rangle_{\pm}$$

The first term is the $\text{He}^+(1s)$ binding energy. The energy of the state relative to the first ionization threshold is

$$E_{1s} = \frac{(Z-1)^2}{8} - \frac{Z(Z-1)}{4} + \langle \frac{1}{r_{12}} \rangle_{\pm} \ (\text{au})$$
Now $\langle \frac{1}{r_{12}} \rangle = \langle \phi^{(3)}_{16} \phi^{(2)}_{12} p | \frac{1}{r_{12}} | \phi^{(3)}_{16} \phi^{(2)}_{12} p \rangle = F_1 \text{ (direct)}$

$= G_1 \text{ (exchange)}$

From Part (a),

$F_1 = \sum_{k} \frac{4\pi}{k} \int dr_1 dr_2 \frac{r_1}{r_2} r_2^k \left| U^{(3)}_{15}(r_1) \right|^2 \left| U^{(2)}_{12}(r_2) \right|^2 \int d\Omega \, Y^x_{\theta_1 \phi_1} Y^y_{\theta_2 \phi_2} Y^z_{\theta_3 \phi_3} Y^z_{\theta_4 \phi_4}$

Only one $k$ value satisfies the triangle inequality, $k = 0$

$Y_{00} = \frac{1}{\sqrt{3}}$

$\Rightarrow F_1 = \int dr_1 dr_2 \frac{1}{r_2} \left| U^{(3)}_{15}(r_1) \right|^2 \left| U^{(2)}_{12}(r_2) \right|^2$

$= \frac{Z^3 (z-1)^5}{6} \int dr_1 \int dr_2 \frac{r_1^2}{r_2} e^{-2zr_1} r_2^4 e^{-2zr_2}$

$= \frac{Z^3 (z-1)^5}{6} \int_0^\infty dr_2 \int_0^\infty r_2^4 e^{-(z-1)r_2} \left\{ \frac{1}{r_2} \int dr_1 \frac{r_1^2}{r_2} e^{-2zr_1} + \int dr_1 \frac{r_1^2}{r_2} e^{-2zr_1} \right\}$

$\left\{ \frac{1}{4z^2 r_2} (1 - e^{-2zr_2}) - \frac{1}{4z^2} e^{-2zr_2} \right\}$

$= \frac{(z-1)^5}{24} \int_0^\infty dr \left[ r_2^3 (e^{-(z-1)r} - e^{-(3z-1)r}) - Zr_2^4 e^{-(3z-1)r} \right]$

$\Rightarrow F_1 = \frac{Z-1}{4} - \frac{(z-1)^5}{4(3z-1)^4} - \frac{Z(z-1)^5}{(3z-1)^4} = \frac{Z-1}{4} - \frac{(z-1)^5(3z-1)}{4(3z-1)^5}$
The exchange term

\[ G = \left< \phi_{15}^{(1)} \phi_{2p}^{(2-1)} \right| \frac{1}{r_{12}} \left| \phi_{15}^{(2-1)} \phi_{2p}^{(2)} \right> \]

\[ = \sum_{k} \frac{4\pi}{2k+1} \int d\mathbf{r}_1 d\mathbf{r}_2 \ u_{15}(\mathbf{r}_1) u_{2p}(\mathbf{r}_2) u_{15}(\mathbf{r}_2) u_{2p}(\mathbf{r}_1) \]

\[ \times \int d\mathbf{R}_1 \ Y_{00}^{*}(1) Y_{k0}^{*}(1) Y_{01}(1) \]

\[ \times \int d\mathbf{R}_2 \ Y_{00}^{*}(2) Y_{k0}^{*}(2) Y_{00}(2) \]

Here only \( k = 1 \), each angular integral is \( \frac{1}{4\pi} \).

\[ \Rightarrow G = \frac{2^3 (2-1)^5}{18} \int_0^\infty d\mathbf{r} \ r^3 e^{-(3z-1)r/2} \int_0^\infty d\mathbf{r}_2 \ \frac{r_2}{r_2^2} \ r_2^3 e^{-(3z-1)r_2/2} \]

by symmetry.

\[ = \frac{2^3 (2-1)^5}{18} \int_0^\infty d\mathbf{r} \ r^4 e^{-(3z-1)r/2} \int_0^\infty d\mathbf{r}' \ r' e^{-(3z-1)r'/2} \]

\[ = \frac{2^3 (2-1)^3}{18} \int_0^\infty d\mathbf{r} \ r^4 e^{-(3z-1)r/2} \left( \frac{2r}{3z-1} + \frac{4}{(3z-1)^2} \right) e^{-(3z-1)r/2} \]

\[ \Rightarrow G = \frac{112}{3} \frac{2^3 (2-1)^5}{(3z-1)^7} \]

\[ \therefore \quad E_\pm = \frac{(2z-1)^2}{8} - \frac{(2-1)^5}{4(3z-1)} (7z-1) \pm \frac{112}{3} \frac{2^3 (2-1)^5}{(3z-1)^7} \]
For the \( Z = 2 \),

1 \( \text{Hartree} = 2.1947 \times 10^5 \ \text{cm}^{-1} \)

\[
E_S = E_{3p} = -0.1222 \ \text{au} = -26,819 \ \text{cm}^{-1} \quad \text{for} \quad 3p
\]

\[
E_S = E_{3p} = -0.1299 \ \text{au} = -28,509 \ \text{cm}^{-1} \quad \text{for} \quad 3p
\]

OK agreement \( \approx 1\%-2\% \) of level energy

10-20\% of splitting

(c) The splitting is twice the exchange interaction

\[
\begin{align*}
\Delta E = 26 &= \frac{224}{3} \left( \frac{(p-1)^5}{(3Z-1)^3} \right) + 2.195 \times 10^5 \ \text{cm}^{-1} / \text{au}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( E_3 ) (cm(^{-1}))</th>
<th>( \left&lt; 3P_2 \right&gt; ) (cm(^{-1}))</th>
<th>( \Delta E_{\text{exp}} ) (cm(^{-1}))</th>
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Better agreement as \( Z \to \infty \)

Error due to single-particle orbital choice
Problem 2: Russell-Saunders Coupling of 3 equivalent p-electrons

Consider a configuration \((np)^3\) as in Nitrogen.

(a) For three equivalent \(p\)-electrons, there are

\[
\frac{6 \cdot 5 \cdot 4}{3!} = 20
\]

sublevels, consistent with the Pauli exclusion principle.

We use the Slater technique of enumerating the possible \(M_l\) and \(M_s\) values, and then assigning to "Terms".

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<th>(M_l)</th>
<th>(M_s)</th>
<th>(M_{l1})</th>
<th>(M_{l2})</th>
<th>(M_{l3})</th>
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</table>
We now tabulate the number of possible sub-levels with total $M_L$ and $M_S$, assign them to terms, remove them, repeat until all are assigned.

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<th>$M_S$</th>
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<th>$M_L$</th>
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</table>

$L = 2$, $S = \frac{1}{2}$

$\Rightarrow$ $M_L$ | $M_S$ | 1 | 0
<table>
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<tbody>
<tr>
<td>2P</td>
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<td>-</td>
</tr>
<tr>
<td>($L = 1$, $S = \frac{1}{2}$)</td>
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</table>

Thus the possible terms, $[2P, 2D, 4S]$

The multiplets: $[2P_{\frac{1}{2}, \frac{3}{2}}, 2D_{\frac{5}{2}, \frac{3}{2}}, 4S_{\frac{3}{2}, \frac{1}{2}}]$

**(b)** The $4S_{\frac{3}{2}}$ state is one in which the spin is totally symmetric under exchange, whereas the spatial state is totally antisymmetric (lowest energy). To examine the nature of the wave function, consider the sub-level with $M_S = \frac{3}{2}$. In this case all three electrons must have different $M_S = J_1 = -1$ (Case 7 in the Slater table).
We thus have as our orbital \( R_{n_2}(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3) \) \( Y_{l,m}(\theta, \phi) \quad m=\ell g-1 \)

Recall \( Y_{l,0} \sim \frac{Z}{r} \quad Y_{l,\pm 1} \sim \pm \frac{(x \mp iy)}{r} \)

The spatial wave function is described by the Slater determinant

\[
\Psi(r_1, r_2, r_3) = f(r_1) f(r_2) f(r_3) \begin{vmatrix}
 z_1 & (x_1 + iy_1) & x_1 - iy_1 \\
 z_2 & (x_2 + iy_2) & x_2 - iy_2 \\
 z_3 & (x_3 + iy_3) & x_3 - iy_3 \\
\end{vmatrix} = f(r_1) f(r_2) f(r_3) \left[ z_1 (i x_2 y_3 - i x_3 y_2) + (x_1 + iy_1) (z_2 x_3 - z_3 x_2) \right.
\]

\[
- (x_1 - iy_1) \left( z_3 y_2 - z_2 y_3 - i (z_2 y_3 - z_3 y_2) \right) \right]
\]

\[
= -2i f(r_1) f(r_2) f(r_3) \left[ z_1 (y_2 z_3 - y_3 z_2) \\
+ y_1 (z_2 x_3 - x_2 z_3) \\
+ z_1 (x_2 y_3 - y_2 x_3) \right]
\]

\[
= -2i f(r_1) f(r_2) f(r_3) \mathbf{r}_1 \cdot (\mathbf{r}_2 \times \mathbf{r}_3)
\]

The vector \( \mathbf{r}_1 \cdot (\mathbf{r}_2 \times \mathbf{r}_3) \) is a scalar under rotation of all vector \( \rightarrow L=0 \), and totally antisymmetric.
Note: The sublevels of $^4\text{S}_{3/2}$ with $M_J = \pm 3/2$

are separable in orbit and spin.

For \( \{ M_J = \pm 3/2 \} \), the spin state is \( \uparrow \downarrow \uparrow \downarrow \).

The \( M_J = \pm 1/2 \) do not have unique spin states.

They are entangled in space and spin.

(c) The term $^2P_{3/2}$ has sublevels \( M_J = 3/2, 1/2, -1/2, -3/2 \).

The sublevel \( M_J = 3/2 \) follows from the addition of angular momentum and exchange symmetry.

From the Slater table, there are two sets of orbitals with \( M_L = 1 \), \( M_S = 1/2 \) \( \rightarrow M_J = 3/2 \), those are (3) + (5). From the table constructed in part (a):
To find the coefficients, let us first ignore exchange symmetry and construct a wave function from these orbitals with \( n_L = 1, \, n_S = \frac{1}{2}, \Rightarrow n_f = \frac{3}{2} \).

We can do this by first adding together the orbital angular momentum of two \( p \)-electrons to get \( I_{1/2} = 0 \) and the adding \( m_S = 1 \). This is the spatial wave function

\[
\frac{R(r_1)R(r_2)\tilde{r}_{12}}{\sqrt{2}} \times (F_1 \cdot F_2) \times (X_3 + iy_3) \times \prod_{m=2}^{1} \left[ \sum_{l=0}^{\infty} Y_{l1}(1) Y_{l1}(1) \right] Y_{11}(3)
\]

At \( m_f = 1/2 \) spin-state is obtained by adding two spins to form a singlet and the tensoring in a third

\[
\uparrow \downarrow_1, \uparrow \downarrow_2 = \downarrow \uparrow_1, \downarrow \uparrow_2 \downarrow \uparrow_3
\]

The total wave function is then a product of space and spin, the anti-symmetrized over perturbations

\[
\mathcal{U}(1,2,3) = \sum_p (-1)^p R(p_1)R(p_2)R(p_3) \tilde{r}_{12} (X_3 + iy_3) (\downarrow_1, \downarrow_2, \uparrow_3)
\]

We see this as arising from the superposition of the two Slater determinants on the previous page with \( c_1 = 1 \) \( c_2 = -1 \).