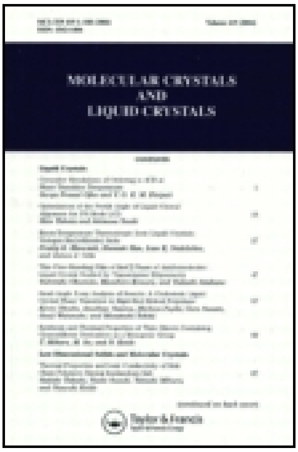

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Biradical Spin, Limited CI, and Heteroatoms

D. J. Klein [a] & S. A. Alexander [b]
[a] Texas A&M University Galveston, Galveston, Texas, 77553-1675
[b] Physics, University of Florida, Gainesville, Florida, 32611

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BIRADICAL SPIN, LIMITED CI, AND HETEROATOMS

D. J. KLEIN* and S. A. ALEXANDER**
*Texas A&M University @ Galveston, Galveston,
Texas 77553-1675

**Physics, University of Florida, Gainesville,
Florida 32611

Abstract For alternant π-network systems both heteroatoms and system size have been imagined to influence ground-state spin multiplicities. Here theoretical and computational evidences are presented against a significant influence of system size and in favor of a notable influence of heteroatoms. Pair-excitation limited configuration interaction (CI) is argued to exhibit artifactual system size effects, so that other computational schemes are recommended to predict splitting patterns of weakly coupled electrons. Full CI computations are reported illustrating the influence of heteratom electronegativity on the splitting pattern of a couple -network structures.

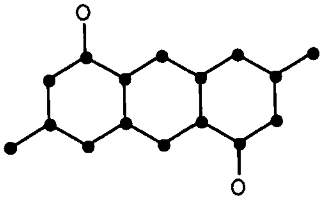
INTRODUCTION

Organic radicals and polyradicals have become much investigated as systems of possibly designable behavior. Best understood are planar homoatomic π-network systems where the readily accessible excitations typically involve just a shift in the pattern of π-orbitals. But the possibilities arising with heteroatoms offer further control parameters in the design of molecular magnets.

Much theory has been developed for the homoatomic case, especially if the π-network is alternant (or bipartite). For instance, several rigorous theorems are known[1,2,3] for the associated simple Pauling-Wheland (homopolar) valence-bond (VB) model, also termed the nearest-neighbor Heisenberg model. In particular for this model the ground-state spin S is given by a VB rule: S is half the difference between the number of "starred" and "unstarred" sites. Further this extends[4] to the "half-filled" (electroneutral) Hubbard model, also known as the Parisier-Parr-Pople (PPP) model limited to on-site Coulomb interactions. Further there is much computational evidence[5,6] that this VB rule extends to more complete PPP models (for the homoatomic alternant electroneutral case). Also modifications of ideas[7] based upon molecular-orbital (MO) theory seem to end up[6] "near" the simple VB rule. Still there is a suggestion[8] that this VB rule applies only for small systems, while for large systems there is reversion back to the simple Hund's rule, whereby the ground-state spin is predicted to be half the number of nonbonding MOs. Evidently with the acceptance of this rule-switching suggestion both the Pauling-Wheland VB model and the Hubbard model (being the "simplest" extension of the Huckel model accounting for explicit electron-electron interaction) would be deemed inadequate. Moreover, the unananimously observed agreement of more complete PPP models with the VB rule would be deemed to indicate either model inadequacy or the inability to yet extend full (or complete) configuration-interaction (CI) techniques to sufficiently large systems. Actually too similar reservations should then extend to a limited number[9,10] of "high quality" ab initio CI computations. Thence the suggestion[8] of VB-rule validity for small systems with a switch to Hund s rule validity for larger systems, beyond making significant predictions for experimental observables, would reveal notable theoretical deficiencies.

Here we look into this rule-switching suggestion. First in section 2 we examine a pair-excitation restricted CI scheme for which computations have been presented[8] to support rule switching. Such limited CI schemes are in fact already accepted[11] to exhibit an artifactual non-size-extensive feature as judged by an analysis of behavior for collections of noninteracting molecular fragments. Here we analyze this simple model in greater detail to show that the singlet-triplet splitting so predicted often artifactually exhibits the rule-switching behavior. Next in section 3 we examine two heteroatomic π-networks related to the quinoid species

Q - 18:



this biradical species having been implicated in an argument[12] favoring rule switching. This argument proceeds: first, noting that this Q - 18 species is experimentably observed to be a spin triplet; second, postulating that the (thermally accessible) state ordering of this quinoid species is the same as the homoatomic species with the same π-network; and third, noting the Hund's-rule prediction for this corresponding homoatomic biradical also is for a triplet spin ground state, contrary to the singlet-spin prediction via the VB rule. The computations we make may however be viewed to suggest that the postulate of like behavior for the corresponding heteroatomic and homoatomic species is not justified. Thus sections 2 and 3 here corrupt the arguments in favor of rule-switching behavior. We believe that theoretical evidence indicates homoatomic alternants ordinarily achieve agreement with the VB rule, independently of molecular size.

PAIR-EXCITATION LIMITED CI

In this section we consider a quantitative computational scheme—that of configuration interaction (CI) amongst all pair-(or double-) excitations above an SCF space of two patterns of MO occupation for a biradical state. Such double-excitation CI schemes evidently have[11] a failing in treating overall energy corrections beyond the SCF level: namely this correction does not seem to scale with the system's size (as measured by the number of electrons). The question of interest here though relates to the singlet-triplet splitting rather than the overall energy for the biradical species.

To address this question we here investigate it for a simple soluble arbitrarily sized model: a collection of noninteracting molecules each of which can be exactly treated (say within the full PPP model). One molecule is taken as a biradical, such as cyclobutadiene, while N remaining molecules are taken as closed-shell singlets, such as ethylene.

The SCF bideterminatal approximants to the singlet (S) and triplet (T) states are denoted by $|\Phi_S\rangle$ and $|\Phi_T\rangle$, and the associated energies are E_S^0 and E_T^0 The consequent double-excitation approximations then are of the form

$$|\Psi_X\rangle = |\Phi_X\rangle + \sum_a c_{Xa}|Xa\rangle \qquad X = S, T \tag{1}$$

with the a -sum being over the excitations $|X\alpha\rangle$ on different noninteracting molecules α. The corresponding energies are

$$E_X = \frac{E_X^0 + 2\sum_a c_{Xa}\langle\Phi_X| H |Xa\rangle + \sum_a c_{Xa}^2\langle Xa| H |Xa\rangle}{1+\sum_a c_{Xa}^2} \tag{2}$$

where we have noted that the excitations in different molecules do not interact (and where for simplicity we have presumed reality of matrix elements and normalization of the $|\Phi_X\rangle$ and $|Xa\rangle$. Now the (N -independent) matrix elements

$$V_{Xa} \equiv \langle\Phi_X| H |Xa\rangle \tag{3}$$

$$\Delta_{Xa} \equiv \langle Xa| H |Xa\rangle - E_X^0$$

are the same for all closed-shell (ethylene) molecules, so that they are abbreviated to V_0 and Δ_0, while the remaining matrix elements for the biradical are abbreviated to V_x and Δ_x. Then, making related abbreviations for the C_{xa}, we have

$$E_x = E_x^0 + \frac{\sum_a \left(2c_{xa}V_a + c_{xa}^2\Delta_a\right)}{1+c_x^2+Nc_0^2} \tag{4}$$

The variational optimization of the CI coefficients implies the partial derivatives of E_x with respect to these coefficients are 0, whence

$$c_{xa} = V_a \big/ \left(E_x - E_x^0 - \Delta_{xa}\right) \tag{5}$$

and substitution of this back into eqn(4)yields

$$E_x - E_x^0 = \frac{\dfrac{2V_x^2}{E_x - E_x^0 - \Delta_x} + \dfrac{V_x^2\Delta_x}{\left(E_x - E_x^0 - \Delta_x\right)^2} + \dfrac{2NV_0^2}{E_x - E_x^0 - \Delta_0} + \dfrac{NV_0^2\Delta_0}{\left(E_x - E_x^0 - \Delta_0\right)^2}}{1 + \dfrac{V_x^2}{\left(E_x - E_x^0 - \Delta_x\right)^2} + \dfrac{NV_0^2}{\left(E_x - E_x^0 - \Delta_0\right)^2}} \tag{6}$$

Now the differences $E_x - E_x^0$ should for large N be dominated by the N ethylene-molecule corrections, so that to leading order in N the $E_x - E_x^0 - \Delta_{xa}$ denominators in eqn. (6) can be simplified and numerators not proportional to N dropped, whence one expects a result of the form

$$E_x - E_x^0 \approx \frac{\dfrac{2NV_0^2}{E_x - E_x^0} + \dfrac{NV_0^2\Delta_0}{\left(E_x - E_x^0\right)^2}}{1 + \dfrac{NV_0^2}{\left(E_x - E_x^0\right)^2}} \tag{7}$$

Anticipating that the terms with denominators $\left(E_x - E_x^0\right)^2$ are quenched, one is lead to

$$E_x - E_x^0 \approx -|V_0|\sqrt{N} \tag{8}$$

the usual result[11] that the overall energy correction lacks size-extensivity.

To deal with the "local" difference $E_T - E_S$ we need to go to finer detail. Eqn. (8) suggests a definition

$$\varepsilon_x \equiv \left(E_x - E_x^0\right)/\sqrt{N} \tag{9}$$

in terms of which eqn. (6) then is developed, say as

$$\varepsilon_x = -|V_0| + f_x(\varepsilon_x) \tag{10}$$

where

$$f_x(\varepsilon) = |V_0| + \frac{\dfrac{2V_x^2/\sqrt{N}}{\varepsilon - \Delta_x/\sqrt{N}} + \dfrac{\Delta_x V_x^2/N^{3/2}}{\left(\varepsilon - \Delta_x/\sqrt{N}\right)^2} + \dfrac{2V_0^2}{\varepsilon - \Delta_0/\sqrt{N}} + \dfrac{\Delta_0 V_0^2/\sqrt{N}}{\left(\varepsilon - \Delta_0/\sqrt{N}\right)^2}}{1 + \dfrac{V_x^2/N}{\left(\varepsilon - \Delta_x/\sqrt{N}\right)^2} + \dfrac{V_0^2}{\left(\varepsilon - \Delta_0/\sqrt{N}\right)^2}} \tag{11}$$

Written in this form one can then make a Lagrange expansion

$$\varepsilon_x = -|V_0| + f_x(-|V_0|) + \frac{1}{2!}\frac{d}{d\varepsilon}\left[f_x(\varepsilon)\right]^2_{\varepsilon=-|V_0|} + \ldots \tag{12}$$

Further elucidation occurs upon expansion of $f_x(\varepsilon)$ in powers of $1/\sqrt{N}$, whence we obtain

$$\varepsilon_x = -|V_0| + \frac{\Delta_0}{2\sqrt{N}} - \frac{2V_x^2 + \Delta_0^2}{4|V_0|N} + O\left(\frac{1}{N^{3/2}}\right) \tag{13}$$

Thus using this in conjunction with eqn. (9), we find

$$E_T - E_S = E_T^0 - E_S^0 + \frac{V_S^2 - V_T^2}{2|V_0|N} + O\left(\frac{1}{N}\right) \tag{14}$$

That is, corrections to the zero-order Hund's-rule-favoring singlet-triplet splitting of $E_T^0 - E_S^0$ becomes quenched as one proceeds to ever larger systems as measured by N. But in fact for a biradical fragment like cyclobutadiene[10] the Hund's-rule $E_T^0 - E_S^0$ splitting is of the wrong sign. Thus pair-excitation limited CI is seen to exhibit artifactual size-dependence of state orderings, so that other computational schemes are recommended for the study of exchange splittings. (For sufficiently small systems the limited CI would be reasonable, but then too improved full CI could be feasible.)

FULL CI RESULTS

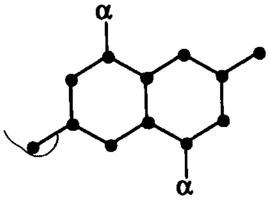
In place of a double-excitation limited CI scheme there are several computational approaches with properly respect system size and presumably yield meaningful corrections to singlet-triplet splittings. Such alternatives include: coupled-cluster theory or (degenerate) many-body perturbation theory. But most reasonable (if feasible) is full CI, for which however the dimensions increase exponentially rapidly with system size. For π-networks with the π-electron number N_e matching the number of sites the numbers $\#_S$ and $\#_T$ of (independent) singlet and triplet states grow rapidly with

N_e	$\#_S$	$\#_T$
2	3	1
6	175	189
10	19404	29700
14	2760615	5010005
18	449141836	901995588

Then one may use[13] an efficient sparse-matrix unitary-group[14] procedure with an iterative "over-relaxation" scheme for eigenvectors[15] to yield (on current supercomputers) one or two low-lying eigenvalues for such systems of up to 14 electrons.

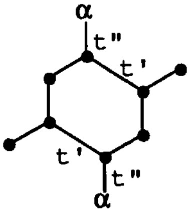
As mentioned in the introduction there is some special interest in an 18-site quinoid biradical structure Q-18. But in light of the (current) difficulty of implementing full-CI computations on such systems, one might instead consider smaller related systems: such as the N=14-site biradical

Q - 14:



where α indicates an electronegativity parameter which may be theoretically varied in a continuous manner from the homoatomic case to a desired heteroatomic case. With even greater computational ease one might perform full-CI computations on the still somewhat related 10-site system

Q - 10:



where now t' and t" indicate electron-hopping parameters which may be changed from the otherwise uniform reference value of t.

Here then we describe the results: first of a variety of computations for the 10-site species Q-10 with several different parameterizations; and second of a more limited number of (more expensive) computations for the Q—14 structure. In both cases we utilize heteroatomic Hubbard models

$$H = \sum_{i\sim j} t_{ij} \sum_{\sigma} a_{i\sigma}^{+} a_{i\sigma} + \alpha \sum_{i}^{\text{hetero}} \sum_{\sigma} a_{i\sigma}^{+} a_{i\sigma} + U \sum_{i} a_{i\uparrow}^{+} a_{i\downarrow}^{+} a_{i\downarrow} a_{i\uparrow} \qquad (15)$$

where the $a_{i\sigma}^{+}$ and $a_{i\sigma}$ are the usual Fermion creation and annihilation operators for an electron of spin $\sigma(=\uparrow,\downarrow)$ in the π-orbital of site i. We somewhat arbitrarily fix the reference t_{ij} electron-hopping integral to take a not unreasonable value of $t = -U/2$ and we vary the site energy α continuously from the homoatomic value of $\alpha = 0$ downward to near $\alpha = -U$. The on-site electron-repulsion parameter U is positive and should be somewhere near 5 eV., but here we report energies in units of U.

For Q-10 we obtain singlet-triplet splittings as indicated in the figure:

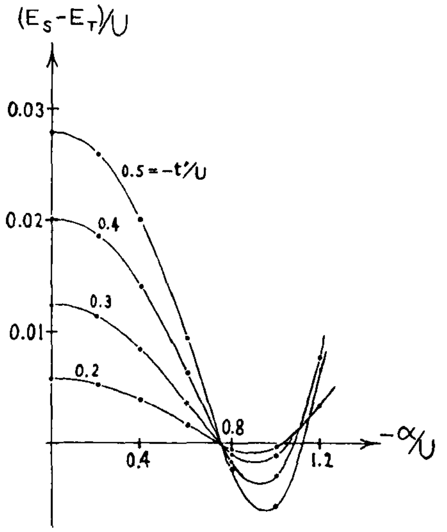


FIGURE 1. Singlet-triplet splittings for Q-10 with various parameterizations

Here the four curves all have $t''= t$ while t'/U takes the indicated values of -0.5, -0.4, -0.3 and -0.2 —this being an attempt to simulate the larger separations between the "radical ends" found in the related Q-18 species. The value of α relevant for O-atoms is not entirely clear a priori, since earlier parameterizations have been developed primarily for the Hückel model, and even then there[16] is a range of recommended values, say with $\alpha/|t|$ in the range from -1.0 to -2.0. Interestingly about half this range corresponds to a triplet ground state in figure 1. Sometimes a modified value of t'' is recommended[16] too, and we have thence carried out some further computations with $t'' = t(1 + \xi\alpha)$. We find that as ξ increases from 0 the splittings near $\alpha = 0$ decrease slightly and at larger ξ, the region exhibiting a triplet ground state becomes less, disappearing altogether near $\xi = 0.4$ For the Q-14 structure we obtain the results of figure 2:

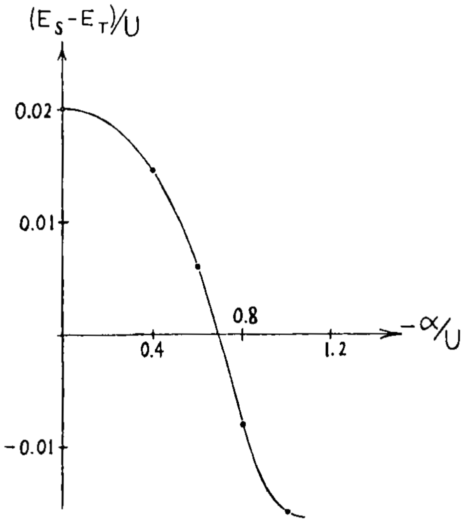


FIGURE 2. Singlet-triplet splitting for Q-14, with uniform t-parameters.

Here all electron-hopping parameters are fixed at $t = -U/2$. Notably the plots for Q-10 and Q-14 appear quite similar, so that it might easily be imagined that a similar plot would also apply for the Q-18 structure.

Evidently for the homoatomic $\alpha = 0$ models which we have treated the ground-state is spin singlet, as indeed Lieb's theorem[4] requires. Further as the heteratoms' electronegativity is increased (i.e. as α is decreased from 0) the spin-triplet falls and eventually crosses under the singlet. This might be rationalized by noting that the higher the electronegativity the more electrons tend to be withdrawn from the outer cycle (of 6-, 10-, or 14-site for Q-10, Q-14 for Q-18), ultimately leaving two fewer electrons than the cycle size, whence "Huckel's rule" (for[17] VB- and PPP-like models) suggests that such 4n-electron containing ionic cycles exhibit triplet ground states. Thus it seems plausable that the Q-(4n + 2) homoatomic and 0-atom heteroatomic species of focal interest here might have different singlet-triplet orderings.

CONCLUSION

Reason has been found to be cautious about the use of pair-excitation limited CI to study exchange splittings. Much more reasonable (if feasible) is full CI.

Exchange splittings have been found to be delicately dependent on the presence and (relative) electronegative strength of heteroatoms. Computational evidence is found that the quinoid O-atom species Q-10, Q-14 and Q-18 might be ground-state triplets, which would agree with experiment[12] for Q-18. Still the corresponding homoatomic species are argued to be ground-state singlets, at least for the Heisenberg (or valence-bond) and Hubbard models. The proper parameterization for heteroatoms seems to us to be a still open question.

For planar homoatomic alternants the VB rule for ground-state spin seems usually to make correct predictions. For heteroatomic species (and perhaps to some extent for homoatomic nonalternants) this rule should not generally hold, because of the accentuated role of "ionic" structures. (Of course, the role of different VB structures depends crucially upon the nature of the AOs from which they are built, and our statement of the preceeding sentence makes the best sense if they are chosen as "antiorthogonalized", say optimally as by Cooper et al[18].) For heteroatom species "simple" spin-symmetry rules do not yet seem well developed.

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