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Electron Correlation and Magnetism: A Simple Molecular Orbital Approach for Predicting Ground-State Spins of Conjugated Hydrocarbons

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A simple molecular orbital (MO) method, the unrestricted Hartree−Fock (UHF) Hubbard method, is proposed to predict the spin preferences of conjugated hydrocarbons. It is shown in this work that this method can account well for ground-state spin multiplicities of not only neutral alternant and nonalternant systems but also ion species. More importantly, the underlying relation between the electron correlation and magnetism in various conjugated systems with different topological characters is revealed by using the present UHF approach. For alternant systems, the magnitude of electron correlation is found to be less important in determining their ground-state spins. Whereas for some nonalternant and ion systems, their ground-state spin multiplicities are shown to depend strongly on the magnitude of electron correlation. In addition, the applicability and limitations of some currently used semiempirical models are analyzed in a unified way.

Introduction

The design and synthesis of high-spin organic molecules and purely organic ferromagnets is a challenging field in current organic chemistry.[1−5] There are several semiempirical theoretical models for predicting ground-state spins of conjugated systems,[6−13] which are very useful in guiding experimentalists to synthesize this new class of molecules and materials. However, these models, which can be classified into two types, the molecular orbital (MO) theory and the valence bond (VB) theory, have varying degrees of difficulty in application. Here we'd like to give brief descriptions for these schemes. The simplest MO theory, the Hückel MO (HMO) theory, assumes that Hund's rule is also operative in molecules; thus the ground-state spin of a considered system is predicted to be just half the number of nonbonding molecular orbitals (NBMOs).[6] Further, Borden and Davidson have demonstrated that in diradicals Hund's rule is obeyed or violated depending on whether two NBMOs have atoms in common or not.[9] When two NBMOs share some common atoms, the Pauli principle keeps the two unpaired electrons from simultaneously appearing in the same atomic orbital (AO), and because there is a high Coulombic repulsion energy associated with the double occupancy of an AO, the triplet is more energetically favorable than the singlet. On the contrary, if two NBMOs can be localized to different sets of atoms, two electrons in two NBMOs need never appear in the same AO regardless of the spins of the two electrons. Consequently, the lowest singlet and triplet states, to first approximation, have the same energy, but the correlation between the electrons in the NBMOs and other electrons in occupied MOs always results in violation of Hund's rule, giving a singlet ground state. Generally speaking, this NBMO analysis is considered to give the correct predictions of spin preferences in most diradicals, but it seems a delicate matter to extend this analysis to polyradicals with more than two NBMOs, although some efforts have been made.[11] Beyond the HMO theory, the full configuration interaction (CI) solutions of the semiempirical Pariser−Parr−Pople (PPP) model and the Hubbard model (which is a further simplification of the PPP model wherein Coulomb interactions are limited to π electrons on the same atom) are successfully applied to small conjugated hydrocarbons with no more than 14 π centers.[8b,c,13] Since the full CI calculations exactly include the correlation effect between electrons, they can always give reliable predictions of ground-state multiplicities. Let's turn to the VB theory. Within the framework of the nearest-neighbor VB model of Pauling and Wheland (being equivalent to the Heisenberg model of solid-state physics), Lieb and Mattis[14] have proven results[7,8a] which for alternant systems the ground-state spin of this model is simply half the difference between the numbers of "starred" and "unstarred" atoms. Unfortunately, this simple rule is invalid in nonalternant systems, and most nonalternant conjugated systems are beyond the capability of this approach because the exact solution of this model is also limited to about 24 π centers.[15]

In the past years, the validity and limitations of these semiempirical schemes have been extensively examined by a large number of experimental[16−20] and theoretical works.[21−30] However, in our opinion, developing a simple and general method that can predict the ground-state spins of various conjugated hydrocarbons including di- and polyradicals, alternant and nonalternant systems, is still necessary and also possible. Summarizing the above discussions on these semiempirical methods, we can find that electron correlation plays a crucial role in determining the spin alignment in the ground state of a system. This point can be extracted from examining the underlying relation of these methods to the Hubbard model. Although this model is a simplified PPP model, it is believed that this model agrees very well with the PPP model for the "homo-polar" states including the lowest state of each spin multiplicity.[31] The Hubbard Hamiltonian is defined as follows:

$$H = -t\sum_{(ij)\sigma} C^{+}_{j\sigma}C_{i\sigma} + U\sum_{i}\hat{n}_{i\alpha}\hat{n}_{i\beta} \tag{1}$$

Where $C_{j\sigma}{}^{+}$ and $C_{i\sigma}$ are the creation operator of spin σ at site j and the annihilation operator of spin σ at site i, respectively. $\hat{n}_{i\alpha(\beta)}(= C^{+}_{i\alpha(\beta)}C_{i\alpha(\beta)})$ denotes the number operator spin $\alpha(\beta)$ at site i, the parameter t represents the nearest-neighbor hopping energy ($-t$ is equal to β of the HMO theory), and U is the on-site Coulomb repulsion energy, which introduces the electron correlation into this model. When U is equal to zero, the Hubbard model reduces exactly to the HMO model, while in the strongly correlated limit ($U/t \rightarrow \infty$), the second-order degenerate perturbation theory[32,33] or a two-site cluster expansion technique[31,34] can be used to map the model onto the nearest-neighbor VB model (displayed below) mentioned above.

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$$H_{\mathrm{VB}} = J\sum_{(ij)}\left(2S_i\cdot S_j - \frac{1}{2}\right) \quad \text{for} \quad U \gg t \tag{2}$$

Where S_i is the spin operator for site i and J $(=2t^2/U)$ is an exchange parameter. Now, it is clear that the NBMO analysis of Borden and Davidson corresponds to the weakly correlated limit of the Hubbard model, and the results of the nearest-neighbor VB model represent those of the Hubbard model in the strongly correlated limit. In fact, real conjugated hydrocarbons, in which the electron correlation parameter U/t is theoretically estimated to be in the range 1.0−4.0,[35] lie intermediate between the HMO and VB antipodes. On the basis of the success of these two approximate schemes, we conjecture that the Hartree−Fock (HF) approximation of the Hubbard model, which takes the partial electron correlation into account, may also give valuable predictions of spin preferences of conjugated hydrocarbons. Obviously, the HF Hubbard model is simple because only the topological symmetry of molecules is required as in the HMO model and it is easy to solve even for quite large systems.

It should be mentioned that in the chemical literature the HF calculations of the generalized Hubbard model were earlier used to predict ground-state spins of a class of high-spin carbenes without detailed discussions of this method.[36] In this work, we show that if the value of the electron correlation parameter U/t is appropriately selected, the HF Hubbard model is a promising tool in predicting the ground-state spin multiplicity not only for neutral conjugated hydrocarbons but also for ion ones. More importantly, we want to employ this model to investigate the electron correlation/magnetism relation in conjugated systems with different topologlical characters. On the basis of this investigation, the applicability and limitations of some currently used semiempirical theoretical models are analyzed in a unified way.

The Hartree−Fock (HF) Hubbard Model

The Hubbard model described previously is essentially a many-electron Hamiltonian, operating in the space of n-electron wave functions (or Slater determinants), whose dimension increases exponentially with the size of molecules. Currently, for larger systems with more than 14 π centers, the Hubbard model can only be solved approximately. In solid-state theory, the HF approximation of this model is widely adopted for discussing the local magnetic moment in ferromagnetic dilute alloys with localized d and delocalized s electrons.[37] This approximation assumes that the deviation between the number operator and its expection value with respect to the desired spin state is small; namely, the last term of the Hubbard model can be expressed by

$$\begin{aligned} U\sum_i \hat{n}_{i\alpha}\hat{n}_{i\beta} &= U\sum_i [\langle\hat{n}_{i\alpha}\rangle + (\hat{n}_{i\alpha} - \langle\hat{n}_{i\alpha}\rangle)][\langle\hat{n}_{i\beta}\rangle + (\hat{n}_{i\beta} - \langle\hat{n}_{i\beta}\rangle)] \\ &= U\sum_i [\hat{n}_{i\alpha}\langle\hat{n}_{i\beta}\rangle + \langle\hat{n}_{i\alpha}\rangle\hat{n}_{i\beta} - \langle\hat{n}_{i\alpha}\rangle\langle\hat{n}_{i\beta}\rangle + (\hat{n}_{i\alpha} - \langle\hat{n}_{i\alpha}\rangle)(\hat{n}_{i\beta} - \langle\hat{n}_{i\beta}\rangle)] \end{aligned} \tag{3}$$

where $\langle\hat{n}_{i\alpha(\beta)}\rangle$ represents the average value of the operator $\hat{n}_{i\alpha(\beta)}$ with respect to the desired spin state. Neglecting the last term of eq 3, the multiplication of two small quantities, results in the HF Hubbard model, which can be rewritten into two coupled Hamiltonians for α and β electrons, respectively.

$$H = H_\alpha + H_\beta - U\sum_i \langle\hat{n}_{i\alpha}\rangle\langle\hat{n}_{i\beta}\rangle \tag{4a}$$

$$H_\alpha = \sum_i U\langle\hat{n}_{i\beta}\rangle C^+_{i\alpha}C_{i\alpha} + \sum_{i-j}(-t)C^+_{j\alpha}C_{i\alpha} \tag{4b}$$

$$H_\beta = \sum_i U\langle\hat{n}_{i\alpha}\rangle C^+_{i\beta}C_{i\beta} + \sum_{i-j}(-t)C^+_{j\beta}C_{i\beta} \tag{4c}$$

From the above equations, it is clearly seen that the on-site electron correlation is automatically considered in an average manner by adding a term to the Coulomb integral t_0[38] of the HMO theory (t_0 is taken to be the zero of energy throughout this work). Essentially, the model we obtain above should be termed the unrestricted Hartree−Fock (UHF) Hubbard model (will be used in the following) because the double occupancy of molecular orbitals is not forced here. Since the solution of this model is the eigenfunction of S_z but not of S^2, the average value of total spin S is usually needed to evaluate the spin contaminations of the UHF wave functions, which can be easily calculated by using the formula below:[39]

$$\langle S^2\rangle = S(S+1) = \frac{p-q}{2}\left(\frac{p-q}{2} + 1\right) + q - \mathrm{tr}(P^\alpha P^\beta) \tag{5}$$

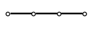
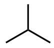
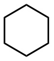
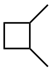
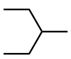
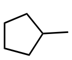
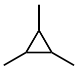
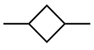
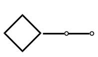
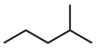
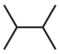
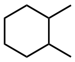
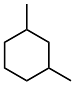
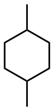
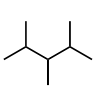
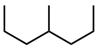
Here $p(q)$ is the number of $\alpha(\beta)$ spin electrons, and $P^{\alpha(\beta)}$ denotes the density matrix associated with $\alpha(\beta)$ spin. Due to the spin contaminations of desired spin states, the energy difference between the ground and first excited states can reflect the strength of spin coupling only if these two states are less spin-contaminated. Generally, the ground-state spin multiplicity derived from the UHF Hubbard calculations depends on the value of the parameter U/t especially in nonalternant or ion systems. So in the following we first determine the realistic value of this parameter for conjugated hydrocarbons by fitting the full CI solutions of the Hubbard model to corresponding values of the PPP model.

With changing the value of the parameter U/t (t is taken to be 2.60 eV given by Schulten, Ohmine, and Karplus[40]), we exactly solve the Hubbard model by using the Lanczos algorithm[41] for a series of conjugated hydrocarbons, in which the exact solutions of the PPP model are also available.[13] We find that if the parameter U/t is chosen to be 2.0, the singlet−triplet (S−T) energy gaps calculated from the Hubbard model are in quantitative agreement with those from the PPP calculations, as shown in Table 1 and Figure 1. In fact, even for those molecules with very narrow energy gaps, such as **12** and **16**, the Hubbard model can also give consistent predictions with the PPP model. On the other hand, the spin distributions obtained from the full CI Hubbard calculations also agree well with corresponding experimental (or PPP if available) values,[42,43] as depicted in Figure 2. Concludingly, it seems likely that the Hubbard model with the parameter U/t of 2.0 can describe very well the low-lying electronic states as the PPP model. Therefore, we'll adopt this parameter in our subsequent UHF Hubbard calculations (unless otherwise addressed). It should be mentioned that this is the same parameter used by Klein et al.[8a]

Results and Discussion

In this section, the UHF Hubbard calculations are carried out for a large number of neutral and ion conjugated molecules (all systems are assumed to be planar). The predicted ground-state spin preferences are compared with those from other semiempirical and even ab initio schemes for predicting the ground-state spin. Meanwhile, the dependence of the electron correlation/magnetism relation on topological characters of π networks is

TABLE 1: The Two Lowest States of a Series of π Systems

molecules	PPP[a] (in eV)	Hubbard[b] (in eV)	HF-Hubbard[c] ($\langle S^2 \rangle$)
 1	$r_0 = r_1 = 1.4$ Å $E_T - E_S = 2.5$	S, −7.48 T, −5.43	S, −2.47 (0.00) T, −1.88 (2.00)
 2	S, −8.04 T, −7.75	S, −7.35 T, −6.98	S, −2.66 (1.10) T, −2.50 (2.00)
 3	S, −5.84 T, −6.72	S, −5.20 T, −6.08	S, −1.95 (1.02) T, −2.23 (2.08)
 4	S, −15.66 T, −11.74	S, −14.06 T, −10.65	S, −5.00 (0.00) T, −3.63 (2.15)
 5	S, −13.75 T, −11.63	S, −12.42 T, −10.57	S, −4.21 (0.00) T, −3.62 (2.08)
 6	S, −13.05 T, −11.03	S, −11.67 T, −9.93	S, −3.90 (0.00) T, −3.48 (2.15)
 7	S, −14.17 T, −12.67	S, −12.73 T, −11.42	S, −4.41 (0.14) T, −4.11 (2.06)
 8	S, −13.91 T, −11.69	S, −12.58 T, −10.63	S, −4.30 (0.28) T, −3.79 (2.08)
 9	S, −11.84 T, −12.55	S, −10.72 T, −11.44	S, −3.93 (1.14) T, −4.15 (2.24)
 10	S, −12.91 T, −12.66	S, −11.75 T, −11.46	S, −4.21 (1.22) T, −4.07 (2.08)
 11	S, −11.29 T, −11.79	S, −10.13 T, −10.65	S, −3.64 (1.12) T, −3.83 (2.20)
 12	S, −11.50 T, −11.41	S, −10.39 T, −10.29	S, −3.72 (1.29) T, −3.63 (2.15)
 13	S, −18.34 T, −17.37	S, −17.29 T, −16.42	S, −5.95 (0.00) T, −5.90 (2.02)
 14	S, −17.25 T, −17.64	S, −16.31 T, −16.67	S, −5.92 (1.01) T, −6.05 (2.18)
 15	S, −18.25 T, −17.32	S, −17.24 T, −16.37	S, −5.92 (0.00) T, −5.88 (2.01)
 16	S, −16.07 T, −16.09	S, −14.49 T, −14.52	S, −5.10 (1.22) T, −5.18 (2.55)
 17	S, −16.49 T, −16.89	S, −14.78 T, −15.20	S, −5.25 (1.17) T, −5.44 (2.31)

[a] The full CI solutions taken from ref 13. [b] The full CI solutions presented in this work. The parameters t and U/t are taken to be 2.60 eV and 2.00, respectively. [c] Calculated from the Hartree−Fock approximation of the Hubbard model (in units of t = 2.60 eV). The expectation value of S^2 ($\langle S^2 \rangle$) is presented to evaluate the spin contaminations of the desired spin states.

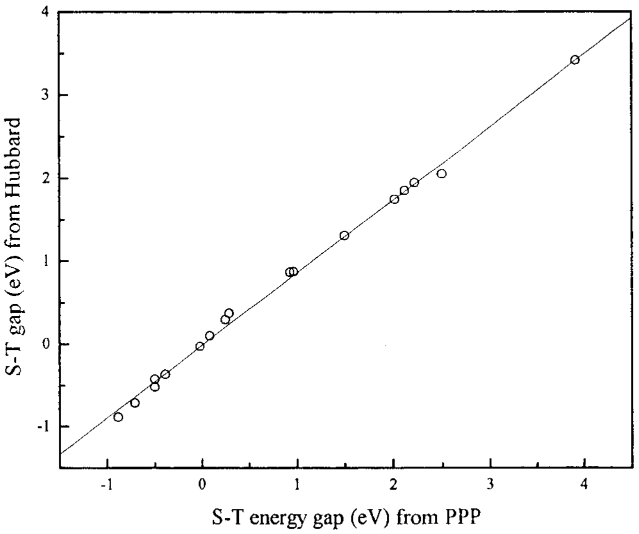


Figure 1. Correlation of the singlet−triplet (S−T) energy difference from the full CI Hubbard calculations with those from the corresponding PPP calculations.

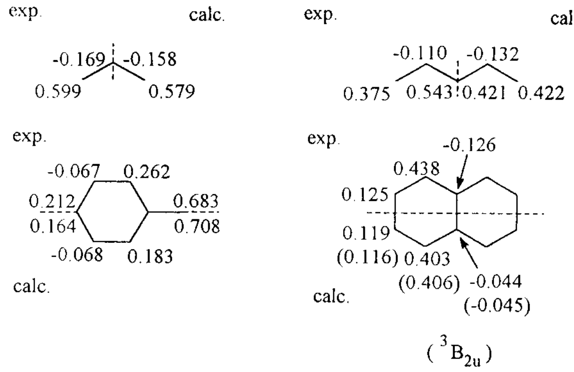


Figure 2. Calculated spin densities in some conjugated hydrocarbons. The corresponding experimental values (from ref 42, ref 43, and references therein) are given for the purpose of comparison. For the $^3B_{2u}$ state of naphthalene, the exact PPP results (from ref 43) are also presented in parentheses.

examined in detail. The applicability and limitations of some semiempirical models are analyzed in a unified way.

Neutral Systems. In the previous section, we have provided the exact solutions of the Hubbard model for species **1**−**17** listed in Table 1, which give us a straightforward chance to verify the applicability of the UHF Hubbard approach. From the results also collected in Table 1, it is clearly seen that for all considered systems even those with nearly degenerate ground states, this approach makes the same predictions as the full CI Hubbard calculations, indicating that the UHF Hubbard model is a promising tool for predicting the ground-state spin multiplicity of conjugaged systems. We'd like to give some further comments on the above results. For those closed-shell alternant molecules like benzene and butadiene, their ground states are always predicted by this method to be pure singlet states. In fact, in this case the UHF Hubbard model gives the same results as the restricted HF (RHF) Hubbard approach with forcing the doubly occupied condition of molecular orbitals. Drastic differences occur in open-shell alternant species (e.g. radicals). For example, this method makes direct predictions that cyclobutadiene (**2**) and tetramethyleneethane (TME, **12**) have singlet ground states, but species **3**, **9**, and **14** prefer triplet ground states, although all these molecules possess two degenerate NBMOs even within the RHF Hubbard model. Generally, for those diradicals with two nondisjoint NBMOs, this method and the NBMO analysis addressed above lead to the same

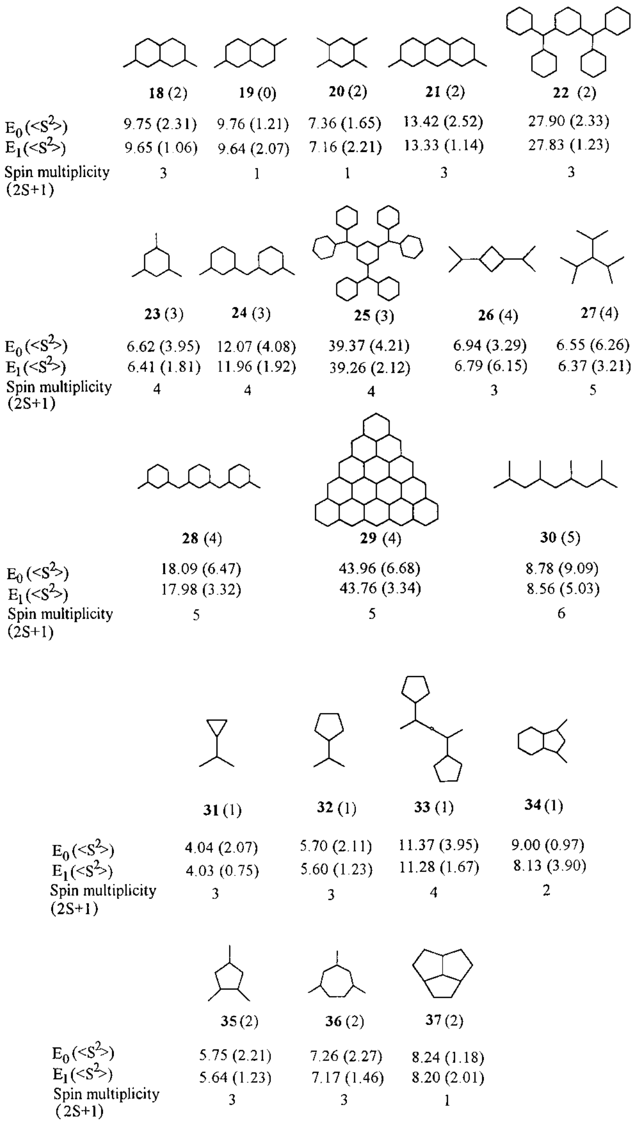


Figure 3. Ground-state spin multiplicity of some neutral conjugated hydrocarbons. The energies (in units of *t*) of the two lowest states are presented for each species. The expectation value of S^2 is included to evaluate the spin contaminations of each spin state. The number of NBMOs of each species (species **37** has two bonding degenerate frontier orbitals instead of NBMOs) is also given in parentheses for the purpose of analysis.

conclusion because these two methods have the same physical background. But for those species in which two NBMOs are disjoint, the NBMO analysis may give unreliable results in some cases[8b,26c] because it is only perturbative in nature. Species **16** provides such an example. The NBMO analysis predicts that it should be a singlet state; however, a triplet ground state is derived from both the exact and UHF Hubbard model. In fact, the failure of the NBMO analysis also occurs in those species with more than two NBMOs, which will be discussed hereafter. In comparison with the perturbed NBMO approach, the UHF Hubbard calculations can always make the correct predictions for these systems by directly using the spin-polarized orbitals. Besides alternant systems, we notice that the present UHF method can also treat nonalternant systems, as illustrated for **7** and **8**. In addition, it is worth commenting on the spin contaminations of the two lowest states listed in Table 1. Generally speaking, we can see that for those molecules with narrow energy gaps their ground states are spin-contaminated to a large extent. Obviously, the mixture of these states with their first excited states is responsible for this phenomenon. It can be expected that if we introduce the more complicate projected UHF method,[29] these spin contaminations may be greatly reduced. Even so, the simple UHF method is adopted in this work because this method usually gives the same ground-state spin predictions as the projected UHF technique. Concludingly, the success of the UHF Hubbard model to the above small systems stimulates us to investigate the application of this method to more extensive neutral and ion conjugated hydrocarbons.

Twenty neutral conjugated hydrocarbons, including alternant and nonalternant systems, are selected for our investigation (Figure 3). For each species, the calculated energies and the expectional value of S^2 of the two lowest states, together with the resulting ground-state spin, are also displayed in Figure 3. At first sight, for all alternant systems considered our predictions of ground-state spins are in full accord with those from the simple "starred" and "unstarred" rule of the VB approach described previously. This implies that ground-state spins of alternant systems may be completely controlled by their topological symmetry rather than the magnitude of electron correlation. To confirm this inference, we perform the UHF Hubbard calculations for these species at different values of the parameter *U*/*t*. Undoubtedly, we find that the ground-state spin of each alternant system does not change at all if only the parameter *U*/*t* is nonzero. Therefore, our results demonstrate that the simple VB rule, although derived from the strongly correlated limit of the Hubbard model, can always give reliable predictions for ground-state spins of alternant conjugated molecules, which belong to the moderately correlated systems. However, the failure of the simple Hund's rule is again observed in species **20** and **26**. Ab initio calculations on **20** at many different levels of theory[26a] also support the results of the UHF Hubbard model and the VB model that this molecule has a singlet ground state. Indeed, the violation of Hund's rule in this species is also verified by recent experiments.[28] Similarly, a triplet is predicted to be the ground state of species **26** by this method (our full CI Hubbard calculations on this species also support this assignment), whereas Hund's rule gives a quintet ground state. On the other hand, the NBMO analysis, which works well in most diradicals, also suffers from the difficulties in polyradicals. For instance, according to our and others' calculations,[8b] the quintet, not the triplet given by the NBMO analysis, is predicted to be the ground state of species **27**. As mentioned above, the breakdown of the NBMO analysis in this case can also be ascribed to its perturbative character. Summarizing the above discussions, the UHF Hubbard model and the simple VB approach can be considered to account very well for ground-state spin multiplicities of alternant systems.

In contrast to that in alternant systems, the spin preferences of nonalternant systems are complicated by not only the spin polarization but also the charge transfer in π networks. Although Radhakrishnan's empirical rule, based solely on the topology of conjugated systems, gives correct predictions on ground-state spins in some nonalternant molecules,[12] a simple theoretical way for predicting the ground-state spins of these systems has not been established yet. The present UHF Hubbard approach is an attempt toward this goal. From the displayed results for species **31**−**37**, we note that there is not a definite relation between the number of NBMOs and the ground-state spin. Consequently, both Hund's rule and the NBMO analysis should be used cautiously. For instances, our calculations predict a triplet ground state for species **32**, although it has only one NBMO in the HMO framework. More sophisticated ab initio results[23b] and the full CI PPP[13] (or the present Hubbard) calculations also support this prediction. For species **35** and **36**, the predictions from our method are also advocated by the

TABLE 2: Hubbard Transition in Species 31 Predicted by the Full CI and Unrestricted Hartree−Fock (UHF) Hubbard Calculations

	1.70[a]		1.95[a]		2.00[a]	
state	full CI	UHF($\langle S^2\rangle$)[b]	full CI	UHF($\langle S^2\rangle$)[b]	full CI	UHF($\langle S^2\rangle$)[b]
singlet	−4.6692	−4.4453 (0.61)	−4.3599	−4.0970 (0.73)	−4.3004	−4.0290 (0.75)
triplet	−4.5900	−4.3929 (2.03)	−4.3588	−4.0999 (2.04)	−4.3142	−4.0427 (2.07)

[a] The value of the parameter U/t. [b] The expectation value of S^2 ($\langle S^2\rangle$) is presented to evaluate the spin contamination of each spin state.

more complex semiempirical CNDO/S-CI method.[26c] Especially, the present method predicts that compound **37**, in which two frontier orbitals (but not NBMOs) are degenerate within the HMO theory, has a singlet ground state, being consistent with the latest experimental facts.[18] Now, as we have done in alternant systems, we want to investigate whether ground-state spins of nonalternant systems are dependent on the magnitude of the electron correlation parameter U/t. We take species **31** as an example. Although both the exact and approximate Hubbard models, in which the present parameter ($U/t = 2.0$) is used, show that the triplet is slightly lower in energy than the singlet (the exact PPP and VB calculations also lead to this prediction), further exact Hubbard calculations reveal that there exists a critical value (≈ 2.0) of the electron correlation parameter U/t (Table 2), below which a singlet ground state is favorable in energy. It should be pointed out that such a transition from a triplet state to a singlet state is termed the Hubbard transition (the changeover of the ground-state spin multiplicity) and has been discussed by Lee.[44] Encouragingly, the present UHF Hubbard approach also yields a critical value extremely close to that from the full CI Hubbard calculations. These calculations on species **31** remind us that for some nonalternant systems, in which the Hubbard transition may exist, their ground-state spins will depend strongly on the magnitude of the parameter U/t. Therefore for such systems, the UHF Hubbard calculations even with the present parametrization ($U/t = 2.0$) may still yield the incorrect results owing to the fact that the model is so simple and nonalterant systems are not simple like alternant species. Despite this, the UHF Hubbard model with the present parametrization scheme is still expected to be the simplest theoretical model for our qualitative predictions of ground-state spins of nonalternant systems. On the basis of the above discussions, we now answer another related question, i.e., in which cases can the VB model operate in nonalternant conjugated hydrocarbons? Clearly, if a nonalternant system has no Hubbard transitions at all or has a Hubbard transition at a critical parameter U/t far below 2.0, the VB model may be anticipated to give a correct prediction of the ground-state spin of this system. For example, species **32** has a Hubbard transition at $U/t \approx 1.48$ (1.48, full CI; 1.44, UHF), whose ground state is correctly predicted by the VB calculations to be the triplet, as mentioned above. Lee[44] has arrived at a qualitative rule to predict whether the Hubbard transition occurs in some nonalternant systems. In fact, by performing the present UHF Hubbard calculations, it is very easy to ascertain the occurrence of the Hubbard transition, as illustrated in **31** and **32**.

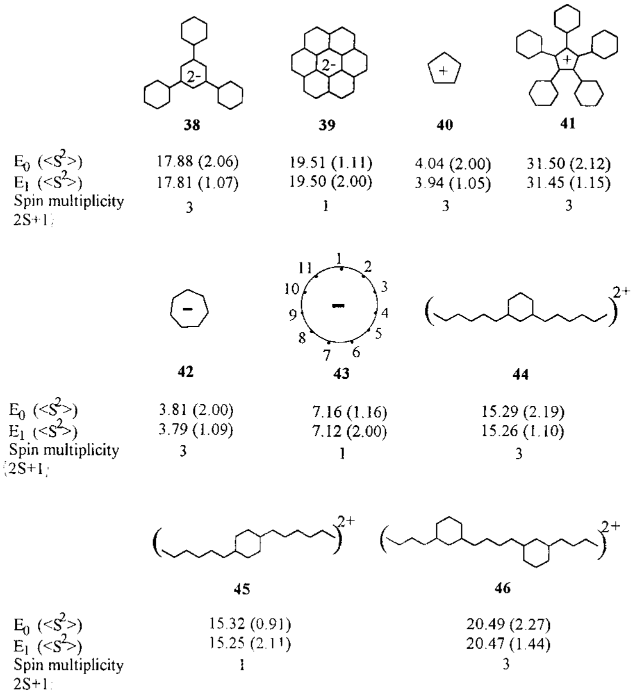


Figure 4. Ground-states spin multiplicity of some ion conjugated hydrocarbons. The energies (in units of t) of the two lowest states are presented for each species. The expectation value of S^2 is included to evaluate the spin contaminations of each spin state.

Ion Systems. Like neutral systems, ion radicals and related polymers have also received noticeable attention in relation to the design and preparation of organic ferromagnets with polaronic ferromagnetism.[45] Recently, Dougherty et al.[17d] have shown experimentally that the high-spin molecules can be constructed by coupling ion radicals with the ferromagnetic coupling units. Therefore, an understanding of the ground-state spins of ion radicals is also desirable. Here, we illustrate that the UHF Hubbard model is also capable of providing reasonable predictions of ground-state spins for most ion conjugated hydrocarbons. Some examples have been presented in Figure 4. From Figure 4, it can be seen that compounds **38**−**43** (except **39** and **43**) are all ground-state triplets from our calculations. We notice that the same predictions can also be obtained from the HMO theory with the aid of Hund's rule because two degenerate orbitals are only half-filled for these species. Experimentally, an ESR spectrum characteristic of a triplet state is indeed observed in species **38**, **40**, and **41**, respectively.[46] The cycloheptatrienyl anion (**42**), although it should be a triplet in the D_{7h} conformation by our and other's works,[47] may prefer a distorted singlet. For species **39** and **43**, however, the divergence between the present method and the HMO theory arises. Based on the HMO theory, these two species should have triplet ground states like those systems discussed above. However, using the parameter U/t of 2.0 determined previously, the UHF Hubbard model predicts that these two molecules are the ground-state singlet species. We note that experimental observations confirm that species **39** is indeed diamagnetic.[46] Although it is very difficult to confirm experimentally the predicted violation of Hund's rule in planar **43** since the equilibrium geometry of this species may be nonplanar, the failure of the HMO theory in larger $4n$ π electron systems, as demonstrated here, has been postulated previously.[47] It is interesting to examine why the HMO theory fails in these cases. For this purpose, we perform the UHF Hubbard calculations for species **39** at different values of U/t. Surprisingly, when the value of U/t is limited to be below 1.90, the present approach also predicts that the triplet state is energetically favorable, consistent with the results of the HMO theory. Therefore, our calculations for this species indicate that the magnitude of electron correlation is also very important in determining ground-state spins of ion radicals. Owing to this reason, the UHF Hubbard model even with the present parametrization may also give unreliable predictions in some ion systems, in which the changeover of ground-state spin multiplicity occurs at the critical parameter U/t around 2.0. Despite this, the UHF Hubbard method with the parameter U/t of 2.0 is expected to work well in most of ion conjugated systems with less negative or positive charge. As expected, the present UHF Hubbard calculations on compounds **44** and **46** show that the *m*-phenylene type units can ferromagnetically couple two ion radical groups with delocalized spins, which is in line with the ab initio UHF results.[29]

Concluding Remarks

This work suggests a simple and general molecular orbital approach, the UHF Hubbard model, to predict the spin preferences of conjugated hydrocarbons. A systematic investigation presented in this work demonstrates that if appropriately parametrized, this method can account very well for ground-state spin multiplicities of not only neutral alternant and nonalternant systems but also ion species. More importantly, the present work sheds light on the underlying relation between the electron correlation and magnetism in various conjugated systems. For alternant systems, the magnitdue of electron correlation (reflected by the value of the parameter U/t) is found to be less important for determining their ground-state spins, so the simple VB model, derived from the Hubbard model in the strongly correlated limit, can be expected to give correct predictions for ground-state spins of these systems. But for nonalternant systems, the situation is not so simple. Our calculations indicate that the ground-state spin multiplicity is strongly dependent on the magnitude of electron correlation in some of these systems, which can be easily detected by use of the present UHF Hubbard calculations. Consequently, the HMO and VB models may break down in these cases. In addition, the magnititude of electron correlation is also shown to have a crucial effect on the ground-state spins of ion systems. Finally, we would like to point out that the similarity between the UHF and full CI predictions of spin orderings, as shown in this paper, is an incentive to the wide application of other semiempirical or ab initio UHF methods for spin preferences in various chemical systems.

In summary, we have made progress in recognizing the electron correlation/magnetism relation in molecular systems and predicting the ground-state spins of conjugated hydrocarbons. The results we obtain may be of considerable use to the design and preparation of high-spin organic molecules and novel magnetic materials.

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