

Answers to Homework Set 6

From lecture 21: Evaluate $\langle \beta(1)\beta(2) | S^2 | \beta(1)\beta(2) \rangle$. Remember to use eq. 20-26 to expand the operator

When we expand the two-electron S^2 operator into its individual components, using atomic units to avoid repeatedly writing \hbar we have

$$\begin{aligned}
 \langle \beta(1)\beta(2) | S^2 | \beta(1)\beta(2) \rangle &= \int \beta(1)\beta(2) S^2(1)\beta(1)\beta(2) d\omega(1)d\omega(2) \\
 &\quad + \int \beta(1)\beta(2) \beta(1) S^2(2)\beta(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) S_x(1)\beta(1) S_x(2)\beta(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) S_y(1)\beta(1) S_y(2)\beta(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) S_z(1)\beta(1) S_z(2)\beta(2) d\omega(1)d\omega(2) \\
 &= \int \beta(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \beta(1)\beta(2) d\omega(1)d\omega(2) \\
 &\quad + \int \beta(1)\beta(2) \beta(1) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \beta(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) \frac{1}{2} \alpha(1) \frac{1}{2} \alpha(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) \frac{i}{2} \alpha(1) \frac{i}{2} \alpha(2) d\omega(1)d\omega(2) \\
 &\quad + 2 \int \beta(1)\beta(2) \frac{1}{2} \beta(1) \frac{1}{2} \beta(2) d\omega(1)d\omega(2) \\
 &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) + 0 + 0 + \frac{1}{2} \\
 &= 2
 \end{aligned}$$

Note how the terms deriving from S_x and S_y become zero since these operators transform the β spin function to the α spin function, and an integration over $\alpha(i)\beta(i)d\omega(i)$ gives zero owing to the orthogonality of the spin functions.

From lecture 22:

Consider the fluorine atom. Its ground state is represented by the determinant ${}^2|1s^2 2s^2 2p_x^2 2p_y^2 2p_z\rangle$. Although fluorine is the most electronegative element, by applying a high enough voltage one can still strip an electron from it to generate F^+ . If two electrons are always kept in the 1s orbital, what are all possible determinants that can be made by ionizing fluorine to F^+ ? Put them in an energy ordering like that of eq. 22-9 and provide a short justification of your choice of order. Note that the F atom has spherical symmetry, so there is no difference between determinants that differ only in the labels x , y , and z on the p orbitals (thus, for instance, there is no difference between ${}^3|1s^2 2s^2 2p_x 2p_y^2 2p_z\rangle$ and ${}^3|1s^2 2s^2 2p_x^2 2p_y 2p_z\rangle$). You can also ignore spin-orbit coupling.

The easiest way to think about this problem is to notice that there are 5 different kinds of electrons that can be taken away from the fluorine atom (since the 1s orbital is left doubly filled). There is (i) a 2s electron of the same spin as the unpaired p electron, (ii) a 2s electron of the opposite spin as the unpaired p electron, (iii) a 2p electron in one of the doubly filled p orbitals that is of the same spin as the unpaired p electron, (iv) a 2p electron in one of the doubly filled p orbitals that is of the opposite spin as the unpaired p electron, and (v) the unpaired p electron. If we ask about the energy by which each of these 5 electrons is bound to the F atom, we have

$$\text{Case i: } \varepsilon_{2s} + J_{2s2s} + 5J_{2s2p} - K_{2s2p}$$

where the logic is that the electron has the potential and kinetic energy of a standard 2s electron (ε_{2s}), Coulomb interactions with the other 2s electron and the 5 2p electrons ($J_{2s2s} + 5J_{2s2p}$), and 3 favorable exchange interactions with 2p electrons of the same spin ($-3K_{2s2p}$) and 2 unfavorable exchange interactions with 2p electrons of opposite spin ($2K_{2s2p}$) for a net exchange energy of K_{2s2p} .

Following the same logic for the other cases gives

$$\text{Case ii: } \varepsilon_{2s} + J_{2s2s} + 5J_{2s2p} + K_{2s2p}$$

$$\text{Case iii: } \varepsilon_{2p} + 2J_{2s2p} + J_{2p2p} + 3J_{2p2p'} - K_{2p2p'}$$

$$\text{Case iv: } \varepsilon_{2p} + 2J_{2s2p} + J_{2p2p} + 3J_{2p2p'} + K_{2p2p'}$$

$$\text{Case v: } \varepsilon_{2p} + 2J_{2s2p} + 4J_{2p2p'}$$

where subscript 2p2p refers to an interaction between 2 2p electrons in the same p orbital, and subscript 2p2p' refers to 2 2p electrons in different p orbitals.

It will be easiest to remove the electron that has the highest energy of the 5 cases. Inspection suggests that this corresponds to case iv, which in addition to being a 2p electron (and thus intrinsically higher in energy than a 2s electron) has a Coulomb repulsion with the other electron in its orbital (worst) and with 3 other p electrons (bad) and a net unfavorable exchange interaction because it is the opposite spin of the unpaired p electron.

It is not easy to decide whether the next highest energy electron will be that of case iii or case v as we do not know the precise values of the various integrals J and K . We will accept that either order could be correct. As for the 2s electrons, it is clear that case ii is higher in energy than case 1, the most difficult electron to remove.

Following this analysis, the energy ordering of the F^+ determinants is

$$\begin{aligned} {}^3|2s^2 2p_x^2 2p_y 2p_z\rangle &< {}^1|2s^2 2p_x^2 \bar{2}p_y 2p_z\rangle \approx {}^1|2s^2 2p_x^2 2p_y^2\rangle \\ &< {}^3|2s 2p_x^2 2p_y^2 2p_z\rangle < {}^1|\bar{2}s 2p_x^2 2p_y^2 2p_z\rangle \end{aligned}$$

where, of course, the triplets can each be written in 3 degenerate ways. In addition, there are two possible singlets for every singlet case, depending on whether the doublet F atom began with a spin up electron in the singly occupied p orbital (as illustrated in all of the above discussion) or a degenerate spin down electron in that orbital.

From lecture 23:

Given eqs. 23-4 and 23-12, prove eq. 23-13.

We are given

$$\Psi_0 = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots$$

and

$$\langle \Psi_0 | \Psi_0^{(0)} \rangle = 1$$

and asked to prove

$$\langle \Psi_0^{(n)} | \Psi_0^{(0)} \rangle = \delta_{n0}$$

Substituting the first equation into the second gives

$$\begin{aligned}
1 &= \langle \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots | \Psi_0^{(0)} \rangle \\
&= \langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle + \lambda \langle \Psi_0^{(1)} | \Psi_0^{(0)} \rangle + \lambda^2 \langle \Psi_0^{(2)} | \Psi_0^{(0)} \rangle \\
&\quad + \lambda^3 \langle \Psi_0^{(3)} | \Psi_0^{(0)} \rangle + \dots \\
&= 1 + \lambda \langle \Psi_0^{(1)} | \Psi_0^{(0)} \rangle + \lambda^2 \langle \Psi_0^{(2)} | \Psi_0^{(0)} \rangle + \lambda^3 \langle \Psi_0^{(3)} | \Psi_0^{(0)} \rangle + \dots
\end{aligned}$$

Subtracting 1 from both sides (note that the 1 on the left came from the normalization of the zeroth-order wave function) gives

$$0 = \lambda \langle \Psi_0^{(1)} | \Psi_0^{(0)} \rangle + \lambda^2 \langle \Psi_0^{(2)} | \Psi_0^{(0)} \rangle + \lambda^3 \langle \Psi_0^{(3)} | \Psi_0^{(0)} \rangle + \dots$$

The only way that this equation can be true for all values of λ is for every integral on the r.h.s. to be zero. This result, together with the normalization of the zeroth-order wave function, may be expressed as

$$\langle \Psi_0^{(n)} | \Psi_0^{(0)} \rangle = \delta_{n0}$$

QED.