22.3.5: v. Exercise Solutions

Q1

Constructing the Slater determinant corresponding to the "state" $1s(\alpha)1s(\alpha)$ with the rows labeling the orbitals and the columns labeling the electrons gives:

$$\begin{aligned} |1s\alpha 1s\alpha| = & \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\alpha(1) & 1s\alpha(2) \\ 1s\alpha(1) & as\alpha(2) \end{vmatrix} && (22.3.5.1) \\ = & \frac{1}{\sqrt{2}}(1s\alpha(1)1s\alpha(2) - 1s\alpha(1)1s\alpha(2)) && (22.3.5.2) \\ = & 0 && (22.3.5.3) \end{aligned}$$

Q2

Staring with the $M_S = 1\ {}^3S$ state which in a "box" for this $M_L = 0,\ M_S = 1$ case would contain only one product function; $|1s\alpha 2s\alpha|)$ and applying S_- gives:

$$\begin{aligned} S_-^3 S(S=1, M_S=1) = & \sqrt{1(1+1) - 1(1-1)}\,\hbar^3 S(S=1, M_S=0) && (22.3.5.4) \\ = & \hbar\sqrt{2}^3 S(S=1, M_S=0) && (22.3.5.5) \\ = & (S_-(1) + S_-(2))\,|1s\alpha 2s\alpha| && (22.3.5.6) \\ = & S_-(1)|1s\alpha 2s\alpha| + S_-(2)|1s\alpha 2s\alpha| && (22.3.5.7) \\ = & \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}-1\right)}\ [|1s\beta 2s\alpha + |1s\alpha 2s\beta|] && (22.3.5.8) \\ = & \hbar\,(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|) && (22.3.5.9) \\ \text{So, } \hbar\sqrt{2}^3 S(S=1, M_S=0) = & \hbar(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|) && (22.3.5.10) \\ {}^3S(S=1, M_S=0) = & \frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|)) && (22.3.5.11) \end{aligned}$$

The three triplet states are then:

$$\begin{aligned} & {}^3S(S=1, M_S=1) = |1s\alpha 2s\alpha|, && (22.3.5.12) \\ & {}^3S(S=1, M_S=0) = \frac{1}{2}(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|)\text{, and} && (22.3.5.13) \\ & {}^3S(S=1, M_S=-1) = |1s\beta 2s\beta|. && (22.3.5.14) \end{aligned}$$

The single state which must be constructed orthogonal to the three singlet states (and in particular to the ${}^3S(S=0, M_S=0)$ state) can be seen to be:

$$ {}^1S(S=0, M_S=0) = \frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| - |1s\alpha 2s\beta|)\,. $$

Applying S^2 and S_z to each of these states gives:

$$\begin{aligned} S_Z|1s\alpha 2s\alpha| = & (S_Z(1) + S_Z(2))\,|1s\alpha 2s\beta| && (22.3.5.15) \\ = & S_Z(1)|1s\alpha 2s\alpha| + S_Z(2)|1s\alpha 2s\alpha| && (22.3.5.16) \\ = & \hbar\left(\frac{1}{2}\right)|1s\alpha 2s\alpha| + \hbar\left(\frac{1}{2}\right)|1s\alpha 2s\alpha| && (22.3.5.17) \\ = & \hbar|1s\alpha 2s\alpha| && (22.3.5.18) \\ S^2|1s\alpha 2s\alpha| = & \left(S_-S_+ + S_Z^2 + \hbar S_Z\right)|1s\alpha 2s\alpha| && (22.3.5.19) \\ = & S_-S_+|1s\alpha 2s\alpha| + S_Z^2|1s\alpha 2s\alpha| + \hbar S_Z|1s\alpha 2s\alpha| && (22.3.5.20) \\ = & 0 + \hbar^2|1s\alpha 2s\alpha| + \hbar^2|1s\alpha 2s\alpha| && (22.3.5.21) \\ = & 2\hbar^2|1s\alpha 2s\alpha| && (22.3.5.22) \end{aligned}$$

$$\begin{aligned} S_Z\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| + |1s\alpha 2s\beta||) = & (S_Z(1) + S_Z(2))\,\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|) && (22.3.5.23) \\ = & \frac{1}{\sqrt{2}}(S_Z(1) + S_Z(2))\,|1s\beta 2s\alpha| + \frac{1}{\sqrt{2}}(S_Z(1) + S_Z(2))\,|1s\alpha 2s\beta| && (22.3.5.24) \\ = & \frac{1}{\sqrt{2}}\left(\hbar\left(-\frac{1}{2}\right) + \hbar\left(\frac{1}{2}\right)\right)|1s\beta 2s\alpha| + \frac{1}{\sqrt{2}}\left(\hbar\left(\frac{1}{2}\right) + \hbar\left(-\frac{1}{2}\right)\right)|1s\alpha 2s\beta| && (22.3.5.25) \\ = & 0\hbar\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| + |1s\alpha 2s\beta|) && (22.3.5.26) \end{aligned}$$

$$\begin{aligned}
S^2\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|+|1s\alpha 2s\beta|) &= \left(S_-S_+ + S_Z^2 + \hbar S_Z\right)\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|+|1s\alpha 2s\beta|) && (22.3.5.27)\\
&= S_-S_+\frac{1}{\sqrt{2}}(|1s\beta 2\alpha|+|1s\alpha 2s\beta|) && (22.3.5.28)\\
&= \frac{1}{\sqrt{2}}(S_-\left(S_+(1)+S_+(2)\right)|1s\beta 2s\alpha| + S_-\left(S_+(1)+S_+(2)\right)|1s\alpha 2s\beta|) && (22.3.5.29)\\
&= \frac{1}{\sqrt{2}}(S_-\hbar|1s\alpha 2s\alpha| + S_-\hbar|1s\alpha 2s\alpha|) && (22.3.5.30)\\
&= 2\hbar\frac{1}{\sqrt{2}}((S_-(1)+S_-(2))|1s\alpha 2s\alpha|) && (22.3.5.31)\\
&= 2\hbar\frac{1}{\sqrt{2}}(\hbar|1s\beta 2s\alpha| + |\hbar|1s\alpha 2s\beta|) && (22.3.5.32)\\
&= 2\hbar^2\frac{1}{\sqrt{2}}(1s\beta 2s\alpha| + |1s\alpha 2s\beta|) && (22.3.5.33)
\end{aligned}$$

$$\begin{aligned}
S^2|1s\beta 2s\beta| &= \left(S_+S_- + S_Z^2 - \hbar S_A\right)|1s\beta 2s\beta| && (22.3.5.34)\\
&= S_+S_-|1s\beta 2s\beta|1s\beta 2s\beta| - \hbar S_Z|1s\beta 2s\beta| && (22.3.5.35)\\
&= 0+\hbar^2|1s\beta 2s\beta| + \hbar^2|1s\beta 2s\beta| && (22.3.5.36)\\
&= 2\hbar^2|1s\beta 2s\beta| && (22.3.5.37)
\end{aligned}$$

$$\begin{aligned}
S_Z\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|-|1s\alpha 2s\beta|) &= (S_Z(1)+S_Z(2))\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|-|1s\alpha 2s\beta|) && (22.3.5.38)\\
&= \frac{1}{\sqrt{2}}(S_Z(1)+S_Z(2))|1s\beta 2s\alpha| - \frac{1}{\sqrt{2}}(S_Z(1)+S_Z(2))|1s\alpha 2s\beta| && (22.3.5.39)\\
&= \frac{1}{\sqrt{2}}\left(\hbar\left(-\frac{1}{2}\right)+\hbar\left(\frac{1}{2}\right)\right)|1s\beta 2s\alpha| - \frac{1}{\sqrt{2}}\left(\hbar\left(\frac{1}{2}\right)+\hbar\left(-\frac{1}{2}\right)\right)|1s\alpha 2s\beta| && (22.3.5.40)\\
&= 0\hbar\frac{1}{\sqrt{2}}(1s\beta 2s\alpha| - |1s\alpha 2s\beta|) && (22.3.5.41)
\end{aligned}$$

$$\begin{aligned}
S^2\frac{1}{\sqrt{2}}(1s\beta 2s\alpha|-|1s\alpha 2s\beta|) &= \left(S_-S_+ S_Z^2 + \hbar S_Z\right)\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|-|1s\alpha 2s\beta|) && (22.3.5.42)\\
&= S_-S_+\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha|-|1s\alpha 2s\beta|) && (22.3.5.43)\\
&= \frac{1}{\sqrt{2}}(S_-\left(S_+(1)+S_+(2)\right)|1s\beta 2s\alpha| - S_-\left(S_+(1)+S_+(2)\right)|1s\alpha 2s\beta|) && (22.3.5.44)\\
&= \frac{1}{\sqrt{2}}(S_-\hbar|1s\alpha 2s\alpha| - S_-\hbar|1s\alpha 2s\alpha|) && (22.3.5.45)\\
&= 0\hbar\frac{1}{\sqrt{2}}\left((S_-(1)+S(2))\,|1s\alpha 2s\alpha|\right) && (22.3.5.46)\\
&= 0\hbar\frac{1}{\sqrt{2}}(\hbar|1s\beta 2s\alpha| - \hbar|1s\alpha 2s\beta|) && (22.3.5.47)\\
&= 0\hbar^2\frac{1}{\sqrt{2}}(|1s\beta 2s\alpha| - |1s\alpha 2s\beta|) && (22.3.5.48)
\end{aligned}$$

Q3

a. Once the spatial symmetry has been determined by multimplication of the irreducible representations, the spon coupling is identical to exercise 2 and gives the result:

$$\frac{1}{\sqrt{2}}(|3_{a1}\alpha 1b_1\beta| - |3_{a1}\beta 1b_1\alpha|)$$

b. There are three states here (again analogous to exercise 2):

$$\begin{aligned}
&1.)|3_{a1}\alpha 1b_1\alpha|, && (22.3.5.49)\\
&2.)\frac{1}{\sqrt{2}}(|3_{a1}\alpha 1b_1\beta| + |3_{a1}\beta 1b_1\alpha|)\text{, and} && (22.3.5.50)\\
&3.)|3_{a1}\beta 1b_1\beta| && (22.3.5.51)
\end{aligned}$$

c.

$$|3_{a1}\alpha 3_{a1}\beta|$$

Q4

As shown in review exercise 1c, for two ewuivalent π electrons one obtains six states:

$$\begin{aligned}
&{}^1\Delta(M_L=2)\text{; one state }(M_S=0), && (22.3.5.52)\\
&{}^1\Delta(M_L=-2)\text{; one state }(M_S=0), && (22.3.5.53)\\
&{}^1\sum(M_L=0)\text{; one state }(M_S=0)\text{, and} && (22.3.5.54)\\
&{}^3\sum(M_L=0)\text{; three states }(M_S=1,0,\text{ and -1}). && (22.3.5.55)
\end{aligned}$$

By inspecting the "box" in review exercise 1c, it should be fairly straightforward to write down the wavefunctions for each of these:

$$^1\Delta(M_L=2); |\pi_1\alpha\pi_1\beta| \tag{22.3.5.56}$$

$$^1\Delta(M_L=-2); |\pi_1\alpha\pi_1\beta| \tag{22.3.5.57}$$

$$^1\sum(M_L=0); \frac{1}{\sqrt{2}}(|\pi_1\beta\pi_{-1}\alpha|-|\pi_1\alpha\pi_{-1}\beta|) \tag{22.3.5.58}$$

$$^3\sum(M_L=0, M_S=1); |\pi_1\alpha\pi_{-1}\alpha| \tag{22.3.5.59}$$

$$^3\sum(M_L=0, M_S=0); \frac{1}{\sqrt{2}}(|\pi_1\beta\pi_{-1}\alpha|+|\pi_1\alpha\pi_{-1}\beta|) \tag{22.3.5.60}$$

$$^3\sum(M_L=0, M_S=-1); |\pi_1\beta\pi_{-1}\beta| \tag{22.3.5.61}$$

Q5

We can conveniently couple another s electron to the states generate from the $1s^12s^1$ configuration in exercise 2:

$$^3S(L=0,S=1)\text{with } 3s^1(L=0,S=\frac{1}{2})giving: \tag{22.3.5.62}$$

$$L=0, S=\frac{3}{2},\frac{1}{2},^4S(4states)and^2S(2states). \tag{22.3.5.63}$$

$$^1S(L=0,S=0)with3s^1(L=0,S=\frac{1}{2})giving: \tag{22.3.5.64}$$

$$L=0, S=\frac{1}{2};^2S(2states). \tag{22.3.5.65}$$

Constructing a "box" for this case would yield:

M_S \ M_L	0
$\frac{3}{2}$	$\|1s\alpha2s\alpha3s\alpha\|$
$\frac{1}{2}$	$\|1s\alpha2s\alpha3s\beta\|$, $\|1s\alpha2s\beta3s\alpha\|$, $\|1s\beta2s\alpha3s\alpha\|$

One can immediately identify the wavefunctions for two of the quartets (they are single entries):

$$^4S(S=\frac{3}{2},M_S=\frac{3}{2}):|1s\alpha2s\alpha3s\alpha| \tag{22.3.5.66}$$

$$^4S(S=\frac{3}{2},M_S=-\frac{3}{2}):|1s\beta2s\beta3s\beta| \tag{22.3.5.67}$$

Applying S_- to $^4S(S=\frac{3}{2},M_S=-\frac{3}{2})$ yields:

$$S_-^4S(S=\frac{3}{2},M_S=\frac{3}{2}) = \hbar\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{3}{2}\left(\frac{3}{2}-1\right)}^4S(S=\frac{3}{2},M_S=\frac{1}{2}) \tag{22.3.5.68}$$

$$= \hbar\sqrt{3}^4S(S=\frac{3}{2},M_S=\frac{1}{2}) \tag{22.3.5.69}$$

$$S_-|1s\alpha2s\alpha3s\alpha| = \hbar(|1s\beta2s\alpha3s\alpha|+|1s\alpha2s\beta3s\alpha|+|1s\alpha2s\alpha3s\beta|) \tag{22.3.5.70}$$

$$\text{So, }^4S(S=\frac{3}{2},M_S=\frac{1}{2}) = \frac{1}{\sqrt{3}}(|1s\beta2s\alpha3s\alpha|+|1s\alpha2s\beta3s\alpha|+|1s\alpha2s\alpha3s\beta|) \tag{22.3.5.71}$$

Applying S_+ to $^S(S=\frac{3}{2},M_S=-\frac{3}{2})$ yields:

Applying S_+ to $^4S(S=\frac{3}{2},M_S=-\frac{3}{2})$ yields:

$$S_+^4S(S=\frac{3}{2},M_S=-\frac{3}{2}) = \hbar\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)--\frac{3}{2}\left(\frac{3}{2}+1\right)}^4S(S=\frac{3}{2},M_S=-\frac{1}{2}) \tag{22.3.5.72}$$

$$= \hbar\sqrt{3}^4S(S=\frac{3}{2},M_S=-\frac{1}{2}) \tag{22.3.5.73}$$

$$S_+|1s\beta2s\beta3s\beta| = \hbar(|1s\alpha2s\beta3s\beta|+|1s\beta2s\alpha3s\beta|+|1s\beta2s\beta3s\alpha|) \tag{22.3.5.74}$$

$$\text{So, }^4S(S=\frac{3}{2},M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}}(|1s\alpha2s\beta3s\beta|+|1s\beta2s\alpha3s\beta|+|1s\beta2s\beta3s\alpha|) \tag{22.3.5.75}$$

Applying S_+ to $^S(S=\frac{3}{2},M_S=-\frac{3}{2})$ yields:

It only remains to construct the doublet states which are orthogonal to these quartet states. Recall that the orthogonal combinations for systems having three equal components (for example when symmetry adapting the 3 sp^2 hybrids in C_{2v} or D_{3h} symmetry) give results of + + +, +2 - -, and 0 + -. Notice that the quartets are the + + + combinations and therefore the doublets can be recognized as:

$$^2S(S=\frac{1}{2},M_S=-\frac{1}{2}) = \frac{1}{\sqrt{6}}(|1s\beta 2s\alpha 3s\alpha| + |1s\alpha 2s\beta 3s\alpha| - 2|1s\alpha 2s\alpha 3s\beta|) \tag{22.3.5.76}$$

$$^2S(S=\frac{1}{2},M_S=-\frac{1}{2}) = \frac{1}{\sqrt{2}}(|1s\beta 2s\alpha 3s\alpha| - |1s\alpha 2s\beta 3s\alpha| + 0|1s\alpha 2s\alpha 3s\beta|) \tag{22.3.5.77}$$

$$^2S(S=\frac{1}{2},M_S=-\frac{1}{2}) = \frac{1}{\sqrt{6}}(|1s\alpha 2s\beta 3s\beta| + |1s\beta 2s\alpha 3s\beta| - 2|1s\beta 2s\beta 3s\alpha|) \tag{22.3.5.78}$$

$$^2S(S=\frac{1}{2},M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}}(|1s\alpha 2s\beta 3s\beta| - |1s\beta 2s\alpha 3s\beta| + 0|1s\beta 2s\beta 3s\alpha|) \tag{22.3.5.79}$$

Q6

As illustrated in this chapter a p^2 configuration (two equivalent p electrons) gives rise to the term symbols: $^3P,^1D$, and ^1S. Coupling an additional electron $(3d^1)$ to this p^2 configureation will give the desired $1s^22s^22p^23d^1$ term symbols:

$$^3P(L=1,S=1) \text{ with } ^D(L=2,S=\frac{1}{2}) generates; \tag{22.3.5.80}$$

$$L=3,2,1, \text{ and } S=\frac{3}{2},\frac{1}{2} \text{ with term symbols } ^4F,^2F,^4D,^2D,^4P, \text{ and } ^2S, \tag{22.3.5.81}$$

$$^1S(L=0,S=0) \text{ with } ^2D(L=2,S=\frac{1}{2}) generates; \tag{22.3.5.82}$$

$$L=2 \text{ and } S=\frac{1}{2} \text{ with term symbol } ^2D. \tag{22.3.5.83}$$

Q7

The notation used for the Slater Condon tules will be the same as used in the test:
(a.) zero (spin orbital) difference;

$$\langle|F+G|\rangle = \langle\phi_i|f|\phi_i\rangle + \sum_{i>j}(\langle\phi_i\phi_j|g|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|g|\phi_j\phi_i\rangle) \tag{22.3.5.84}$$

$$= \sum_i f_{ii} + \sum_{i>j}(g_{ijij} - g_{ijji}) \tag{22.3.5.85}$$

(b.) one (spin orbital) difference $(\phi_p \neq \phi_{p'}$;

$$\langle|F+G|\rangle = \langle\phi_p|f|\phi_{p'}\rangle + \sum_{j\neq p;p'}(\langle\phi_p\phi_j|g|\phi_{p'}\phi_j\rangle - \langle\phi_p\phi_j|g|\phi_j\phi_{p'}\rangle) \tag{22.3.5.86}$$

$$= f_{pp'} + \sum_{j\neq p;p'}(g_{pjp'j} - g_{pjjp'}) \tag{22.3.5.87}$$

(c.) two (spin orbital) differences $(\phi_p \neq \phi_{p'}$ and $\phi_q \neq \phi_{q'})$;

$$\langle|F+G|\rangle = \langle\phi_p\phi_q|g|\phi_{p'}\phi_{q'}\rangle - \langle\phi_p\phi_q|g|\phi_j\phi_{p'}\rangle \tag{22.3.5.88}$$

$$= g_{pqp'q'} - g_{pqq^{-\prime}p'} \tag{22.3.5.89}$$

(d.) three or more (spin orbital) differences;

$$\langle|F+G|\rangle = 0$$

i. $^3P(M_L=1,M_S=1) = |p_1\alpha p_0\alpha|$
$\langle|p_1\alpha p_0\alpha|H|p_1\alpha p_0\alpha|\rangle =$
Error!. Using the Slater Condon rule (a.) above (SCa):

$$\langle|10|H|10|\rangle = f_{11} + f_{00} + g_{1010} - g_{1001}$$

ii. $^3P(M_L=0,M_S=0) = \frac{1}{\sqrt{2}}(|p_1\alpha p_{-1}\beta| + |p_1\beta p_{-1}\alpha|)$

$$\langle^3P(M_L=0,M_S=0)|H|^3P(M_L=0,M_S=0)\rangle = \tag{22.3.}$$

$$= \frac{1}{2}(\langle|p_1\alpha p_{-1}\beta|H|p_1\alpha p_{-1}\beta|\rangle + \langle|p_1\alpha p_{-1}\beta|H|p_1\beta p_{-1}\alpha|\rangle + \langle|p_1\beta p_{-1}\alpha|H|p_1\alpha p_{-1}\beta|\rangle + \langle|p_1\beta p_{-1}\alpha|H|p_1\beta p_{-1}\alpha|\rangle) \tag{22.3.}$$

Evaluating each matrix element gives:

$$\langle|p_1\alpha p_{-1}\beta|H|p_1\alpha p_{-1}\beta|\rangle = f_{1\alpha 1\alpha} + f_{-1\beta -1\beta} + g_{1\alpha -1\beta 1\alpha -1\beta} - g_{1\alpha -1\beta -1\beta 1\alpha}(SCA) \tag{22.3.5.92}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.93}$$

$$\langle|p_1\alpha p_{-1}\beta|H|p_1\beta p_{-1}\alpha|\rangle = g_{1\alpha -1\beta 1\beta -1\alpha} - g_{1\alpha -1\beta -1\alpha 1\beta}(SCc) \tag{22.3.5.94}$$

$$= 0 - g_{1-1-11} \tag{22.3.5.95}$$

$$\langle|p_1\beta p_{-1}\alpha|H|p_1\alpha p_{-1}\beta|\rangle = g_{1\beta -1\alpha 1\alpha -1\beta} - g_{1\beta -1\alpha -1\beta 1\alpha}(SCc) \tag{22.3.5.96}$$

$$= 0 - g_{1-1-11} \tag{22.3.5.97}$$

$$\langle|p_1\beta p_{-1}\alpha|H|p_1\beta p_{-1}\alpha|\rangle = f_{1\beta 1\beta} + f_{-1\alpha -1\alpha} + g_{1\beta -1\alpha 1\beta -1\alpha} - g_{1\beta -1\alpha -1\alpha 1\beta}(SCa) \tag{22.3.5.98}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.99}$$

Substitution of these expressions give:

$$\langle^3P(M_L=0,M_S=0)|H|^3P(M_L=0,M_S=0)\rangle = \frac{1}{2}(f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} - g_{1-1-11} + f_{11} + f_{-1-1} + g_{1-11-1}) \tag{22.3.5.100}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} \tag{22.3.5.101}$$

iii. $^1S(M_L=0,M_S=0); \frac{1}{\sqrt{3}}(|p_0\alpha p_0\beta| - |p_1\alpha p_{-1}\beta| - |p_{-1}\alpha p_1\beta|)$

$$\begin{aligned}\langle ^1S(M_L=0,M_S=0)|H|^1S(M_L=0,M_S=0)\rangle &= \frac{1}{3}\Big(\langle|p_0\alpha p_0\beta|H|p_0\alpha p_0\beta|\rangle - \langle|p_0\alpha p_0\beta|H|p_1\alpha p_{-1}\beta|\rangle \quad - \quad \langle|p_0\alpha p_0\beta|H|p_{-1}\alpha p_1\beta|\rangle - \langle|p_1\alpha p_{-1}\beta|H|p_0\alpha p_0\beta|\rangle \quad (22 \\ &+ \quad \langle|p_1\alpha p_{-1}\beta|H|p_1\alpha p_{-1}\beta|\rangle + \langle|p_1\alpha p_{-1}\beta|H|p_{-11}\alpha p_1\beta|\rangle \quad (22 \\ &- \quad \langle|p_{-1}\alpha p_1\beta|H|p_0\alpha p_0\beta|\rangle + \langle|p_{-1}\alpha p_1\beta|H|p_1\alpha p_{-1}\beta|\rangle \quad (22 \\ &+ \quad \langle|p_{-1}\alpha p_1\beta|H|p_{-1}\alpha p_1\beta|\rangle\Big) \quad (22\end{aligned}$$

Evaluating each matrix element gives:

$$\langle|P_0\alpha p_0\beta|H|p_0\alpha p_0\beta|\rangle = f_{0\alpha0\alpha} + f_{0\beta0\beta} + g_{0\alpha0\beta0\alpha0\beta} - g_{0\alpha0\beta0\beta0\alpha}(SCa) \tag{22.3.5.106}$$
$$= f_{00} + f_{00} + g_{0000} - 0 \tag{22.3.5.107}$$
$$\langle|p_0\alpha p_0\beta|H|p_1\alpha p_{-1}\beta|\rangle = \langle|p_1\alpha p_{-1}\beta|H|p_0\alpha p_0\beta|\rangle \tag{22.3.5.108}$$
$$= g_{0\alpha0\beta1\alpha-1\beta} - g_{0\alpha0\beta-1\beta1\alpha}(SCc) \tag{22.3.5.109}$$
$$= g_{001-1} - 0 \tag{22.3.5.110}$$
$$\langle|p_0\alpha p_0\beta|H|p_{-1}\alpha p_1\beta|\rangle = \langle|p_{-1}\alpha p_1\beta|H|p_0\alpha p_0\beta|\rangle \tag{22.3.5.111}$$
$$= g_{0\alpha0\beta-1\alpha1\beta} - g_{0\alpha0\beta1\beta-1\alpha}(SCc) \tag{22.3.5.112}$$
$$= g_{00-11} - 0 \tag{22.3.5.113}$$
$$\langle|p_1\alpha p_{-1}\beta|H|p_1\alpha p_{-1}\beta|\rangle = f_{1\alpha1\alpha} + f_{-1\beta-1\beta} + g_{1\alpha-1\beta1\alpha-1\beta} - g_{1\alpha-1\beta-1\beta1\alpha}(SCa) \tag{22.3.5.114}$$
$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.115}$$
$$\langle|p_1\alpha p_{-1}\beta|H|p_{-1}\alpha p_1\beta|\rangle = \langle|p_{-1}\alpha p_1\beta|H|p_1\alpha p_{-1}\beta|\rangle \tag{22.3.5.116}$$
$$= g_{1\alpha-\beta-1\alpha1\beta} - g_{1\alpha-1\beta1\beta-1\alpha}(SCc) \tag{22.3.5.117}$$
$$= g_{1-1-11} - 0 \tag{22.3.5.118}$$
$$\langle|p_{-1}\alpha p_1\beta|H|p_{-1}\alpha p_1\beta|\rangle = f_{-1\alpha-1\alpha} + f_{1\beta1\beta} + g_{-1\alpha1\beta-1\alpha1\beta} - g_{-1\alpha1\beta1\beta-1\alpha}(SCa) \tag{22.3.5.119}$$
$$= f_{-1-1} + f_{11} + g_{-11-11} - 0 \tag{22.3.5.120}$$

Substitution of these expressions give:

$$\langle ^1S(M_L=0,M_S=0) \quad |H|^1S(M_L=0,M_S=0)\rangle \tag{22.3.5.121}$$
$$= \frac{1}{3}(f_{00} + f_{00} + g_{0000} - g_{001-1} - g_{00-11} - g_{001-1} + f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11} - g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} + g_{-11-11}) \tag{22.3.5.122}$$
$$= \frac{1}{3}(2f_{00} + 2f_{11} + 2f_{-1-1} + g_{0000} - 4g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11}) \tag{22.3.5.123}$$

iv. $^1D(M_L=0,M_S=0) = \frac{1}{\sqrt{6}}(2|p_0\alpha p_0\beta| + |p_1\alpha p_{-1}\beta| + |p_{-1}\alpha p_1\beta|)$

Evaluating $\langle ^1D(M_L=0,M_S=0)|H|^1D(M_L=0,M_S=0)\rangle$ we note that all the Slater Condon matrix elements generated are the same as those evaluated in part iii. (the sign for the wavefunction components and the multiplicative factor of two for one of the components, however, are different).

$$\langle ^1D\,(M_L=0,M_S=0)\,|H|^1D\,(M_L=0,M_S=0)\rangle \tag{22.3.5.124}$$
$$\frac{1}{6}(4f_{00} + 4f_{00} + 4g_{0000} + 2g_{001-1} + 2g_{00-11} + 2g_{001-1} + f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11} + 2g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} + g_{-11-11}) \tag{22.3.5.125}$$
$$= \frac{1}{6}(8f_{00} + 2f_{11} + 2f_{-1-1} + 4g_{0000} + 8g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11}) \tag{22.3.5.126}$$

Q8

i. $^\Delta\,(M_L=2,M_S=0) = |\pi_1\alpha\pi_1\beta|$

$$\langle ^1\Delta\,(M_L=2,M_S=0)\,|H|^1\Delta\,(M_L=2,M_S=0)\rangle \tag{22.3.5.127}$$
$$= \langle|\pi_1\alpha\pi_1\beta|H|\pi_1\alpha\pi_1\beta|\rangle \tag{22.3.5.128}$$
$$= f_{1\alpha1\alpha} + f_{1\beta1\beta} + g_{1\alpha1\beta1\alpha1\beta} - g_{1_{alpha1\beta1\beta1\alpha}}(SCa) \tag{22.3.5.129}$$
$$= f_{11} + f_{11} + g_{1111} - 0 \tag{22.3.5.130}$$
$$= 2f_{11} + g_{1111} \tag{22.3.5.131}$$

ii. $^1\sum(M_L=0,M_S=0) = \frac{1}{\sqrt{2}}(|\pi_1\alpha\pi_{-1}\beta| - |\pi_1\beta\pi_{-1}\alpha|)$

$$\langle ^3\sum(M_L=0,M_S=0)\,|H|^3\sum(M_L=0,M_S=0)\rangle$$
$$= \frac{1}{2}(\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\alpha\pi_{-1}\beta|\rangle - \langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\beta\pi_{-1}\alpha|\rangle - \langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\alpha\pi_{-1}\beta|\rangle + \langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\beta\pi_{-1}\alpha|\rangle)$$

Evaluating each matrix element gives:

$$\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\alpha\pi_{-1}\beta|\rangle = f_{1\alpha 1\alpha} + f_{-1\beta -1\beta} + g_{1\alpha -1\beta 1\alpha -1\beta} - g_{1\alpha -1\beta -1\beta 1\alpha}(SCa) \tag{22.3.5.134}$$
$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.135}$$
$$\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\beta\pi_{-1}\alpha|\rangle = g_{1\alpha -1\beta 1\beta -1\alpha} - g_{1\alpha -1\beta -1\alpha 1\beta}(SCc) \tag{22.3.5.136}$$
$$= 0 - g_{1-1-11} \tag{22.3.5.137}$$
$$\langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\alpha\pi_{-1}\beta|\rangle = 0 - g_{1-1-11} \tag{22.3.5.138}$$
$$\langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\beta\pi_{-1}\beta|\rangle = f_{1\beta 1\beta} + f_{-1\alpha -1\alpha} + g_{1\beta -1\alpha 1\beta -1\alpha} - g_{1\beta -1\alpha -1\alpha 1\beta}(SCa) \tag{22.3.5.139}$$
$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.140}$$

Substitution of these expressions give:

$$\langle {}^3\sum(M_L=0,M_S=0)\,|H|^3\sum(M_L=0,M_S=0)\rangle = \frac{1}{2}(f_{11}+f_{-1-1}+g_{1-11-1}+g_{1-1-11}+g_{1-1-11}+f_{11}+f_{-1-1}+g_{1-11-1}) \tag{22.3.5.141}$$
$$= f_{11}+f_{-1-1}+g_{1-11-1}+g_{1-1-11} \tag{22.3.5.142}$$

iii. ${}^3\sum(M_L=0,M_S=0) = \frac{1}{\sqrt{2}}(|\pi_1\alpha\pi_{-1}\beta| + |\pi_1\beta\pi_{-1}\alpha|)$

$$\langle {}^3\sum(M_L=0,M_S=0)\,|H|^3\sum(M_L=0,M_S=0)\rangle$$
$$= \frac{1}{2}(\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\alpha\pi_{-1}\beta|\rangle + \langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\beta\pi_{-1}\alpha|\rangle + \langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\alpha\pi_{-1}\beta|\rangle + \langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\beta\pi_{-1}\alpha|$$

Evaluating each matrix element gives:

$$\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\alpha\pi_{-1}\beta\rangle = f_{1\alpha 1\alpha} + f_{-1\beta -1\beta} + g_{1\alpha -1\beta 1\alpha -1\beta} - g_{1\alpha -1\beta -1\beta 1\alpha}(SCa) \tag{22.3.5.145}$$
$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.146}$$
$$\langle|\pi_1\alpha\pi_{-1}\beta|H|\pi_1\beta\pi_{-1}\alpha|\rangle = g_{1\alpha -1\beta 1\beta -1\alpha} - g_{1\alpha -1\beta -1\alpha 1\beta}(SCc) \tag{22.3.5.147}$$
$$= 0 - g_{1-1-11} \tag{22.3.5.148}$$
$$\langle|\pi_1\beta\pi_{-1}\alpha|H|\pi_1\alpha\pi_{-1}\alpha|\rangle = f_{1\beta 1\beta} + f_{-1\alpha -1\alpha} + g_{1\beta -1\alpha 1\beta -1\alpha} - g_{1\beta -1\alpha -1\alpha 1\beta}(SCa) \tag{22.3.5.149}$$
$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \tag{22.3.5.150}$$

Substitution of these expressions give:

$$\langle \quad \Sigma(M_L=0,M_S=0)\,|H|^3\sum(M_L=0,M_S=0)\rangle \tag{22.3.5.151}$$
$$= \frac{1}{2}(f_{11}+f_{-1-1}+g_{1-11-1}-g_{1-1-11}+f_{11}+f_{-1-1}+g_{1-11-1}) \tag{22.3.5.152}$$
$$= f_{11}+f_{-1-1}+g_{1-11-1}-g_{1-1-11} \tag{22.3.5.153}$$