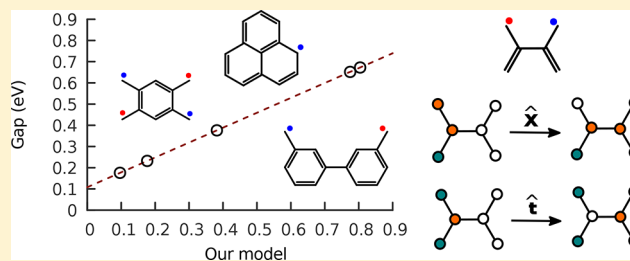


Energy Gaps of Polyradicals from an Effective and Transferable Hamiltonian with through-Bond Interactions

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ABSTRACT: Current model Hamiltonians and *ab initio* many-body quantum treatments of π -conjugated polyradicals formed from hydrocarbons produce divergent results because of numerical complexity and large size of the basis-function set used. We propose an alternative, three-term Hamiltonian, to describe these various polyradicals that simplifies considerably the computational cost while providing a physical interpretation for all three terms and a high degree of model universality. The essential feature of this Hamiltonian is a term, not present in previous models, describing the three-sited through-bond interaction that governs the noninteracting spin-up and spin-down sectors. A computation of the lowest energy gaps and spin configurations for the smaller polyradicals demonstrates the efficacy of the model and its potential in applications in revealing electrical conductivity and ferromagnetism of the more complicated substituted polyradicals.



Hydrocarbons polyradicals with high/low-spin ground states are of central interest to chemistry and physics, as they form the basis of many substituted polyradicals.^{1–3} Their polyradical character arises when some unpaired electrons occupy almost-degenerate molecular orbitals; this is an important distinguishing trait in the electronic structure^{1–3} with applications in metal-free functional organic molecular magnetism.^{4–8} The insights obtained with these simple molecules are employed to understand the effects of topology and electronic interactions of more complicated molecules.^{9,10} Nevertheless, the physics and the computation of energy gaps between pairs of magnetic states of the organic polyradicals still represent a challenge both in quantum chemistry and for Hamiltonian modeling.

It is usually necessary to employ high-level *ab initio* techniques to obtain accurate estimates of these spin gaps; although an accurate quantum chemistry many-body treatment of these molecules becomes tricky, the behavior is erratic and diverse from one methodology to another as well as having a large dependence on the size of the Gaussian basis set used.¹¹ Improving the accuracy of the *ab initio* theoretical methods is possible but comes at a huge computational cost.¹²

From the Hamiltonian modeling perspective, the Heisenberg–Dirac model based on Hamiltonian^{13–15} $\hat{H}_{\text{HD}} = \sum_{i \neq j} J_{ij} (2\vec{S}_i \cdot \vec{S}_j - 1/2)$ has a truncated covalent configuration space^{16,17} that limits its applicability. Many extensions have been suggested to improve its usefulness concerning more general systems.^{18,19} Recently some good progress has been made with these extended models when applied to tetradicals.¹⁸ Furthermore, a rigorous procedure to create alternative magnetic Hamiltonians was also worked out by Malrieu¹⁹ et al. These extended Heisenberg models are effective in describing strongly correlated molecules but are not adequate to characterize weakly correlated systems.¹⁸ More-

over, these extended models produce expressions that are cumbersome and in effect do not provide new insights into the physics of the problem.¹⁸

In contrast, the Hubbard²⁰ model based on Hamiltonian $\hat{H}_{\text{Hub}} = \sum_{\sigma(ij)} -t(\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c.) + \sum_k U \hat{n}_{k\uparrow} \hat{n}_{k\downarrow}$ can describe the charge and spin states of polycyclic aromatic hydrocarbons (PAHs)²¹ as well as radicals,¹⁸ although at a cost of a very large configuration space that limits its applicability and a parameter U that lacks to some degree transferability among the different molecules.^{18,21} An improvement over the Hubbard model is achieved with the Pariser–Parr–Pople (PPP) Hamiltonian,^{22,23} that is more effective in describing PAH molecules^{21,24} and seems to have a more transferable set of parameters but suffers from the same computational scaling problems of the Hubbard model.

An expansion at the high U/t limit of the Hubbard model^{25,26} leads to a Hamiltonian with two new correlated hopping terms. The first is a two-sites correlated hopping^{27–29} of general form $(\hat{n}_i + \hat{n}_j) \hat{c}_i^\dagger \hat{c}_j$, where i, j are first neighbors, and the second one is a three-sites^{19,30} term like $\hat{c}_i^\dagger \hat{c}_k^\dagger \hat{c}_k \hat{c}_m$, where l and m are next-nearest-neighbors and k is an intermediate site between them. These correlated hopping mechanisms were studied at 1D systems,^{31,32} and they were also applied to model cuprates.^{33–35} Moreover, the three-sites mechanism was recently realized on an optical lattice which manifested a string order not observed before.³⁶

The objective of this Letter is to report an alternative model Hamiltonian applicable to describe the basic physics of π -conjugated polyradicals. Our model uses only two free parameters and a very simplifying hypothesis of noninteracting spin sectors associated with spin-up (\uparrow) and spin-down (\downarrow)

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states, that yields a considerable reduction in the number of basis states necessary to diagonalize the Hamiltonian. The effectiveness of this model is possible because of a *through-bond* three-site term used in the model that does not appear in the Heisenberg-like and Hubbard-like models or any other model that we know aimed at describing isolated radical organic molecules but still gives an easy to understand and interpretable expression. Our results are assessed by comparison with *ab initio* quantum chemistry computations reported in the literature, with our model predicting very good values for the spin gaps of each molecule considered. Moreover, we use one set of parameter values to describe all molecules, an indication of the applicability of our model to other similar quantum chemistry problems.

Our model Hamiltonian is expressed in the form

$$\hat{H} = \sum_{\sigma=\uparrow,\downarrow} \left[\sum_{\langle i,j \rangle} (-t(\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}) + V \hat{n}_{i\sigma} \hat{n}_{j\sigma}) + \sum_{\langle\langle l,(k),m \rangle\rangle} X(\hat{c}_{l\sigma}^\dagger \hat{n}_{k\sigma} \hat{c}_{m\sigma} + \hat{c}_{m\sigma}^\dagger \hat{n}_{k\sigma} \hat{c}_{l\sigma}) \right] \quad (1)$$

where $\hat{c}_{i\sigma}^\dagger$ ($\hat{c}_{i\sigma}$) is the Fermion creation (annihilation) operator for spin σ on the i th site, obeying the anticommutation relations $\{\hat{c}_{i\sigma}, \hat{c}_{j\sigma}^\dagger\} = \delta_{ij}\delta_{\sigma\sigma}$ and $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$ is the number operator.

The first term proportional to t corresponds to the nearest-neighbor (NN) \hat{t} hopping mechanism, and the term proportional to V is the NN charge(σ)–charge(σ) interaction. The last term proportional to X is the extended correlated hopping operator \hat{X} , where two next-to-nearest neighbor sites labeled $\langle\langle l, m \rangle\rangle$ are connected by an intermediate site (k) shared between them; see Figure 1(A). Despite the widely used tight-

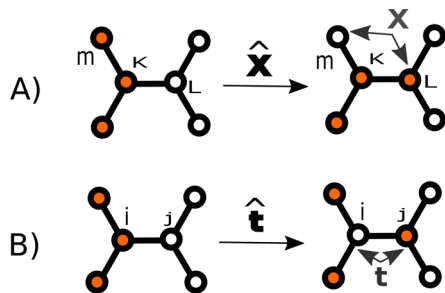


Figure 1. Action of operators \hat{X} , A) and \hat{t} , B) on the initial states (left column) with three particles with \uparrow or \downarrow for the singlet sector of the TME molecule. The resulting states are given in the right column. Observe that the through-bond operator \hat{X} maintains a pair of adjacent sites (red dots) occupied, whereas a direct hopping may create holes (white dots).

binding hopping mechanism, we are not aware of the use of these last two terms in eq 1 in any similar model Hamiltonian aimed at describing isolated π -conjugated organic radical molecules, as the key characteristic of our model requires noninteracting \uparrow and \downarrow spin sectors. These independent spin sectors distinguish fundamentally our model from the Hubbard-like models and enable the separate diagonalization of eq 1 for one particle spin type (\uparrow and \downarrow) at once, which is subsequently combined with the other to give the desired spin sector. This reduces considerably the number of basis states and the computational effort necessary to describe any system and

moreover enables its application to be extended to larger molecules.

We observe in Figure 1(B) that the action of \hat{t} creates states with holes, whereas the action of \hat{X} , Figure 1(A), always keeps a string of two NN sites occupied. This feature of the \hat{X} operator of always keeping two NN sites connected is called *through-bond* hopping. Observe that two NN occupied sites also imply a nonzero value for \hat{V} , and the competition between these two terms is the key point in our model design.

From a computational perspective, the operators of eq 1 can be represented in matrix form using the Fock space basis formed by the states with a fixed number of particles without the use of any other symmetry constraint. Our strategy to obtain the ground state is based on an exact diagonalization of the matrix representation of the Hamiltonian, where the implicitly restarted Lanczos method^{37,38} was used to obtain the 25 smallest eigenvalues and their corresponding eigenvectors for the biggest systems and a simple standard direct methods for smaller molecules.

The molecules studied are depicted in Figure 2. They are a challenge for both, experiment and the application of *ab initio*

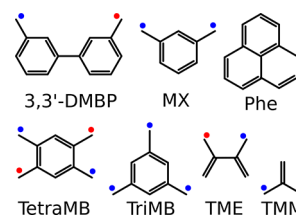


Figure 2. Polyradicals molecules. Non-Kekulé nondisjoint ferromagnetic diradicals TMM and MX and triradical TriMB. Non-Kekulé disjoint antiferromagnetic radicals TME and 3,3'-DMBP and TetraMB. Polyaromatic radical phenenyl (Phe). Blue (red) dots indicate the expected \uparrow (\downarrow) spin configuration of the ground state.

methods, and from a quantum chemistry perspective only recently have accurate predictions been obtained for some of them regarding their electronic properties. Precise model Hamiltonians describing them are to the best of our knowledge nonexistent. These molecules are polyradicals composed only of π electrons (orbitals); because of the specificities of each system, we shall describe details of each below when we also present our results.

The methodology we adopted was to search for values of the parameters given in eq 1 for TMM, TriMB, and TME in Figure 2 that give qualitative results in agreement with *ab initio* quantum chemistry computations concerning only the spin multiplicities of the ground and first excited states. The parameter ratios $0 < V/t < 10$ and $0 < X/t < 15$ were varied in steps of 0.25 and 0.01, respectively. This initial screening revealed that only a restricted area, indicated in Figure 3, has the expected physical behavior of the correct spin multiplicities of the ground and excited states. This marked area is robust, in the sense that it nearly remains unchanged when a different set of reference molecules was chosen, being constrained to $V/t = 10.0$ and $X/t = 6.1$ corresponding to the right upper corner. The remaining molecules, MX, TetraMB, 3,3'-DMBP, and Phe, are used as a test set of the general applicability of our model.

In performing a quantitative comparison, we have the basic problem of the choice of conversion from the arbitrary scale of our model to the units used in quantum chemistry. A simple

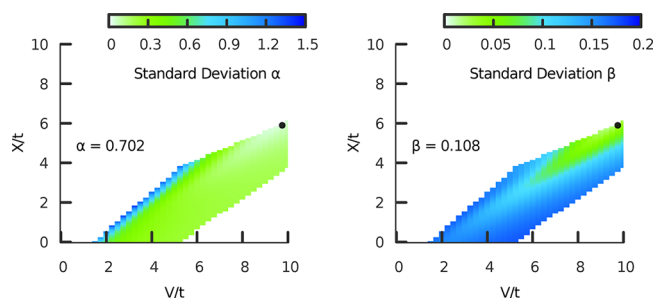


Figure 3. Parameter ratio values of the model Hamiltonian where we have the expected physical behavior. To convert the arbitrary units of our model to electron volt units, a linear function $f(x) = \alpha x + \beta$ was used. The figures show the standard deviation of the fitted gaps. The black circle at $V/t = 9.75$ and $X/t = 5.90$ is the point chosen to make the quantitative analysis.

linear function was fitted to convert the arbitrary scale of our model to reference gaps in electron volts; see Figure 4. We have

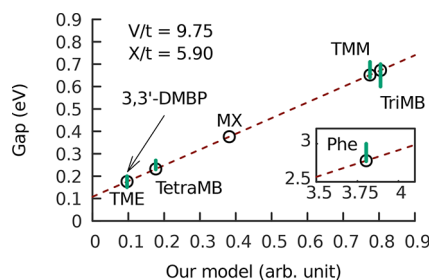


Figure 4. Vertical bars are visual guides for the range of gaps predicted using *ab initio* quantum chemistry methods found in the literature (see text); the results of our model are marked with circles. The dashed line is the fitted linear conversion $f(x) = 0.702x + 0.108$ from the arbitrary units of our model to electron volts (see also Figure 3). The gap predicted for TME and 3,3'-DMBP is superposed, but the vertical bar refers to the TME molecule. The absence of reference values for MX is because the variation of the theoretical predictions is large. The inset shows our result for the Phe molecule.

chosen these reference values using predictions from *ab initio* quantum chemistry computations reported in the literature; a more detailed discussion is made when we describe each molecule. Indeed, these reference energies are not essential, and slight variations of their values leave our results little changed, with the proviso that reasonable values for the gaps are used.

The linear function used is given by $f(x) = \alpha x + \beta$, where x is the energies of our model and $f(x)$ is the reference values. This screening of parameters shows a standard deviation for α and β that decreases when we increase the parameters X/t and V/t of our model, indicating that the converted energies values are improved with respect to the reference values. The coloring in Figure 3 indicates that this behavior is robust, such that both α and β monotonically reduce their deviations for the same parameters. Indeed, the reference energies used to fit $f(x)$ do not change the qualitative structure of Figure 3, provided that reasonable reference gaps are used. The black dot in Figure 3 marks the values $V/t = 9.75$ and $X/t = 5.90$ we shall use in our quantitative analysis. This point is exactly at the region of minimal deviation from the reference values for both parameters $\alpha = 0.702$ and $\beta = 0.108$ that have standard deviations 0.065 and 0.042, respectively. Hereafter, we shall focus on these parameters for our discussion of all molecules. This same set of values for the parameter ratios is used for all

molecules, which is an indication of the transferability and robustness of our model to different organic PAH radicals. The parameter ratio values $V/t = 9.75$ and $X/t = 5.90$ provide a linear fit that interpolates the reference range of spin gaps of all molecules considered in this Letter, and consequently our predictions cannot be improved without more accurate values of spin gaps or a bigger set of molecules.

The structure of eq 1 can be understood as follows. A general Hamiltonian in the absence of spin–orbit coupling and external fields is given by the sum of a noninteracting

$$\hat{H}_0 = \sum_{s_1 s_2} \sum_{\sigma} h_{s_1 s_2} \hat{c}_{s_1 \sigma}^{\dagger} \hat{c}_{s_2 \sigma} \quad (2)$$

part and an interaction

$$\hat{H}_{\text{int}} = \frac{1}{2} \sum_{s_1 s_2 s_3 s_4} \sum_{\sigma \sigma'} v_{s_1 s_2 s_3 s_4} \hat{c}_{s_1 \sigma}^{\dagger} \hat{c}_{s_2 \sigma}^{\dagger} \hat{c}_{s_3 \sigma'} \hat{c}_{s_4 \sigma'} \quad (3)$$

term.^{39,40}

If we consider two first neighbors sites i, j , then the standard direct term of \hat{H}_{int} is given by the choice $v_{s_1 s_2 s_3 s_4} = v_{ijij}$, such that eq 3 becomes $\sum_{(ij)} V_{ij} \hat{n}_i \hat{n}_j$, where $\hat{n}_k = \hat{n}_{k\uparrow} + \hat{n}_{k\downarrow}$. We obtain the standard *exchange coupling*⁴⁰ setting $v_{s_1 s_2 s_3 s_4} = v_{ijij}$,

$$\hat{V}_{\text{ex}} = \sum_{i \neq j} J_{ij} \left(\hat{S}_i \cdot \hat{S}_j + \frac{1}{4} \hat{n}_i \hat{n}_j \right), \quad \text{which also reads}$$

$$\hat{V}_{\text{ex}} = \sum_{i \neq j} J_{ij} \left(\hat{S}_i^X \hat{S}_j^X + \hat{S}_i^Y \hat{S}_j^Y + \frac{1}{2} \sum_{\sigma} \hat{n}_{i\sigma} \hat{n}_{j\sigma} \right) \quad (4)$$

We get the exchange coupling of a through-bond three-sites term \hat{X}_{ex} with the choice $v_{s_1 s_2 s_3 s_4} = v_{lkmk}$ such that

$$\hat{X}_{\text{ex}} = \sum_{l, (k), m} X_{lm} (\hat{c}_{l\uparrow}^{\dagger} \hat{S}_k^{-} \hat{c}_{m\downarrow} + \hat{c}_{l\downarrow}^{\dagger} \hat{S}_k^{+} \hat{c}_{m\uparrow} + \sum_{\sigma} \hat{c}_{l\sigma}^{\dagger} \hat{n}_{k\sigma} \hat{c}_{m\sigma}) \quad (5)$$

where $\hat{S}_k^{+} = \hat{c}_{k\uparrow}^{\dagger} \hat{c}_{k\downarrow}$, $\hat{S}_k^{-} = \hat{S}_k^{+}$, $\hat{S}_k^X = 1/2(\hat{S}_k^{+} + \hat{S}_k^{-})$, and $\hat{S}_k^Y = 1/2i(\hat{S}_k^{+} - \hat{S}_k^{-})$.

Observe that eqs 4 and 5 have essentially the same physical interpretation, namely, a nonclassical exchange coupling, where eq 4 is defined at first neighbors and eq 5 is defined at through-bond second neighbors. They also commute with the total spin operator \hat{S}^2 and \hat{S}^Z such that the total spin S and m_s are good quantum numbers.

Our model, eq 1, is an approximation given by the noninteracting spin sectors of the two and three sites exchange model Hamiltonian

$$\hat{H}_{\text{ex}} = \hat{H}_0 + \hat{V}_{\text{ex}} + \hat{X}_{\text{ex}} \quad (6)$$

We realize that the term $\sum_{(ij)} \sum_{\sigma} \hat{n}_{i\sigma} \hat{n}_{j\sigma}$ keeps like spins at next nearest neighbors to reduce the Coulomb repulsion. However, this two sites term can produce a charge density wave with alternating double occupied sites and holes that obviously does not describe the molecules studied in this Letter. To remedy, the three-site term $\sum_{(l, (k), m)} X(\hat{c}_{l\sigma}^{\dagger} \hat{n}_{k\sigma} \hat{c}_{m\sigma} + \hat{c}_{m\sigma}^{\dagger} \hat{n}_{k\sigma} \hat{c}_{l\sigma})$ avoids configurations with a string of like spins, which effectively favors spin alternating configurations. These spin alternating states were described by Ovchinnikov⁴¹ as a good starting point to the qualitative description of polyradicals.

We stress that \hat{V} and \hat{X} in eq 1 are complementary and must be thought of as a unit, because they describe essentially the same physics, as we have discussed above. We can see in Figure 3 that these operators must be used together to accurately describe the molecules studied in this Letter. Additionally, we can see in Table 1 that the values of $\langle 9.75\hat{V} + 5.90\hat{X} \rangle$ are much

Table 1. Electronic Structure and Energy of Each Term in the Hamiltonian for All Molecules, Computed at $V/t = 9.75$ and $X/t = 5.90^a$

state	$\langle S_z \rangle$	gap (eV)	$\langle -1.0\hat{t} \rangle$	$\langle 9.75\hat{V} \rangle$	$\langle 5.90\hat{X} \rangle$
TMM					
1	1.0		-2.442670	0.858377	-0.519428
2 (4)	0.0	0.65	-2.317030	2.502041	-1.514056
TME					
1 (4)	0.0		-4.743549	3.197755	-2.345680
5	1.0	0.18	-4.721297	4.306811	-3.380465
MX					
1	1.0		-7.834366	12.635298	-11.443846
2	0.0	0.38	-8.237676	14.120934	-12.144212
TriMB					
1	1.5		-7.765113	10.462697	-9.431934
2 (2)	0.5	0.67	-8.249382	13.392391	-11.073300
TetraMB					
1	0.0		-9.909312	13.129138	-11.322499
2 (2)	0.0		-9.893638	13.392710	-11.592160
4	0.0		-9.877964	13.656282	-11.861820
5	1.0	0.23	-9.927434	14.786886	-12.785534
3,3'-DMBP					
1	0.0		-15.989330	31.744048	-29.275513
2 (2)	0.0		-15.965735	31.881703	-29.428034
4	0.0		-15.942141	32.019359	-29.580556
5	1.0	0.18	-16.084022	32.833646	-30.172780
Phe					
1	0.5		-16.858519	39.470016	-36.504265
9 (2)	0.5	2.78	-14.299265	41.958610	-37.748587

^aThe ground state is labeled 1, and the excited states are labeled by increasing numbers with the associated degeneracy in brackets. The expected value of the z-component of spin $\langle S_z \rangle = 1/2 \langle \sum_k \hat{n}_{k\uparrow} - \hat{n}_{k\downarrow} \rangle$ is given as well as our estimate spin gap scaled as in Figure 4.

smaller than the values of the first neighbors hopping mechanism. It is an indication that the principal mechanism governing the physics of these molecules could be described by the delocalized π electrons, as expected by π -conjugate molecules.

We show in Figure 4 and Table 1 that the approximation of \hat{H}_{ex} by eq 1 gives very good quantitative results, despite not commuting with \hat{S}^2 . In fact, e.g., if we consider a triplet ground state, then we cannot distinguish the $m_s = 0$ triplet state from the singlet $m_s = 0$ excited states. However, we are interested in the spin gaps, and we show in Figure 4 that our simple approximation consistently predicts accurate spin gaps based only on the difference between the number of particles at each spin sector. Observe that wave functions that do not commute with \hat{S}^2 are routinely used by quantum chemistry methods to describe organic radicals,^{42–44} and eq 1 reproduces the “different orbitals for different spins” *ansatz* from a very simple many-body perspective.

It is also convenient to compare the results of our model with the Hubbard model, which showed good results in describing radical molecules.^{19,24} We have used the same methodology as before to fit the linear function $f_{\text{Hub}}(x) = \alpha_{\text{Hub}}x + \beta_{\text{Hub}}$ used to convert from the arbitrary units of the Hubbard model to electron volts. We study this model with the molecules TMM, TME, MX, TriMB, and TetraMB. The eigenstates of the two biggest molecules, Phe and 3,3'-DMBP, are beyond our computational limits, but the results obtained with the five smaller molecules are sufficient for our purposes.

We can see in Figure 5 that the smallest standard deviations (SD) for the Hubbard model are at approximately the

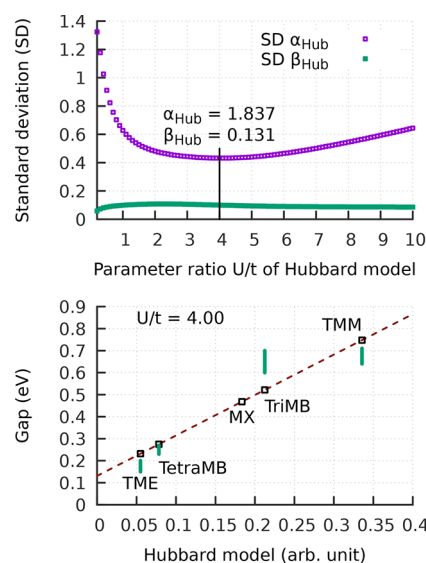


Figure 5. Results for the Hubbard model. Vertical bars are described in Figure 4. Top: standard deviations of parameters α_{Hub} and β_{Hub} of the fitted function $f_{\text{Hub}}(x) = \alpha_{\text{Hub}}x + \beta_{\text{Hub}}$ that convert from the arbitrary energy scale of the Hubbard model to electron volts. Bottom: results of $f_{\text{Hub}}(x)$ for five molecules represented by open squares.

parameter ratio $U/t = 4.0$. In agreement with our results, this parameter ratio was found also in the work of Vergés et al., when they studied the electronic structure of a phenalenyl derivative with the Hubbard and PPP models.²¹

The fitted parameters are given by $\alpha_{\text{Hub}} = 1.837$ and $\beta_{\text{Hub}} = 0.131$, with standard deviations 0.4 and 0.1, respectively. These SDs are 1 order of magnitude larger than we have obtained for our model. We expect that these larger SDs will affect the converted gaps.

In fact, the converted gaps, Figure 5, have unacceptable values far from reference values for four of the five molecules considered. Only TetraMB has a converted gap close to the one predicted by the literature.

Moreover, our model, eq 1, gives energy gaps very close to the *ab initio* values, which the Hubbard model does not exhibit for the parameters considered. In particular, for TriMB the Hubbard model completely mispredicts the gap, that is close to the MX molecule, whereas *ab initio* values are close to the TMM molecule.

Our simple methodology shows that it is difficult to fit the spin gaps of the molecules considered in this Letter with a unique set of parameters of the Hubbard model. In particular, our model has a transferable set of parameters, contrary to the more general Hubbard model.¹⁸

The first molecule analyzed is tetramethyleneethane (TME in Figure 2). It is the simplest *disjoint non-Kekulé* diradical with a singlet ground state that violates Hund's rule.⁴⁵ As a non-Kekulé molecule, TME cannot be represented by a valence bond structure where the electrons are delocalized into a network of conjugated double bonds. This work considers only a zero twist (dihedral) angle, where all atoms are in the same plane and the symmetry of the molecule corresponds to the D_{2h} point group. This is necessary to ensure the π conjugation and the homogeneous parameters of eq 1 that describe all molecules considered in this Letter.

Uncovering the nature of the electronic ground state of this diradical has proven to be both experimentally and theoretically challenging. Experimentally, the torsional angle is not zero, making it difficult to compare results from theory and experiment. Ion photoelectrons spectroscopy experiments⁴⁶ reported a singlet ground state, contradicting an early experiment based on electron paramagnetic resonance that reported a triplet ground state.⁴⁷

Using the cc-pVTZ basis set, the methods RHF, PBE0, and MP2 give a triplet ground state for this system, whereas CCSD(T) gives almost-degenerate singlet and triplet states.⁴⁸ A more accurate CASPT2 gives a singlet ground state that lies 0.20–0.15 eV below the triplet state depending on the active space and basis set used.⁴⁸ The NEVPT2 method also agrees with a singlet ground state at approximately 0.20 eV below the first triplet state.⁴⁹

Because the spin sectors of our model are noninteracting, the 6 π electrons were described using our Hamiltonian for the network corresponding to the TME molecule and 4, 3, and 2 participating particles with only 15, 20, and 15 Fock states, respectively. The singlet states are given by a combination of energies of the 3-particle sector, whereas the triplet state is given by a combination of the 4- and 2-particle sectors. Observe that even if we diagonalize eq 1 with all spin sectors at the same time (this is not necessary because our model conserves the total number of particles), the total number of basis states is only 50, in contrast with the $20 \cdot 20 + 15 \cdot 15 = 625$ basis states required by the Hubbard-like models to describe the same spin sectors.

After the diagonalization of eq 1, our model correctly describes a singlet ground state. The first triplet state is immediately above the ground state and is nondegenerate. The energies of each term in eq 1 are given in Table 1, where we observe that the noninteracting spin-sector term remains almost unchanged from the singlet to the triplet state, whereas the interacting spin-sector part is in fact responsible for the physical difference. Moreover, we predict a gap of 0.18 eV, that is within the range of *ab initio* calculation results; see Figure 4.

Trimethylenemethane (TMM) has four π electrons and a triplet ground state. In photoelectron spectrum experiments,⁵⁰ an energy gap of 0.79 eV was obtained that was attributed to the second excitation of this molecule. A theoretical prediction by Slipchenko and Krylov⁵¹ using a spin-flip coupled-cluster approach and recent papers based on the incremental full configuration interaction⁵² showed that the quantum chemistry basis set used has a strong influence on the obtained theoretical energy gaps as well as the methodology considered,⁵³ giving 0.64–0.71 eV for the first transition and 0.74–0.87 eV for the second excited state.⁵²

Our results for this molecule are a triplet ground state and a first excited state that is a tetradegenerate spin singlet; see Table 1. In contrast with the other molecule discussed above, the energies of the interacting terms of the Hamiltonian have a strong increasing variation by a factor of approximately three (see Table 1), whereas by comparison the noninteracting term reduces its value by a small amount. The energy gap obtained after scaling is 0.65 eV that also agrees with the result obtained from quantum chemistry estimations for the first gap.^{52,53}

1,3,5-Trimethylenebenzene (TriMB on Figure 2) is the basis of many high-spin polyradicals described in the literature and has a quartet ground state.^{3,54} With few experiments available, it was only recently studied using matrix isolation spectroscopy.⁵⁵ Theoretical computations based on CASSCF and CASPT2N

found an adiabatic doublet-quartet energy splitting of 0.6–0.7 eV^{56,57} that has been corroborated in a recent work based on the DDCI CAS(3,3) methodology.⁵⁸

We show in Table 1 that our model Hamiltonian correctly predicts a spin quartet ground state with a double-degenerate spin doublet state immediately above. It is known that these double-degenerate excited states are in fact a Jahn–Teller pair.^{54,55} The energy gap predicted is 0.67 eV, which is also within quantum chemistry values.

m-Xylylene (MX in Figure 2), also known as *meta*-benzoquinodimethane, has a triplet ground state. It is one of the most important diradicals, providing insights necessary to understand more complex systems.^{59,60}

An early characterization by Platz⁶¹ et al. using ESR gave evidence of a triplet ground state that was subsequently confirmed.⁶² The experimental value of the triplet-singlet gap is 0.41 ± 0.09 eV (9.6 ± 0.2 kcal/mol), and the order of the electronic states is correctly predicted from qualitative arguments as well as *ab initio* calculations and methods from density functional theory, but the energy gap is proving very challenging to estimate.^{2,60} CASPT2 computations⁶³ predicted an adiabatic gap of 0.5 eV, and the diverse many-body multireference methods provide no further approximation from that obtained by experiment,⁶⁰ despite the considerable variation in methodologies. This is the reason we have not drawn a corresponding vertical bar in Figure 4, where only our predicted gap is shown.

The ground state obtained using eq 1 is a spin triplet, with a spin singlet state immediately above it. This molecule has an intermediate-sized gap compared with others of this work, with a predicted value of 0.38 eV. Fortunately, this value is only 0.03 eV below that obtained from experiment and is in fact a better prediction than many quantum chemistry estimates.⁶⁰

TetraMB was the first non-Kekulé disjoint molecule found that violated Hund's rule.⁶⁴ We predict a gap of 0.23 eV, with a singlet ground state, followed by a double-degenerate singlet state, then another singlet state, and finally the first triplet state; see Table 1. The CASSCF and CASPT2N predictions of Hrovat and Borden⁶⁵ are an energy gap of 0.22–0.26 eV.⁶⁴ Hence, our result for the energy gap fully corroborates the theoretical quantum chemistry prediction as well as the singlet ground state obtained in experiments.⁶⁶

Based on an analogous chemical compound 4-*tert*-butylphenyl, which has additional aryls at the spin centers of the 3,3'-DMBP, the singlet–triplet gap of the diradical 3,3'-DMBP was predicted^{1,67} as ≈ 0.1 kcal/mol. However, our estimate is slightly larger, ≈ 4 kcal/mol, 0.18 eV (Table 1), being close to that obtained for TME. This discrepancy can be attributed to using a close chemical analogue to infer the gap of a specific molecule. This is clear from the comparison of TME, with the theoretical prediction of ≈ 4 kcal/mol, and the analogous 2,3-dimethylenecyclohexane-1,4-diyl (DMCHD), which was measured to have a gap of only ≈ 0.002 kcal/mol.¹ Hence, it seems that we cannot compare directly a closely related chemical compound to estimate the gap, and, compared with the theoretical prediction of TME and the other molecules considered in this study, our estimative seems to be reliable.

This large molecule has a Hubbard-like Hilbert space of approximately $20 \cdot 10^6$ states. With our model, we only need $3003 + 3432 + 3003 = 9438$ basis states for the 6-, 7-, and 8-particle sectors to describe the singlet and triplet states of this system.

Moreover, the condensed radical PAH phenalenyl (Phe in Figure 2) is a promising candidate as a new advanced material.^{68–70} Its *ab initio* studies are challenging due to its 13 π electrons. With our model, we can describe the doublet ground state of the radical of this molecule using two sectors, one with 7 (\uparrow) particles and the other with 6 (\downarrow) particles, and only 3432 basis states. In a recent work,⁶⁸ the CAS(7,7) MR-CISD gap prediction for the ground and first double degenerate excited state is 2.78–3.08 eV, depending on the basis set used. Considering the 7 electrons as the active space of *ab initio* computation, we compared the result of our model for the first degenerate excited state of the 7-particle sector, which gave a gap of 2.78 eV, a value that completely agrees with the literature result; see Table 1 and Figure 4.

Therefore, our model proves to be robust and has transferable parameters that are found to be widely applicable to diverse chemical situations. We studied radicals, diradicals, and triradicals with very challenging chemical configurations, as well as the polyaromatic radical phenalenyl, with very good results. A drawback of our method is that it relies on the qualitative description of charges and spin densities at each site (a problem similarly encountered for Hubbard-like models²⁴) and the inclusion of σ -electron interactions. Nevertheless, the inclusion of local terms and a small perturbative \uparrow and \downarrow spin interaction seems to solve these problems and will be treated in a forthcoming paper. Moreover, a new study must include a mechanism to describe substituted (hetero)atoms and its consequences on the electronic structure⁷¹ of these systems.

To conclude, we constructed a simple model Hamiltonian with two free parameters and a new *through-bond* hopping mechanism assuming the hypotheses of noninteracting \uparrow and \downarrow sectors. We showed that the best values for these two free parameter ratios of our model are robustly given by $V/t = 9.75$ and $X/t = 5.90$, when we used a simple linear function $f(x) = \alpha x + \beta$ to convert the energy gap values in arbitrary units of our model to electron volts provided by *ab initio* calculation methods in the literature, with fitted parameters of $\alpha = 0.702$ and $\beta = 0.108$. The converted predicted gaps of 0.65 eV for TMM, 0.18 eV for TME, 0.38 eV for MX, 0.67 for TriMB, 0.23 eV for TetraMB, 0.18 eV for 3,3'-DMBP, and 2.78 eV for Phe by our model are in agreement with those given in the literature for all molecules considered. Moreover, our model represents a huge computational savings compared with Hubbard-like models, which enables it to be applied to study large molecular systems.

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Notes

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