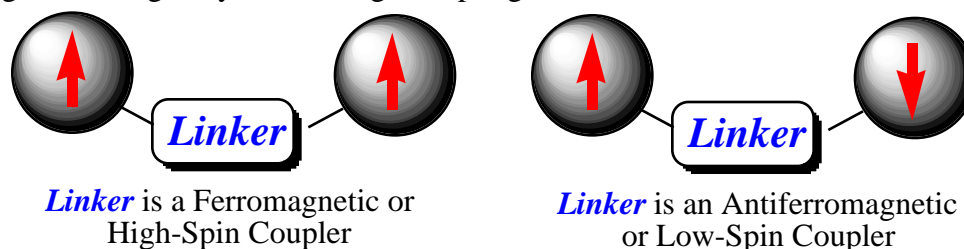


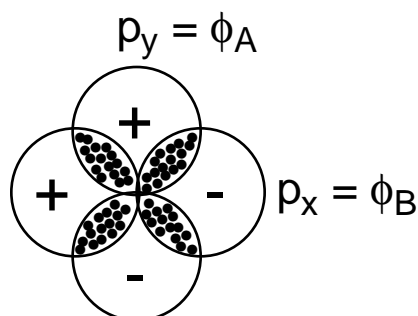
A central issue in our molecular design principles is taken from some excellent research on organic biradicals over the past twenty years.¹ As noted by Dougherty,² a biradical can be thought of as two spin-containing units bridged by an exchange-coupling unit:



The pi-topology and conformation of the biradical are central to understanding the electronic structure, *i.e.*, whether the ground-state is a triplet (above left) or a singlet (above right).

Hund's Rule, Singlet and Triplet Energies, and the Pauli Exclusion Principle

Consider two electrons in two orbitals, ϕ_A and ϕ_B (*e.g.*, two orthogonal 2p orbitals).



A wavefunction for this system is:

$$\Psi = \phi_A(1)\phi_B(2) \quad (1)$$

Now, let's calculate the probability of finding an electron using this wavefunction:

$$\text{Electron Density} \approx \text{Probability of finding an electron} = \Psi^2 = \phi_A(1)^2\phi_B(2)^2 \quad (2)$$

This corresponds to finding electron 1 localized in orbital 1 and electron 2 localized in orbital 2. This electronic localization is forbidden by quantum mechanics. Stated another, more common way, electrons must be indistinguishable: if we label the electrons above, we can clearly distinguish 1 from 2 because electron 1 is in ϕ_A and electron 2 is in ϕ_B . In quantum mechanics, this reason is stated mathematically by using a permutation operator (P_{12}), a math function that switches electron labels. When P_{12} operates on acceptable wavefunctions, the result is \pm the original wavefunction (obtaining $-\Psi$ is acceptable since $(-\Psi)^2 = \Psi^2$).

$$\text{If } \Psi \text{ is an acceptable wavefunction: } P_{12}\Psi = \pm \Psi \quad (3)$$

$$\text{If } \Psi \text{ is an unacceptable wavefunction: } P_{12}\Psi \neq \pm \Psi \quad (4)$$

Let's try P_{12} on our original wavefunction:

$$P_{12}\Psi = \phi_A(2)\phi_B(1) = \Psi' \neq \Psi \quad (5)$$

Thus, Ψ is an unacceptable wavefunction. How can we create an acceptable wavefunction? Let's try a linear combination of Ψ and Ψ' .

$$\Psi_+ = 0.707[\Psi + \Psi'] \quad (0.707 \text{ is the normalization factor}) \quad (6)$$

$$\Psi_+ = 0.707[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)] \quad (7)$$

Now, let's use P_{12} to determine if Ψ_+ is acceptable.

$$P_{12}\Psi_+ = 0.707[\phi_A(2)\phi_B(1) + \phi_B(2)\phi_A(1)] = \Psi_+ \quad (8)$$

Upon careful inspection, it is clear that the permuted Ψ_+ is the same as Ψ_+ . Therefore, Ψ_+ is an acceptable wavefunction. Now let's try the other linear combination of Ψ and Ψ' .

$$\Psi_- = 0.707[\Psi - \Psi'] \quad (0.707 \text{ is the normalization factor}) \quad (9)$$

$$\Psi_- = 0.707[\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)] \quad (10)$$

Again, let's use P_{12} to determine if Ψ_- is acceptable.

$$P_{12}\Psi_- = 0.707[\phi_A(2)\phi_B(1) - \phi_B(2)\phi_A(1)] = -\Psi_- \quad (11)$$

Upon inspection, it is clear that the permuted Ψ_- is $-\Psi_-$. Therefore, Ψ_- is an acceptable wavefunction. Thus, there are two acceptable wavefunctions for two electrons in two different orbitals.

$$\Psi_+ = 0.707[\Psi + \Psi'] \quad (12)$$

$$\Psi_- = 0.707[\Psi - \Psi'] \quad (13)$$

Because permuted Ψ_+ is equal to Ψ_+ , Ψ_+ is called a symmetric spacial wavefunction (spatial because the wavefunction describes the motion of the electron in a particular region of space). By the same token, because permuted Ψ_- is equal to $-\Psi_-$, Ψ_- is called an antisymmetric spacial wavefunction.

Now, let's consider that the total wave function is a product of spatial (Ψ) and spin wavefunctions (γ). The total wavefunction must be antisymmetric with respect to electron exchange.

$$\Psi_{\text{tot}} = \Psi_{\text{space}}\gamma_{\text{spin}} \quad (14)$$

$$P_{12}\Psi_{\text{tot}} = -\Psi_{\text{tot}} \quad (15)$$

Spin wavefunctions describe the spin angular momentum of the electrons. For two spins, the allowable wavefunctions are:

$$\gamma_{\uparrow\uparrow,+} = \alpha(1)\alpha(2) \quad (16)$$

$$\gamma_{\downarrow\downarrow,+} = \beta(1)\beta(2) \quad (17)$$

$$\gamma_{\uparrow\downarrow,+} = 0.707[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (18)$$

and

$$\gamma_{\uparrow\downarrow,-} = 0.707[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (19)$$

The origin of equations 18 and 19 are similar to their spatial counterparts, and the rules for creating the spin wavefunctions are the same as those for creating allowable spatial wavefunctions. Again, by inspection, spin wavefunctions 16 — 18 are symmetric and spin wavefunction 19 is antisymmetric.

Because the Ψ_{tot} must be antisymmetric, the allowed total wavefunctions are:

$$\Psi_{\text{tot}} = \Psi_{-} \gamma_{\uparrow\uparrow,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (20)$$

$$\Psi_{\text{tot}} = \Psi_{-} \gamma_{\downarrow\downarrow,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (21)$$

$$\Psi_{\text{tot}} = \Psi_{-} \gamma_{\uparrow\downarrow,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (22)$$

$$\Psi_{\text{tot}} = \Psi_{+} \gamma_{\uparrow\downarrow,-} \quad (\text{symmetric spatial and antisymmetric spin}) \quad (23)$$

The first three total wavefunctions (20 — 22) correspond to the three microstates of the **triplet** manifold, while the final total wavefunction (23) corresponds to an open-shell **singlet** state. Most notable is that the **triplet** states have antisymmetric *spatial* wavefunctions while the **singlet** state has a symmetric *spatial* wavefunction. The reason that this is noteworthy is that it is the spatial wavefunctions that are used to determine energies. In fact, the energies we wish to compute are the electron-electron repulsion energies since these are the essence of the energy difference between the **singlet** and **triplet** states.

Two closed-shell zwitterionic singlet states are also possible ($\Psi_{S^{+},CS}$ and $\Psi_{S^{-},CS}$), and are given below. In what follows, the ϕ has been dropped from the designations for the orbitals. Therefore, from two orbitals and two electrons, a total of four electronic states are formed:

$$\Psi_A = \frac{1}{\sqrt{2}}(a(1)b(2) - b(1)a(2)) \quad (\text{Triplet}) \quad (24)$$

$$\Psi_{S,OS} = \frac{1}{\sqrt{2}}(a(1)b(2) + b(1)a(2)) \quad (\text{Open-shell Singlet}) \quad (25)$$

$$\Psi_{S^{+},CS} = \frac{1}{\sqrt{2}}(a(1)a(2) + b(1)b(2)) \quad (\text{Closed-shell Singlet}) \quad (26)$$

$$\Psi_{S^{-},CS} = \frac{1}{\sqrt{2}}(a(1)a(2) - b(1)b(2)) \quad (\text{Closed-shell Singlet}) \quad (27)$$

Next, let's use the zero-order Hamiltonian (one-electron energy operators), Eqn. 28, and calculate the energies of the four states.

$$H^{(0)} = h(1) + h(2) \quad (28)$$

The energy of the open-shell triplet is:

$$E^{(0)}(\Psi_A) = \frac{1}{2} \langle a(1)b(2) - b(1)a(2) | h(1) + h(2) | a(1)b(2) - b(1)a(2) \rangle$$

$$\begin{aligned}
&= \frac{1}{2} [\langle a(1)b(2)|h(1) + h(2)|a(1)b(2) \rangle - \langle a(1)b(2)|h(1) + h(2)|b(1)a(2) \rangle - \\
&\quad \langle b(1)a(2)|h(1) + h(2)|a(1)b(2) \rangle + \langle b(1)a(2)|h(1) + h(2)|b(1)a(2) \rangle] \\
&= \frac{1}{2} [\langle b(2)|b(2) \rangle \langle a(1)|h(1)|a(1) \rangle + \langle a(1)|a(1) \rangle \langle b(2)|h(2)|b(2) \rangle \\
&\quad - \langle b(2)|a(2) \rangle \langle a(1)|h(1)|b(1) \rangle - \langle a(1)|b(1) \rangle \langle b(2)|h(2)|a(2) \rangle \\
&\quad - \langle a(2)|b(2) \rangle \langle b(1)|h(1)|a(1) \rangle - \langle b(1)|a(1) \rangle \langle a(2)|h(2)|b(2) \rangle \\
&\quad + \langle a(2)|a(2) \rangle \langle b(1)|h(1)|b(1) \rangle + \langle b(1)|b(1) \rangle \langle a(2)|h(2)|a(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha - 0 - 0 - 0 - 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{29}$$

The energy of the open-shell singlet is:

$$\begin{aligned}
E^{(0)}(\Psi_{s,os}) &= \frac{1}{2} \langle a(1)b(2) + b(1)a(2)|h(1) + h(2)|a(1)b(2) + b(1)a(2) \rangle \\
&= \frac{1}{2} [\langle a(1)b(2)|h(1) + h(2)|a(1)b(2) \rangle + \langle a(1)b(2)|h(1) + h(2)|b(1)a(2) \rangle + \\
&\quad \langle b(1)a(2)|h(1) + h(2)|a(1)b(2) \rangle + \langle b(1)a(2)|h(1) + h(2)|b(1)a(2) \rangle] \\
&= \frac{1}{2} [\langle b(2)|b(2) \rangle \langle a(1)|h(1)|a(1) \rangle + \langle a(1)|a(1) \rangle \langle b(2)|h(2)|b(2) \rangle \\
&\quad + \langle b(2)|a(2) \rangle \langle a(1)|h(1)|b(1) \rangle + \langle a(1)|b(1) \rangle \langle b(2)|h(2)|a(2) \rangle \\
&\quad + \langle a(2)|b(2) \rangle \langle b(1)|h(1)|a(1) \rangle + \langle b(1)|a(1) \rangle \langle a(2)|h(2)|b(2) \rangle \\
&\quad + \langle a(2)|a(2) \rangle \langle b(1)|h(1)|b(1) \rangle + \langle b(1)|b(1) \rangle \langle a(2)|h(2)|a(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha + 0 + 0 + 0 + 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{30}$$

The energy of the first closed-shell singlet is:

$$\begin{aligned}
E^{(0)}(\Psi_{s+,cs}) &= \frac{1}{2} \langle a(1)a(2) + b(1)b(2)|h(1) + h(2)|a(1)a(2) + b(1)b(2) \rangle \\
&= \frac{1}{2} [\langle a(1)a(2)|h(1) + h(2)|a(1)a(2) \rangle + \langle a(1)a(2)|h(1) + h(2)|b(1)b(2) \rangle + \\
&\quad \langle b(1)b(2)|h(1) + h(2)|a(1)a(2) \rangle + \langle b(1)b(2)|h(1) + h(2)|b(1)b(2) \rangle] \\
&= \frac{1}{2} [\langle a(2)|a(2) \rangle \langle a(1)|h(1)|a(1) \rangle + \langle a(1)|a(1) \rangle \langle a(2)|h(2)|a(2) \rangle \\
&\quad + \langle a(2)|b(2) \rangle \langle a(1)|h(1)|b(1) \rangle + \langle a(1)|b(1) \rangle \langle a(2)|h(2)|b(2) \rangle \\
&\quad + \langle b(2)|a(2) \rangle \langle b(1)|h(1)|a(1) \rangle + \langle b(1)|a(1) \rangle \langle b(2)|h(2)|a(2) \rangle \\
&\quad + \langle b(2)|b(2) \rangle \langle b(1)|h(1)|b(1) \rangle + \langle b(1)|b(1) \rangle \langle b(2)|h(2)|b(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha + 0 + 0 + 0 + 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{31}$$

The energy of the second closed-shell singlet is:

$$\begin{aligned}
E^{(0)}(\Psi_{s-,cs}) &= \frac{1}{2} \langle a(1)a(2) - b(1)b(2) | h(1) + h(2) | a(1)a(2) - b(1)b(2) \rangle \\
&= \frac{1}{2} [\langle a(1)a(2) | h(1) + h(2) | a(1)a(2) \rangle - \langle a(1)a(2) | h(1) + h(2) | b(1)b(2) \rangle - \\
&\quad \langle b(1)b(2) | h(1) + h(2) | a(1)a(2) \rangle + \langle b(1)b(2) | h(1) + h(2) | b(1)b(2) \rangle] \\
&= \frac{1}{2} [\langle a(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle a(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle \\
&\quad - \langle a(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle \\
&\quad - \langle b(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle - \langle b(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle \\
&\quad + \langle b(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle b(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha - 0 - 0 - 0 - 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{32}$$

So, to zeroth order, all four states have the same energy: 2α . This is obvious by inspection, two electrons in identical orbitals have the same orbital energies (in the absence of electron-electron repulsion) irrespective of how they are occupied.

Now, let's use a perturbed Hamiltonian to account for electron-electron repulsion:

$$H = H^{(0)} + H^{(1)} = H^{(0)} + 1/r_{12} \tag{33}$$

and calculate the first-order corrected energies.

The first-order corrected energy of the open-shell triplet is:

$$\begin{aligned}
E^{(1)}(\Psi_A) &= \frac{1}{2} \left\langle a(1)b(2) - b(1)a(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)b(2) - b(1)a(2) \right\rangle \\
&= 2\alpha + \frac{1}{2} \left\langle a(1)b(2) - b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) - b(1)a(2) \right\rangle \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle - \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle - \right. \\
&\quad \left. \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle - \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle - \right. \\
&\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} [j - k - k + j] = 2\alpha + j - k
\end{aligned} \tag{34}$$

The first-order corrected energy of the open-shell singlet is:

$$\begin{aligned}
E^{(1)}(\Psi_{s,os}) &= \frac{1}{2} \left\langle a(1)b(2) + b(1)a(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)b(2) + b(1)a(2) \right\rangle \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) + b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) + b(1)a(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle + \right. \\
&\quad \left. \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle + \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \right. \\
&\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} [j + k + k + j] = 2\alpha + j + k
\end{aligned} \tag{35}$$

The first-order corrected energy of the first closed-shell singlet is:

$$\begin{aligned}
E^{(1)}(\Psi_{s+,cs}) &= \frac{1}{2} \left\langle a(1)a(2) + b(1)b(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) + b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle + \right. \\
&\quad \left. \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle + \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \right. \\
&\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle \right] \\
&= 2\alpha + \frac{1}{2} [j^0 + k + k + j^0] = 2\alpha + j^0 + k
\end{aligned} \tag{36}$$

The first-order corrected energy of the second closed-shell singlet is:

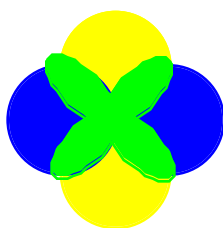
$$\begin{aligned}
 E^{(1)}(\Psi_{s-,cs}) &= \frac{1}{2} \left\langle a(1)a(2) - b(1)b(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)a(2) - b(1)b(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left\langle a(1)a(2) - b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) - b(1)b(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle - \left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle - \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} [j^0 - k - k + j^0] = 2\alpha + j^0 - k
 \end{aligned} \tag{37}$$

In the last four energy expressions, j is a two-center coulomb integral, k is the exchange integral, and j^0 is the one-center coulomb integral ($j^0 \gg j$). These integrals are displayed pictorially in the Figure below.

Yellow = ϕ_A

Blue = ϕ_B

Overlap density = Green



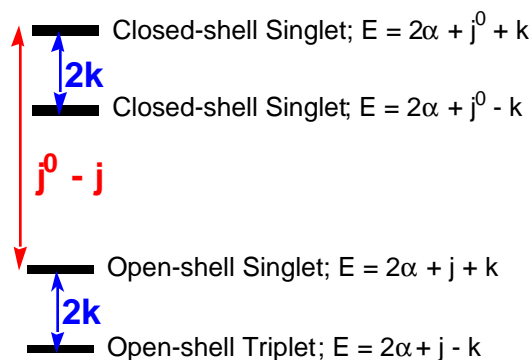
j = coulomb integral = electron-electron repulsion between yellow and blue

k = exchange integral = electron-electron repulsion **within green volume element**

j^0 = one-center coulomb integral = electron-electron repulsion within yellow or within blue

I = hybrid coulomb integral = electron-electron repulsion between yellow and green and between blue and green

These energies give the following energy level diagram:



The final step is to calculate the second order energies that arise via configuration interaction. The second order corrections take the form:

$$E^{(2)} = \frac{\langle \Psi_i | H^{(1)} | \Psi_j \rangle^2}{E_i - E_j} \quad (38)$$

We will mix the high-lying closed-shell states into the low-lying states, and begin by calculating the matrix elements in the numerator of Eqn. 38.

For the highest closed-shell singlet mixing into the open-shell singlet, we have:

$$\begin{aligned} & \left\langle \Psi_{s,os} \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{s+,cs} \right\rangle^2 \\ &= \left\langle \frac{1}{\sqrt{2}} [a(1)b(2) + b(1)a(2)] \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \frac{1}{\sqrt{2}} [a(1)a(2) + b(1)b(2)] \right\rangle^2 \\ &= \left\{ \left[\frac{1}{2} \langle a(1)b(2) + b(1)a(2) | h(1) | a(1)a(2) + b(1)b(2) \rangle + \langle a(1)b(2) + b(1)a(2) | h(2) | a(1)a(2) + b(1)b(2) \rangle + \right. \right. \\ & \left. \left. \left\langle a(1)b(2) + b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \right] \right\}^2 \\ &= \left\{ \left[\frac{1}{2} \langle a(1)b(2) | h(1) | a(1)a(2) \rangle + \langle a(1)b(2) | h(1) | b(1)b(2) \rangle + \langle b(1)a(2) | h(1) | a(1)a(2) \rangle + \right. \right. \\ & \langle b(1)a(2) | h(1) | b(1)b(2) \rangle + \langle a(1)b(2) | h(2) | a(1)a(2) \rangle + \langle a(1)b(2) | h(2) | b(1)b(2) \rangle + \\ & \langle b(1)a(2) | h(2) | a(1)a(2) \rangle + \langle b(1)a(2) | h(2) | b(1)b(2) \rangle + \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \\ & \left. \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \right\}^2 \\ &= \left\{ \left[\frac{1}{2} \langle b(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle b(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle + \langle a(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle + \right. \right. \\ & \langle a(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle + \langle a(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle + \\ & \langle b(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle + \langle b(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle + \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \\ & \left. \left. \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle + \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle \right] \right\}^2 \\ &= \frac{1}{2} [0 + \beta + \beta + 0 + \beta + 0 + 0 + \beta + l + l + l + l]^2 \\ &= \frac{1}{2} [4\beta + 4l]^2 = 4(\beta + l)^2 \end{aligned} \quad (39)$$

The second order correction to the energy is thus:

$$E^{(2)}(\Psi_{s,os}) = \frac{4(\beta + l)^2}{j^0 - j} \quad (40)$$

For the lower closed-shell singlet mixing into the open-shell singlet, we have:

$$\begin{aligned} & \left\langle \Psi_{s,os} \left| h(1) + h(2) + \frac{1}{r_{12}} \Psi_{s-,cs} \right. \right\rangle^2 \\ &= \left\langle \frac{1}{\sqrt{2}} [a(1)b(2) + b(1)a(2)] \left| h(1) + h(2) + \frac{1}{r_{12}} \frac{1}{\sqrt{2}} [a(1)a(2) - b(1)b(2)] \right. \right\rangle^2 \\ &= \left\{ \left[\frac{1}{2} \langle a(1)b(2) + b(1)a(2) | h(1) | a(1)a(2) - b(1)b(2) \rangle + \langle a(1)b(2) + b(1)a(2) | h(2) | a(1)a(2) - b(1)b(2) \rangle + \right. \right. \\ & \quad \left. \left. \left\langle a(1)b(2) + b(1)a(2) \left| \frac{1}{r_{12}} \left[a(1)a(2) - b(1)b(2) \right] \right. \right\rangle \right]^2 \\ &= \left\{ \left[\frac{1}{2} \langle a(1)b(2) | h(1) | a(1)a(2) \rangle - \langle a(1)b(2) | h(1) | b(1)b(2) \rangle + \langle b(1)a(2) | h(1) | a(1)a(2) \rangle - \right. \right. \\ & \quad \langle b(1)a(2) | h(1) | b(1)b(2) \rangle + \langle a(1)b(2) | h(2) | a(1)a(2) \rangle - \langle a(1)b(2) | h(2) | b(1)b(2) \rangle + \\ & \quad \langle b(1)a(2) | h(2) | a(1)a(2) \rangle - \langle b(1)a(2) | h(2) | b(1)b(2) \rangle + \left. \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \left[a(1)a(2) \right] \right. \right\rangle - \right. \right. \\ & \quad \left. \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \left[b(1)b(2) \right] \right. \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \left[a(1)a(2) \right] \right. \right\rangle - \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \left[b(1)b(2) \right] \right. \right\rangle \right]^2 \\ &= \left\{ \left[\frac{1}{2} \langle b(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle b(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle + \right. \right. \\ & \quad \langle a(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle - \langle a(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle + \langle a(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle - \\ & \quad \langle b(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle - \langle b(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle + \left. \left. \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \left[a(2)b(2) \right] \right. \right\rangle - \right. \right. \\ & \quad \left. \left. \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \left[b(2)b(2) \right] \right. \right\rangle + \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \left[a(2)a(2) \right] \right. \right\rangle - \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \left[a(2)b(2) \right] \right. \right\rangle \right]^2 \\ &= \frac{1}{2} [0 - \beta + \beta - 0 + \beta - 0 + 0 - \beta + l - l + l - l]^2 \\ &= \left\{ \frac{1}{2} [0] \right\}^2 = 0 \end{aligned} \quad (41)$$

The second order correction to the energy is thus:

$$E^{(2)}(\Psi_{s,os}) = \frac{0}{j^0 - j} = 0 \quad (42)$$

For the highest closed-shell singlet mixing into the triplet, we have:

$$\begin{aligned}
& \left\langle \Psi_A \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{S+,CS} \right\rangle^2 \\
&= \left\langle \frac{1}{\sqrt{2}} [a(1)b(2) - b(1)a(2)] \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \frac{1}{\sqrt{2}} [a(1)a(2) + b(1)b(2)] \right\rangle^2 \\
&= \left\{ \left[\frac{1}{2} \langle a(1)b(2) - b(1)a(2) | h(1) | a(1)a(2) + b(1)b(2) \rangle + \langle a(1)b(2) - b(1)a(2) | h(2) | a(1)a(2) + b(1)b(2) \rangle + \right. \right. \\
& \quad \left. \left. \left\langle a(1)b(2) - b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \left[\frac{1}{2} \langle a(1)b(2) | h(1) | a(1)a(2) \rangle + \langle a(1)b(2) | h(1) | b(1)b(2) \rangle - \langle b(1)a(2) | h(1) | a(1)a(2) \rangle - \right. \right. \\
& \quad \langle b(1)a(2) | h(1) | b(1)b(2) \rangle + \langle a(1)b(2) | h(2) | a(1)a(2) \rangle + \langle a(1)b(2) | h(2) | b(1)b(2) \rangle - \\
& \quad \langle b(1)a(2) | h(2) | a(1)a(2) \rangle - \langle b(1)a(2) | h(2) | b(1)b(2) \rangle + \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \\
& \quad \left. \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle - \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle - \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \left[\frac{1}{2} \langle b(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle b(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle - \right. \right. \\
& \quad \langle a(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle + \langle a(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle - \\
& \quad \langle b(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle - \langle b(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle + \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \\
& \quad \left. \left. \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle - \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle - \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \frac{1}{2} [0 + \beta - \beta - 0 + \beta + 0 - 0 - \beta + l + l - l - l] \right\}^2 \\
&= \left\{ \frac{1}{2} [0] \right\}^2 = 0
\end{aligned} \tag{43}$$

The second order correction to the energy is thus:

$$E^{(2)}(\Psi_A) = \frac{0}{j^0 - j} = 0 \tag{44}$$

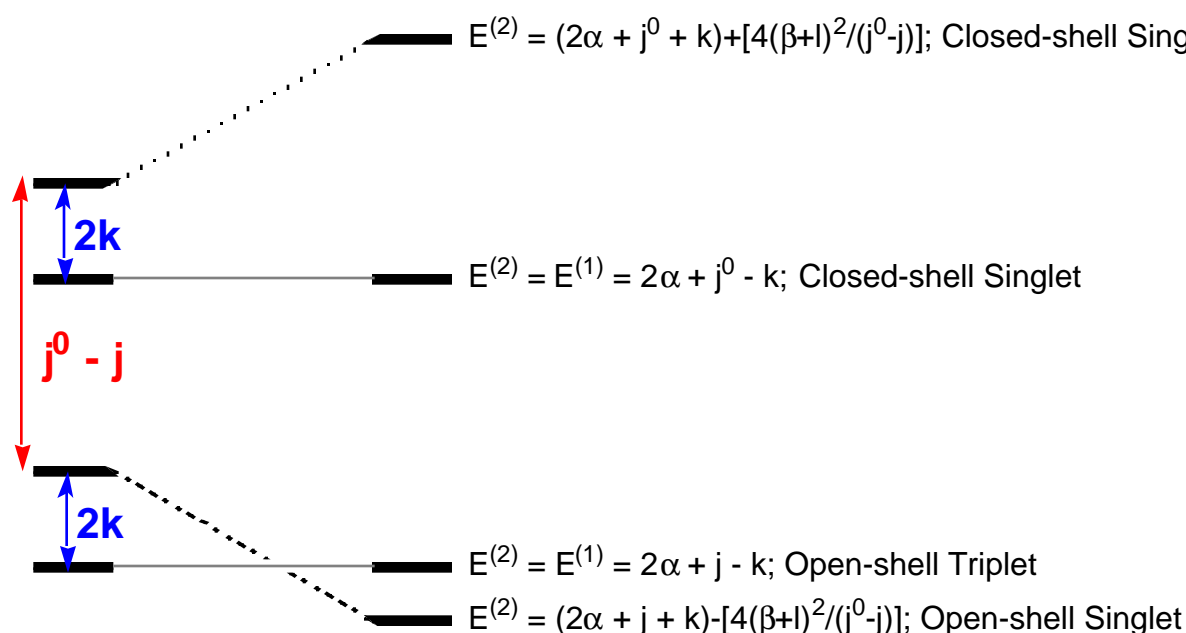
For the lower closed-shell singlet mixing into the triplet, we have:

$$\begin{aligned}
& \left\langle \Psi_A \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{S-,CS} \right\rangle^2 \\
&= \left\langle \frac{1}{\sqrt{2}} [a(1)b(2) - b(1)a(2)] \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \frac{1}{\sqrt{2}} [a(1)a(2) - b(1)b(2)] \right\rangle^2 \\
&= \left\{ \left[\frac{1}{2} \langle a(1)b(2) - b(1)a(2) | h(1) | a(1)a(2) - b(1)b(2) \rangle + \langle a(1)b(2) - b(1)a(2) | h(2) | a(1)a(2) - b(1)b(2) \rangle + \right. \right. \\
& \quad \left. \left. \left\langle a(1)b(2) - b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) - b(1)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \left[\frac{1}{2} \langle a(1)b(2) | h(1) | a(1)a(2) \rangle - \langle a(1)b(2) | h(1) | b(1)b(2) \rangle - \langle b(1)a(2) | h(1) | a(1)a(2) \rangle + \right. \right. \\
& \quad \langle b(1)a(2) | h(1) | b(1)b(2) \rangle + \langle a(1)b(2) | h(2) | a(1)a(2) \rangle - \langle a(1)b(2) | h(2) | b(1)b(2) \rangle - \\
& \quad \langle b(1)a(2) | h(2) | a(1)a(2) \rangle + \langle b(1)a(2) | h(2) | b(1)b(2) \rangle + \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle - \right. \\
& \quad \left. \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle - \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \left[\frac{1}{2} \langle b(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle - \langle b(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle + \right. \right. \\
& \quad \langle a(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle - \langle a(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle - \\
& \quad \langle b(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle + \langle b(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle + \left. \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle - \right. \\
& \quad \left. \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle - \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle \right] \right\}^2 \\
&= \left\{ \frac{1}{2} [0 - \beta - \beta + 0 + \beta - 0 - 0 + \beta + l - l - l + l] \right\}^2 \\
&= \left\{ \frac{1}{2} [0] \right\}^2 = 0
\end{aligned} \tag{45}$$

The second order correction to the energy is thus:

$$E^{(2)}(\Psi_A) = \frac{0}{j^0 - j} = 0 \tag{46}$$

Therefore, configuration interaction only operates for the singlet manifold. In Eqn. 16, l is the hybrid coulomb integral. These corrections give the following energy level diagram:



Thus, the orthogonal magnetic orbital, active-electron approximation gives ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contribution to the exchange parameter (J) as:³

$$J = J_F + J_{AF} = 2k - \frac{4(\beta + l)^2}{j^0 - j} \quad (47)$$

Net ferromagnetic coupling occurs when J_F dominates, while net antiferromagnetic occurs when the J_{AF} term outweighs the J_F term. The ferromagnetic contribution is simply twice the exchange integral, and the antiferromagnetic contribution is embodied in the configuration interaction term. Remember that the exchange integral is the electron-electron repulsion in the *overlap region*. This is the amount of energy the system "saves" by aligning its electrons in a parallel, high-spin fashion. The greater the overlap region, the more stable the **triplet** state. This is the essence of Hund's Rule: place unpaired electrons into each degenerate orbital (to maximize M_S) before doubly occupying an orbital.

Another way of explaining ferromagnetic exchange that two electrons of the same spin avoid each other. *Remember, that the region of space where two different electrons co-exist is the overlap region.* Thus, when two orbitals share a common volume element, spin-aligned electrons avoid this region of shared space and experience less electron-electron repulsion.

Yet another way of expressing the correlated motion of spin-aligned electrons is to examine the spatial wavefunctions that describe their motion.

$$\Psi_S = 0.707[a(1)b(2) + b(1)a(2)] \quad (24)$$

$$\Psi_{A,OS} = 0.707[a(1)b(2) - b(1)a(2)] \quad (25)$$

When two electrons approach each other, their coordinates become nearly identical. In this case, consider the limit of each spatial wavefunction when the coordinates of electron 1 approach those of electron 2:

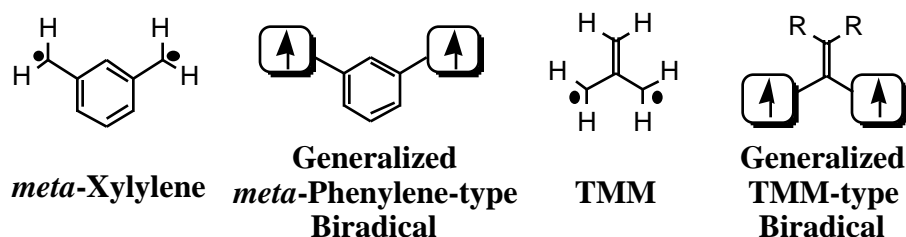
$$\lim \Psi_- = \lim \{0.707[\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)]\} \approx 0.707[\phi_A(2)\phi_B(2) - \phi_B(2)\phi_A(2)] = 0 \quad (48)$$

$$\lim \Psi_+ = \lim \{0.707[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)]\} \approx 0.707[\phi_A(2)\phi_B(2) + \phi_B(2)\phi_A(2)] \neq 0 \quad (49)$$

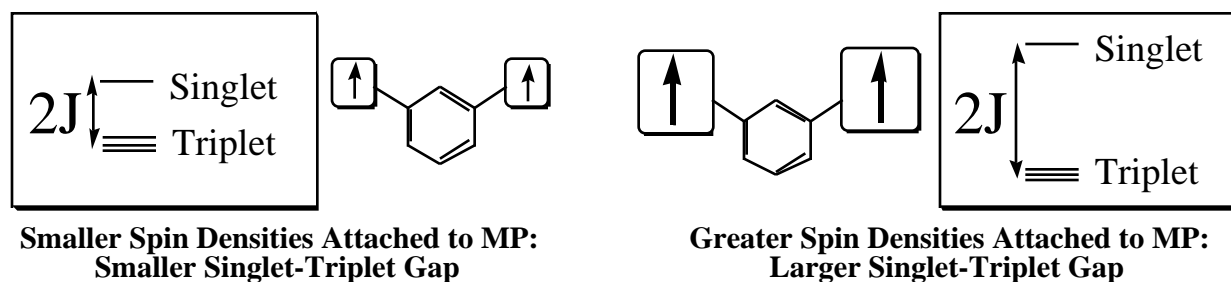
In a sense, spin-aligned electrons avoid each other to prevent the wavefunction from vanishing, while spin-paired electrons do not have to avoid each other. This is my personal vision of the Pauli Exclusion Principle (no two electrons can have the same four quantum numbers). Of course, the result is a lower energy when two, orthogonal, singly-occupied orbitals that share a common volume element have unpaired electrons that are spin-parallel (*i.e.*, a **triplet** state).

Disjoint and Nondisjoint Biradicals

The material presented above gives you the quantum mechanical explanation of a singlet-triplet gap. Biradicals that have degenerate or nearly isoenergetic SOMOs and that and whose eigenvectors (coefficients) cannot be relegated to different sets of atoms are said to be nondisjoint.⁴ Such biradicals are expected to have nonzero exchange integrals and triplet ground states. Many examples of nondisjoint biradicals are *meta*-phenylene-type biradicals (from the parent *meta*-xylylene) and trimethylenemethane (TMM)-type biradicals (from the parent trimethylenemethane).

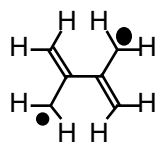


The effectiveness of a ferromagnetic coupling group is based on (1) its π -topology, (2) the spin density at the carbons attached to the coupler: the smaller the spin density, the smaller the gap ($2J$) between the ground-state triplet and the higher-energy singlet state (spin density in the coupler is directly proportional to the exchange integral); and



(3) the presence of steric interactions that attenuate conjugation of the spin-containing unit with the coupler fragment. Several groups have synthesized biradicals in which the triplet stability was decreased, or in which the singlet is lowered below the triplet because of steric interactions between a *meta*-phenylene coupler and the spin-containing groups.⁵ We demonstrated this in TMM-type biradicals.

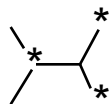
There are many types of disjoint biradicals — those in which the coefficients of the SOMOs can be isolated on different molecular fragments. These biradicals are expected to have vanishingly small singlet-triplet gaps or singlet ground states. The most studied disjoint biradical is tetramethyleneethane and its derivatives.



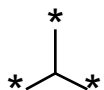
Tetramethyleneethane

You may recognize tetramethyleneethane as two allyl radicals joined at nodal C2. In fact, any biradical linked by nodal carbons is disjoint and is expected to be a singlet ground state molecule.

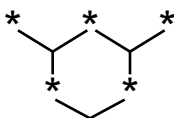
Not surprisingly, there are topology rules for high-spin molecules. The most popular is the “star, non-star rule.” It works only for even alternant systems. Star, or label alternant atoms of the biradical, such that no two starred atoms are contiguous. The ground state spin is thus, $S = (\text{star} - \text{non star})/2$.



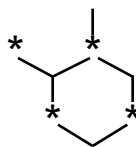
Tetramethyleneethane: $S = (3 - 3)/2 = 0$, a singlet ground state



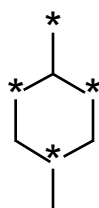
Trimethylenemethane: $S = (3 - 1)/2 = 1$, a triplet ground state



meta-Xylylene: $S = (5 - 3)/2 = 1$, a triplet ground state



ortho-Xylylene: $S = (4 - 4)/2 = 0$, a singlet ground state



para-Xylylene: $S = (4 - 4)/2 = 0$, a singlet ground state

The latter two are special examples since they are Kekule hydrocarbons: the unpaired electrons can be paired into pi-bonds.

References

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