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SUPPORTING INFORMATION

Quantitative prediction and interpretation of spin energy gaps in polyradicals: the virtual magnetic balance

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Orbital modification

A restricted Hartree-Fock (HF)calculation of the high spin quintet state was carried out with the cc-pVDZ basis set (the same considered for geometry optimization at B3LYP level), using the Gamess program.[1] The resulting 1162 canonical molecular orbitals (MOs) were then treated with the QUIOLA program [2] to prepare a new set of MOs suitable for post-HF calculations. The strategies implemented in the QUIOLA program are connected with the variational/perturbative approach implemented in the BALOO program. According to this recipe, the orbital space considered for CI calculations is reduced with respect to the whole orbital set by cutting out a number of empty orbitals at highest energy and a number of double occupied orbitals at lowest energy. The resulting MOs form the variational active space and the resulting Slater determinants (SD) are used for CI calculations. The SDs involved in the remaining orbital space are instead treated in a perturbative way according to the Complementary Space Perturbative Approach (CSPA)[3-4] implemented in the BALOO program. In this context the QUIOLA program was used to make the following unitary transformations involving the orbitals as arising from the HF calculation.

A. The four half-filled magnetic π orbitals were localized on the nitrogen atoms in order to get a better understanding of the post-HF calculations. Both the canonical and localized MOs are displayed in Fig. 2. Such localization revealed that the magnetic MOs are roughly distributed for 60% on the nitrogen atoms whereas the remaining 40% of charge is delocalized on the π basis set of the neighboring atoms of the skeleton. This limited localization on the spin centers was already found for the corresponding aminyl diradical and gives rises to important effects on the exchange integral between magnetic MOs. The obtained localized orbitals were no more changed in the following steps.
B. The doubly occupied and empty orbitals were separately localized over two fragments: the pendant phenyls and the remaining atoms. The orbitals pertaining to the pendant phenyls were discarded and never considered in post-HF calculations, neither in the following steps.
C. A further localization of the considered orbitals was performed taking as fragments the π and the σ atomic orbitals of the scaffold. This was done separately for the doubly occupied and virtual orbitals in order not to mix orbitals with different occupancy.
D. The matrix of a modified Fock operator in the spaces spanned by the virtual π and σ atomic orbitals, was separately diagonalized, according to the Modified Virtual Orbitals (MVO) protocol,[4] devised in our group. Concretely, a modified Fock operator was obtained by adding to the original Fock operator, the Coulombic potential arising from a supplementary nuclear charge of 0.6*e* on each of the four nitrogen atoms. Owing to this artificial attractive potential, the lowest energy eigenvectors of this operator are expected to have an enhanced contribution on the magnetic centers and, consequently, to provide a relevant interaction with the magnetic orbitals. This stratagem has proved to improve the convergence of the energy gap vs. the number of

virtual MVOs considered in the CI treatment in the mixed variational/perturbative approach.[4] We stress that this unitary transformation does not alter the localization properties of the new empty orbitals, as it was done separately for the π and σ manifolds.

E. Finally the modified localized orbitals were arranged in such a way that the π ones both occupied and virtual are adjacent to the frontier orbitals. Thus the resulting orbital ordering is σ(2)–π(2)-π(1)-π(0)-σ(0) where the number in parentheses is the orbital occupancy. These changes were aimed to arrange the MOS in such a way that their importance on the energy splitting increases as the orbital index approaches to the Fermi level. Therefore the first occupied and last empty orbitals should play a minor role and the resulting SDs can be safety treated at perturbative level, according to CSPA.

The localization was done according to the Pipek-Mezey recipes but using a global rotation rather than the 2x2 rotation as suggested in the original paper, and using a fourth power functional.[5] This recently tested method [6] has proven to be more effective than the original one.

All the 1s orbitals and even the MOs localized on the pendant phenyls were not included in the post-HF calculations. As a consequence, the model system used for post-HF calculations does not include electronic correlation within the pendant phenyls. By considering that the magnetic orbitals have negligible components on the pendants, this stratagem is expected to have negligible effects on the spin properties. Yet, the pendants were indeed included in the initial HF calculation, hence, apart from correlation, their effect on the canonical MOs has been accounted for. The remaining 588 MOs were then used to transform the one- and two-electron matrices from the atomic to the molecular basis set.

Owing to the high number of MOs considered herein and to the high dimension of the atomic basis set, the integral transformation step is rather time consuming, but can be performed in about three days by exploiting the high efficiency and parallelization of the code inserted in the BALOO package. The one- and two-electron matrices are the only data needed by BALOO for CI and perturbative treatment of electronic correlation.

The DDCI scheme

In the following table the DDCI scheme used to evaluate the energy gaps between the three lowest spin states is reported in some details. Any DDCI space for a system of four spin centers can be generated by applying suitable excitations to all SDs included in the primary CAS(4,4) configurational space. The excitation classes can be grouped to form the DDCI1, DDCI2 and DDCI3 protocols, at increasing level of accuracy and computational demand. The excitation classes may be labelled in several ways. The first (first column)[3] consists in giving the number of core, magnetic and unoccupied molecular orbitals, whereas the original convention,[7] reported in the second column, is based on the number of holes (h) in the core orbitals and particles (p) on the virtual orbitals. In the third column a short description of the excitation classes is reported, where the labels C,M,E indicate core, magnetic, empty orbitals, respectively. Within this framework, the last columns show pictorially the increase of the configurational space on going from the simplest DDCI1 to the most accurate DDCI3 protocols.

N.4.0		The primary CAS(4,4) space (includes kinetic exchange)	DDCI1	DDCI2	DDCI3
N-1.5.0	1h	C→M (related to superexchange)			
N.3.1	1p	M→E (polarization)			
N-1.4.1	1h+1p	C→M, M→E (include spin polarization)			
N-2.6.0	2h	CC→MM			
N.2.2	2p	MM→EE			
N-2.5.1	2h+1p	CC→MM, M→E			
N-1.3.2	1h+2p	C→M, MM→EE			

Appendix: the simplest calculation

In this Appendix some of the most relevant features that lead to the energy splitting between the three lowest spin states of the considered tetraradical are discussed in some detail. As the CAS(4,4) was found to yield results similar to the ones obtained through more sophisticated treatments, it may be useful analyzing the former results, exploiting the conciseness of such simple model to give a simple rationale of the observed energy splitting among the lowest energy spin states.

Let's consider only the active orbitals on the nitrogen atoms, which we call *a,b,c,d* on going from left to right in Fig. 1. Thus *ab*, *bc* and *cd* are the nearest pair of orbitals. The four electron wave function and the energy of the quintet state (taken for simplicity with the maximum projection along *z*, *Ms*=2) are

$$\left|\Phi_Q\right\rangle = \left|core\ a_\alpha, b_\alpha, c_\alpha, d_\alpha\right\rangle$$
$$E_Q = E_{core} + \varepsilon + J_{ab} + J_{ac} + J_{ad} + J_{bc} + J_{bd} + J_{cd} - K_{ab} - K_{ac} - K_{ad} - K_{bc} - K_{bd} - K_{cd}$$

where *core* represents all the doubly occupied inactive orbitals and E_{core} is its energy. ε expresses the interaction energy of the four active electrons with the *core* ($\varepsilon = \varepsilon_a + \varepsilon_b + \varepsilon_c + \varepsilon_d$) and *J* and *K* are the usual coulombic and exchange integrals. As the configurations considered in the following have all the same occupancy (one electron in each active orbital), the coulombic contributions can be collected in a single term, which is independent from the spin of the active orbital

$$E_0 = E_{core} + \varepsilon + J_{ab} + J_{ac} + J_{ad} + J_{bc} + J_{bd} + J_{cd}$$

The total energy may be rewritten as

$$E_Q = E_0 - K_{ab} - K_{ac} - K_{ad} - K_{bc} - K_{bd} - K_{cd}$$

As the four orbitals are roughly aligned on a straight line and equidistant, the higher exchange contributions come from the integrals involving nearest centers, and in particular

$$K = K_{ab} = K_{bc} = K_{cd} \approx 1000\, cm^{-1} \qquad K_{ac} = K_{ad} = K_{bd} \approx 0$$

Therefore the energy of the quintet state is

$$E_Q = E_0 - 3K$$

with the stabilizing exchange energy arising from the aligned spins.

For the triplet state let's consider the spin states of four electrons each in a different orbital, having spin projection along *z* equal to 1, which are reported in Table A1, together with their energy. It is

apparent that they are stabilized in different way by exchange interaction depending on the number of consecutive orbitals with aligned spin.

Table A1 –Slater Determinants and coefficients of the quintet and triplet spin states, arising from four electrons in four different orbitals, having projection along *z* equal to 1.

Spin of *abcd*	Energy	Quintet	Lowest Triplet
$\beta\alpha\alpha\alpha$	$E_0 - 2K$	0.5	-0.6533
$\alpha\beta\alpha\alpha$	$E_0 - K$	0.5	-0.2706
$\alpha\alpha\beta\alpha$	$E_0 - K$	0.5	0.2706
$\alpha\alpha\alpha\beta$	$E_0 - 2K$	0.5	0.6533

The resulting Hamiltonian matrix (reported in Table A2) is tridiagonal and the eigenvectors corresponding to the lowest eigenvalues are reported in Table A1. The eigenvalue of the lowest triplet state is -2.4142*K*, which is higher than the quintet energy of -3*K*. Consequently the ground state is always the quintet state, irrespectively of the *K* value. By this simple model the energy splitting can be estimated to be 0.5858K corresponding to about 585 cm^{-1}, in good agreement with the value computed at CAS(4,4) and more sophisticated levels of theory. The inclusion of a number of charge transfer Slater determinants like *aabc, abbc* etc, which contribute to the triplet but not to the quintet, should stabilize the triplet state, which eventually may become the ground state. Yet, nothing similar occurs for the tetraradical under study, due to the low impact of the charge transfer Slater determinants.

Table A2 –Hamiltonian matrix in the basis of SDs reported in Table A1.

$E_0 - 2K$	$-K$	0	0
$-K$	$E_0 - K$	$-K$	0
0	$-K$	$E_0 - K$	$-K$
0	0	$-K$	$E_0 - 2K$

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