

11.4: Examples of Applying the Slater-Condon Rules

It is wise to gain some experience using the Slater-Condon rules, so let us consider a few illustrative example problems.

1. What is the contribution to the total energy of the 3P level of Carbon made by the two 2p orbitals alone? Of course, the two 1s and two 2s spin-orbitals contribute to the total energy, but we artificially ignore all such contributions in this example to simplify the problem.

Because all nine of the 3P states have the same energy, we can calculate the energy of any one of them; it is therefore prudent to choose an "easy" one

$$^3P(M_L = 1, M_S = 1) = |p_1\alpha p_0\alpha|.$$

The energy of this state is $\langle p_1\alpha p_0\alpha | H | p_1\alpha p_0\alpha \rangle$. The SC rules tell us this equals:

$$I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle,$$

where the short hand notation $\langle I_j | f | j \rangle$ is introduced.

If the contributions from the two 1s and two 2s spin-orbitals are now taken into account, one obtains a **total** energy that also contains $2I_{1s} + 2I_{2s} + \langle 1s1s | 1s1s \rangle + 4 \langle 1s2s | 1s2s \rangle - 2 \langle 1s2s | 2s1s \rangle + \langle 2s2s | 2s2s \rangle + 2 \langle 1s2p_1 | 1s2p_1 \rangle - \langle 1s2p_1 | 2p_11s \rangle + 2 \langle 1s2p_0 | 1s2p_0 \rangle - \langle 1s2p_0 | 2p_01s \rangle + 2 \langle 2s2p_1 | 2s2p_1 \rangle - \langle 2s2p_1 | 2p_12s \rangle + 2 \langle 2s2p_0 | 2s2p_0 \rangle - \langle 2s2p_0 | 2p_02s \rangle$.

2. Is the energy of another 3P state equal to the above state's energy? Of course, but it may prove informative to prove this. Consider the $M_S = 0, M_L = 1$ state whose energy is:

$$\begin{aligned} \frac{1}{\sqrt{2}} \langle [p_1\alpha p_0\beta] + [p_1\beta p_0\alpha] | H | [p_1\alpha p_0\beta] + [p_1\beta p_0\alpha] \rangle &= \frac{1}{\sqrt{2}} \\ &= \frac{1}{2} [I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle + I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle] \\ &\quad - \frac{1}{2} [\langle 2p_1 2p_0 | 2p_0 2p_1 \rangle + \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle] \\ &= I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle. \end{aligned}$$

Which is, indeed, the same as the other 3P energy obtained above

3. What energy would the singlet state $\frac{1}{\sqrt{2}} \langle [p_1\alpha p_0\beta] - [p_1\beta p_0\alpha] \rangle$ have?

The $^3P_{M_S=0}$ example can be used (changing the sign on the two determinants) to give

$$E = I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle + \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle.$$

Note, this is the $M_L = 1$ component of the 1D state; it is, of course, not a $1P$ state because no such state exists for two equivalent p electrons

4. What is the CI matrix element coupling $|1s^2 2s^2|$ and $|1s^2 3s^2|$?

These two determinants differ by two spin-orbitals, so

$$\langle 1s\alpha 1s\beta 2s\alpha 2s\beta | H | 1s\alpha 1s\beta 3s\alpha 3s\beta \rangle = \langle 2s2s | 3s3s \rangle = \langle 2s3s | 3s2s \rangle$$

(note, this is an exchange-type integral).

5. What is the CI matrix element coupling $|\pi\alpha\pi\beta\rangle$ and $|\pi^*\alpha\pi^*\beta\rangle$?

These two determinants differ by two spin-orbitals, so

$$\langle \pi\alpha\pi\beta | H | \pi^*\alpha\pi^*\beta \rangle = \langle \pi\pi | \pi^*\pi^* \rangle = \langle \pi\pi^* | \pi^*\pi \rangle$$

(note, again this is an exchange-type integral).

6. What is the Hamiltonian matrix element coupling $|\pi\alpha\pi\beta\rangle$ and $\frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle - |\pi\beta\pi^*\alpha\rangle]$?

The first determinant differs from the π^2 determinant by one spin-orbital, as does the second (after it is placed into maximal coincidence by making one permutation), so

$$\begin{aligned} & \langle \pi\alpha\pi\beta | H | \frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle - |\pi\beta\pi^*\alpha\rangle] \rangle \\ &= \frac{1}{\sqrt{2}} \left[\langle \pi | f | \pi^* \rangle + \langle \pi\pi | \pi^*\pi \rangle \right] - (-1) \frac{1}{\sqrt{2}} \left[\langle \pi | f | \pi^* \rangle + \langle \pi\pi | \pi^*\pi \rangle \right] \\ &= \sqrt{2} [\langle \pi | f | \pi^* \rangle + \langle \pi\pi | \pi^*\pi \rangle]. \end{aligned}$$

7. What is the element coupling $|\pi\alpha\pi\beta\rangle$ and $\frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle + |\pi\beta\pi^*\alpha\rangle]$?

$$\begin{aligned} & \langle \pi\alpha\pi\beta | H | \frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle + |\pi\beta\pi^*\alpha\rangle] \rangle = \frac{1}{\sqrt{2}} \left[\langle \pi | f | \pi^* \rangle + \langle \pi\pi | \pi^*\pi \rangle \right] \\ &+ (-1) \frac{1}{\sqrt{2}} \left[\langle \pi | f | \pi^* \rangle + \langle \pi\pi | \pi^*\pi \rangle \right] = 0. \end{aligned}$$

This result should not surprise you because $|\pi\alpha\pi\beta\rangle$ is an $S=0$ singlet state while $\frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle + |\pi\beta\pi^*\alpha\rangle]$ is the $M_S = 0$ component of the $S=1$ triplet state.

8. What is the $\mathbf{r} = \sum_j e\mathbf{r}_j$ electric dipole matrix element between $|p_1\alpha p_1\beta\rangle$ and $\frac{1}{\sqrt{2}}[|p_1\alpha p_0\beta\rangle + |p_0\alpha p_1\beta\rangle]$? Is the second function a singlet or triplet? It is a singlet in disguise; by interchanging the $p_0\alpha$ and $p_1\beta$ and thus introducing a (-1) , this function is clearly identified as $\frac{1}{\sqrt{2}}[|p_1\alpha p_0\beta\rangle - |p_1\alpha p_0\alpha\rangle]$ which is a singlet.

The first determinant differs from the latter two by one spin orbital in each case, so

$$\langle p_1\alpha p_1\beta | \mathbf{r} | \frac{1}{\sqrt{2}}[|p_1\alpha p_0\beta\rangle + |p_0\alpha p_1\beta\rangle] \rangle = \frac{1}{\sqrt{2}} [\langle p_1 | \mathbf{r} | p_0 \rangle + \langle p_1 | \mathbf{r} | p_0 \rangle] = \frac{1}{\sqrt{2}} \langle p_1 | \mathbf{r} | p_0 \rangle.$$

9. What is the electric dipole matrix elements between the $^1\Delta = |\pi_1\alpha\pi_1\beta\rangle$ state and the $^1\Sigma = \frac{1}{\sqrt{2}}[|\pi_1\alpha\pi_{-1}\beta\rangle + |\pi_{-1}\alpha\pi_1\beta\rangle]$ state?

$$\begin{aligned} & \langle \frac{1}{\sqrt{2}}[|\pi_1\alpha\pi_{-1}\beta\rangle + |\pi_{-1}\alpha\pi_1\beta\rangle] | \mathbf{r} | \pi_1\alpha\pi_1\beta \rangle \\ &= \frac{1}{\sqrt{2}} [\langle \pi_{-1} | \mathbf{r} | \pi_1 \rangle + \langle \pi_{-1} | \mathbf{r} | \pi_1 \rangle] \\ &= \sqrt{2} \langle \pi_{-1} | \mathbf{r} | \pi_1 \rangle. \end{aligned}$$

10. As another example of the use of the SC rules, consider the configuration interaction which occurs between the $1s^2 2s^2$ and $1s^2 2p^2$ CSFs in the Be atom.

The CSFs corresponding to these two configurations are as follows:

$$\Phi_1 = |1s\alpha 1s\beta 2s\alpha 2s\beta|$$

and

$$\Phi_2 = \frac{1}{\sqrt{3}} [|1s\alpha 1s\beta 2p_0\alpha 2p_0\beta| - |1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta| - |1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta|].$$

The determinantal Hamiltonian matrix elements needed to evaluate the 2×2 $H_{K,L}$ matrix appropriate to these two CSFs are evaluated via the SC rules. The first such matrix element is:

$$\langle |1s\alpha 1s\beta 2s\alpha 2s\beta| H |1s\alpha 1s\beta 2s\alpha 2s\beta \rangle = 2h_{1s} + 2h_{2s} + J_{1s,2s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s},$$

where

$$h_i = \langle \phi_i | \left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{4e^2}{r} \right) | \phi_i \rangle,$$

$$J_{i,j} = \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_i \phi_j \rangle,$$

and

$$K_{ij} = \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_j \phi_i \rangle$$

are the orbital-level **one-electron**, **coulomb**, and **exchange integrals**, respectively.

Coulomb integrals J_{ij} describe the coulombic interaction of one charge density (ϕ_i^2 above) with another charge density (ϕ_j^2 above); exchange integrals K_{ij} describe the interaction of an **overlap** charge density (i.e., a density of the form $\phi_i \phi_j$) with itself ($\phi_i \phi_j$ with $\phi_i \phi_j$ in the above).

The spin functions α and β which accompany each orbital in $|1s\alpha 1s\beta 2s\alpha 2s\beta|$ have been eliminated by carrying out the spin integrations as discussed above. Because H contains no spin operators, this is straightforward and amounts to keeping integrals $\langle \phi_i | f | \phi_j \rangle$ only if ϕ_i and ϕ_j are of the same spin and integrals $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ only if ϕ_i and ϕ_k are of the same spin **and** ϕ_j and ϕ_l are of the same spin. The physical content of the above energy (i.e., Hamiltonian expectation value) of the $|1s\alpha 1s\beta 2s\alpha 2s\beta|$ determinant is clear: $2h_{1s} + 2h_{2s}$ is the sum of the expectation values of the one-electron (i.e., kinetic energy and electron-nuclear coulomb interaction) part of the Hamiltonian for the four occupied spin-orbitals; $J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s}$ contains the coulombic repulsions among all pairs of occupied spin-orbitals minus the exchange interactions among pairs of spin-orbitals with like spin.

The determinantal matrix elements linking Φ_1 and Φ_2 are as follows:

$$\langle |1s\alpha 1s\beta 2s\alpha 2s\beta| H |1s\alpha 1s\beta 2p_0\alpha 2p_0\beta \rangle = \langle 2s2s | 2p_0 2p_0 \rangle,$$

$$\langle |1s\alpha 1s\beta 2s\alpha 2s\beta| H |1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta \rangle = \langle 2s2s | 2p_1 2p_{-1} \rangle,$$

$$\langle 1s\alpha 1s\beta 2s\alpha 2s\beta | H | 1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta \rangle = \langle 2s2s | 2p_{-1}2p_1 \rangle,$$

where the Dirac convention has been introduced as a shorthand notation for the two electron integrals (e.g., $\langle 2s2s | 2p_0 2p_0 \rangle$ represents $\int 2s^*(r_1)2s^*(r_2)\frac{e^2}{r_{12}}2p_0(r_1)2p_0(r_2)dr_1dr_2$).

The three integrals shown above can be seen to be equal and to be of the exchange integral form by expressing the integrals in terms of integrals over cartesian functions and recognizing identities due to the equivalence of the $2p_x$, $2p_y$, and $2p_z$ orbitals. For example,

$$\begin{aligned} \langle 2s2s | 2p_1 2p_{-1} \rangle &= \frac{1}{\sqrt{2}} [\langle 2s2s | [2p_x + i2p_y][2p_x - i2p_y] \rangle] = \\ \frac{1}{2} [\langle 2s2s | xx \rangle + \langle 2s2s | yy \rangle + i \langle 2s2s | yx \rangle - i \langle 2s2s | xy \rangle] &= \langle 2s2s | xx \rangle = K_{2s,x} \end{aligned}$$

(here the two imaginary terms cancel and the two remaining real integrals are equal);

$$\langle 2s2s 2p_0 2p_0 \rangle = \langle 2s2s | zz \rangle = \langle 2s2s | xx \rangle = K_{2s,x}$$

this is because $K_{2s,z} = K_{2s,x} = K_{2s,y}$;

$$\begin{aligned} \langle 2s2s | 2p_{-1} 2p_1 \rangle &= \frac{1}{2} [\langle 2s2s | [2p_x - i2p_y][2p_x + i2p_y] \rangle] = \\ \langle 2s2s | xx \rangle &= \int 2s^*(r_1)2s^*(r_2)\frac{e^2}{r_{12}}2p_x(r_1)2p_x(r_2)dr_1dr_2 = K_{2s,x}. \end{aligned}$$

These integrals are clearly of the exchange type because they involve the coulombic interaction of the $2s2p_{x,y,orz}$ overlap charge density with itself.

Moving on, the matrix elements among the three determinants in Φ_2 are given as follows:

$$\langle 1s\alpha 1s\beta 2p_0\alpha 2p_0\beta | H | 1s\alpha 1s\beta 2p_0\alpha 2p_0\beta \rangle = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p}$$

($J_{1s,2p}$ and $K_{1s,2p}$ are independent of whether the $2p$ orbital is $2p_x$, $2p_y$, or $2p_z$);

$$\langle 1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta | H | 1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta \rangle = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + \langle 2p_1 2p_{-1} | 2p_1 2p_{-1} \rangle;$$

$$\langle 1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta | H | 1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta \rangle = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + \langle 2p_{-1} 2p_1 | 2p_{-1} 2p_1 \rangle;$$

$$\langle 1s\alpha 1s\beta 2p_0\alpha 2p_0\beta | H | 1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta \rangle = \langle 2p_0 2p_0 | 2p_1 2p_{-1} \rangle$$

$$\langle 1s\alpha 1s\beta 2p_0\alpha 2p_0\beta | H | 1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta \rangle = \langle 2p_0 2p_0 | 2p_{-1} 2p_1 \rangle$$

$$\langle 1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta | H | 1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta \rangle = \langle 2p_1 2p_{-1} | 2p_{-1} 2p_1 \rangle$$

Certain of these integrals can be recast in terms of cartesian integrals for which equivalences are easier to identify as follows:

$$\langle 2p_0 2p_0 | 2p_1 2p_{-1} \rangle = \langle 2p_0 2p_0 | 2p_{-1} 2p_1 \rangle = \langle zz | xx \rangle = K_{z,x};$$

$$\langle 2p_1 2p_{-1} | 2p_{-1} 2p_1 \rangle = \langle xx | yy \rangle + \frac{1}{2} [\langle xx | xx \rangle - \langle xy | xy \rangle]$$

$$= K_{x,y} + \frac{1}{2} [J_{x,x} - J_{x,y}];$$

$$\langle 2p_1 2p_{-1} | 2p_1 2p_{-1} \rangle = \langle 2p_{-1} 2p_1 | 2p_{-1} 2p_1 \rangle = \frac{1}{2} [J_{x,x} + J_{x,y}].$$

Finally, the 2x2 CI matrix corresponding to the CSFs Ψ_1 and Ψ_2 can be formed from the above determinantal matrix elements; this results in:

$$H_{11} = 2h_{1s} + 2h_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s};$$

$$H_{12} = \frac{-K_{2s,x}}{\sqrt{3}};$$

$$H_{22} = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + J_{Z,Z} - \frac{2}{3}K_{Z,X}.$$

The lowest eigenvalue of this matrix provides this CI calculation's estimate of the groundstate 1S energy of Be; its eigenvector provides the CI amplitudes for Φ_1 and Φ_2 in this ground-state wavefunction. The other root of the 2x2 secular problem gives an approximation to another 1S state of higher energy, in particular, a state dominated by the $\frac{1}{\sqrt{3}} [|1s\alpha 1s\beta 2p_0\alpha 2p_0\beta| - |1s\alpha 1s\beta 2p_1\alpha 2p_{-1}\beta| - |1s\alpha 1s\beta 2p_{-1}\alpha 2p_1\beta|]$ CSF.

11. As another example, consider the matrix elements which arise in electric dipole transitions between two singlet electronic states:

$\langle \Psi_1 | \mathbf{E} \cdot \sum_i e\mathbf{r}_i | \Psi_2 \rangle$. Here $\mathbf{E} \cdot \sum_i e\mathbf{r}_i$ is the one-electron operator describing the interaction of an electric field of magnitude and polarization \mathbf{E} with the instantaneous dipole moment of the electrons (the contribution to the dipole operator arising from the nuclear charges $-\sum_a Z_a e^2 \mathbf{R}_a$ does not contribute because, when placed between Ψ_1 and Ψ_2 , this zero-electron operator yields a vanishing integral because Ψ_1 and Ψ_2 are orthogonal).

When the states Ψ_1 and Ψ_2 are described as linear combinations of CSFs as introduced earlier ($\Psi_i = \sum_K C_{iK} \Psi_K$), these matrix elements can be expressed in terms of CSF-based matrix elements $\langle \Psi_K | \sum_i e\mathbf{r}_i | \Psi_L \rangle$. The fact that the electric dipole operator is a one-electron operator, in combination with the SC rules, guarantees that only states for which the dominant determinants differ by at most a single spin-orbital (i.e., those which are "singly excited") can be connected via electric dipole transitions through first order (i.e., in a one-photon transition to which the $\langle \Psi_1 | \sum_i e\mathbf{r}_i | \Psi_2 \rangle$ matrix elements pertain). It is for this reason that light with energy adequate to ionize or excite deep core electrons in atoms or molecules usually causes such ionization or excitation rather than double ionization or excitation of valence-level electrons; the latter are two-electron events.

In, for example, the $\pi \rightarrow \pi^*$ excitation of an olefin, the ground and excited states are dominated by CSFs of the form (where all but the "active" π and π^* orbitals are not explicitly written) :

$$\Psi_1 = |\dots \pi \alpha \pi \beta|$$

and

$$\Phi_2 = \frac{1}{\sqrt{2}} [|\dots \pi \alpha \pi^* \beta| - |\dots \pi \beta \pi^* \alpha|].$$

The electric dipole matrix element between these two CSFs can be found, using the SC rules, to be

$$\frac{e}{\sqrt{2}} \left[\langle \pi | \mathbf{r} | \pi^* \rangle + \langle \pi | \mathbf{r} | \pi^* \rangle \right] = \sqrt{2} e \langle \pi | \mathbf{r} | \pi^* \rangle.$$

Notice that in evaluating the second determinantal integral $\langle |\dots \pi \alpha \pi \beta| e \mathbf{r} | \dots \pi \beta \pi^* \alpha \rangle$, a sign change occurs when one puts the two determinants into maximum coincidence; this sign change then makes the minus sign in Φ_2 yield a positive sign in the final result.

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