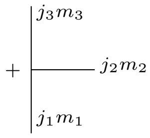
1. Derive the identity



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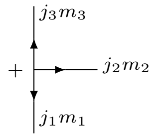
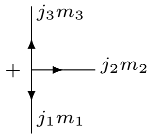
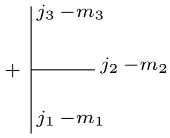
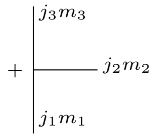


Proof:



$= (-1)^{j_1+j_2+j_3-m_1-m_2-m_3}$


$= (-1)^{2(j_1+j_2+j_3)-m_1-m_2-m_3}$


Now, $m_1 + m_2 + m_3 = 0$ and $j_1 + j_2 + j_3$ is always an integer.
Therefore, the phase factor $(-1)^{2(j_1+j_2+j_3)-m_1-m_2-m_3} = 1$.

2. Show that the spherical harmonics $Y_{kq}(\theta, \phi)$, $q = -k,\ -k+1,\ \cdots,\ k$ are components of an irreducible tensor operator (ITO) of rank k.

Verification:

$$\begin{aligned}
[L_z, Y_{kq}] &= L_z Y_{kq} = qY_{kq} \\
[L_+, Y_{kq}] &= L_+ Y_{kq} = \sqrt{(k-q)(k+q+1)}\,Y_{k\,q+1} \\
[L_-, Y_{kq}] &= L_- Y_{kq} = \sqrt{(k+q)(k-q+1)}\,Y_{k\,q-1}
\end{aligned}$$

Thus, Y_{kq} satisfies the conditions for an ITO.

3. Consider the 12-fold degenerate set of product wave functions:

$$\psi_{2p,m,\sigma}(\boldsymbol{r}_1)\psi_{1s,\mu}(\boldsymbol{r}_2) = \frac{1}{r_1 r_2} P_{2p}(r_1)P_{1s}(r_2)Y_{1m}(\hat{r}_1)Y_{00}(\hat{r}_2)\chi_\sigma(1)\chi_\mu(2).$$

(a) Combine these wave functions to give eigenstates of L^2, L_z, S^2, S_z, where $\boldsymbol{L} = \boldsymbol{L}_1 + \boldsymbol{L}_2$ and $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$.

The products

$$|l, m\rangle_l = \frac{1}{r_1 r_2} P_{2p}(r_1)P_{1s}(r_2)Y_{1m}(\hat{r}_1)Y_{00}(\hat{r}_2)$$

are already eigenstates of L^2 and L_z with eigenvalues 2 and m, respectively. Eigenstates of S^2 and S_z are constructed using the table of CGC'c. They are

$$\begin{aligned}
|0,0\rangle_s &= \frac{1}{\sqrt{2}}\left[\chi_{1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{1/2}(2)\right] \\
|1,1\rangle_s &= \chi_{1/2}(1)\chi_{1/2}(2) \\
|1,0\rangle_s &= \frac{1}{\sqrt{2}}\left[\chi_{1/2}(1)\chi_{-1/2}(2) + \chi_{-1/2}(1)\chi_{1/2}(2)\right] \\
|1,-1\rangle_s &= \chi_{-1/2}(1)\chi_{-1/2}(2)
\end{aligned}$$

The unsymmetrized angular momentum eigenstates are, therefore

$$|1, m, S, M_s\rangle = |1, m\rangle_l |S, M_s\rangle_s$$

(b) With the aid of the above result, write down all possible *antisymmetric* angular momentum eigenstates describing $1s2p$ levels of helium. What is the number of such states?

Note that the symmetric and antisymmetric combinations of orbital angular momentum eigenfunctions are again orbital angular momentum eigenfunctions. Antisymmetric wave functions are constructed by combining the antisymmetric spin eigenfunction $|0, 0\rangle_l$ above with symmetric L eigenfunctions, and combining symmetric spin eigenfunctions $|1, M_z\rangle_s$ with antisymmetric L eigenfunctions:

Therefore, we have in the following possible antisymmetric wave functions:

$$\begin{aligned} |1, m, 0, 0\rangle &= \frac{1}{\sqrt{2}} \frac{1}{r_1 r_2} \big(P_{2p}(r_1) P_{1s}(r_2) Y_{1m}(\hat{r}_1) Y_{00}(\hat{r}_2) + P_{2p}(r_2) P_{1s}(r_1) Y_{1m}(\hat{r}_2) Y_{00}(\hat{r}_1)\big) |0, 0\rangle_s \\ |l, m, 1, M_s\rangle &= \frac{1}{\sqrt{2}} \frac{1}{r_1 r_2} \big(P_{2p}(r_1) P_{1s}(r_2) Y_{1m}(\hat{r}_1) Y_{00}(\hat{r}_2) - P_{2p}(r_2) P_{1s}(r_1) Y_{1m}(\hat{r}_2) Y_{00}(\hat{r}_1)\big) |1, M_s\rangle_s \end{aligned}$$

There are (as before) $3 \times 1 + 3 \times 3 = 12$ states!

4. Show that the ionization energy of an atom with one valence electron is $-\epsilon_v$ in the "frozen-core" Hartree-Fock approximation. (Here, ϵ_v is the eigenvalue of the valence electron Hartree-Fock equation.)

The ionization energy ΔE in the frozen-core approximation is

$$\Delta E = E_{\text{ion}} - E_{\text{atom}} = -\langle h_0 \rangle - \sum_b (g_{vbvb} - g_{vbba})$$

The expression an the rhs can be written simply as

$$-\int_0^\infty P_v(r) \left[-\frac{1}{2} \frac{d^2 P_v}{dr^2} + \left(-\frac{Z}{r} + \frac{l_a(l_a+1)}{2r^2} + V_{HF} \right) P_v(r) \right]$$

By virtue of the frozen-core HF equations, the expression inside the square brackets reduces to $\epsilon_v P_v(r)$. Therefore, we find

$$\Delta E = -\int_0^\infty P_v(r)\, \epsilon_v P_v(r) = -\epsilon_v$$