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A distance-dependent parameterization of the extended Hubbard model for conjugated and aromatic hydrocarbons derived from stretched ethene

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The Hubbard model, which is widely used in physics but is mostly unfamiliar to chemists, provides an attractive yet simple model for chemistry beyond the self consistent field molecular orbital approximation. The Hubbard model adds an effective electron-electron repulsion when two electrons occupy the same atomic orbital to the familiar Hückel Hamiltonian. Thus it breaks the degeneracy between excited singlet and triplet states and allows an explicit treatment of electron correlation. We show how to evaluate the parameters of the model from high-level *ab initio* calculations on two-atom fragments and then to transfer the parameters to large molecules and polymers where accurate *ab initio* calculations are difficult or impossible. The recently developed MS-RASPT2 method is used to generate accurate potential energy curves for ethene as a function of carbon-carbon bond length, which are used to parameterize the model for conjugated hydrocarbons. Test applications to several conjugated/aromatic molecules show that even though the model is very simple, it is capable of reasonably accurate predictions for bond lengths, and predicts molecular excitation energies in reasonable agreement with those from the MS-RASPT2 method. © 2011 American Institute of Physics. [doi:10.1063/1.3659294]

I. INTRODUCTION

As Dirac once remarked, with the advent of quantum mechanics most of chemistry can in principle be considered a solved problem. But in practice, though we know how to write down the Schrödinger equation for any problem of chemical interest, it is too complicated to solve exactly for any but the simplest systems. There are then two routes open to theoretical chemists. One is to seek an approximate solution to the exact Schrödinger equation. Undeniably, substantial progress is being made along this route through the development of new methods coupled with increases in computing power. But there are, and probably always will be, interesting chemical problems beyond the reach of accurate approximate methods. Thus there continues to be a role for the other route to theoretical understanding, the construction of model chemistries. Additionally, models furnish the mental furniture of the chemist's mind: concepts such as molecular orbitals, valence bonds, and the like come from models of how chemistry works, not from numerical solutions of the Schrödinger equation. In the model chemistry approach, one attempts to substitute an exact (or at least highly accurate) solution to an approximate problem for the approximate solution of the exact problem. The essence of a chemical model is that it focuses on what are believed to be the most important physical effects in the problem at hand. Contributions of weaker interactions not explicitly included in the model are accounted for through the use of renormalized parameters in the model

Hamiltonian. These renormalization effects may be evaluated directly from *ab initio* calculations (see, for example, the series of papers by Freed and co-workers¹ on π -electron models or recent work² on the Pariser-Parr-Pople (PPP) model), or the model parameters may simply be adjusted semiempirically to give agreement with experimental data.

Chemists are generally familiar with the Hückel model which represents one of the simplest attempts to model the most important effects of chemical bonding. It has a pedigree which extends back to the earliest days of quantum mechanics,³ but in various guises continues to play a central role in chemistry and physics to this day. Originally conceived as a model for the mobile π electrons in conjugated hydrocarbons, it was extended to all valence electrons by Hoffmann,⁴ and under the name tight binding model, an orthogonalized version continues to be extensively used in the study of crystals⁵ and polymers.⁶ The Hückel model retains just two types of terms: a site energy α_i which represents the attraction of an electron in atomic orbital i to its atom, and a bonding parameter β_{ij} which measures the strength of a covalent bond between atomic orbital i and atomic orbital j . Even in its most primitive form, with β_{ij} taken as constant for all chemically identical bonded pairs of atoms, it often provides a qualitatively correct description of the molecular orbital structure of a molecule which has been extremely fruitful, leading to such important developments as the Woodward-Hoffmann rules⁷ and Fukui's frontier orbital theory.⁸

While the Hückel model captures the essence of chemical bonding, it suffers from at least two serious limitations as a conceptual chemical model. To begin with, it predicts that singlet and triplet transitions to excited states that share the

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same initial and final molecular orbitals will be degenerate. Experimentally, triplet states are often found a full electron volt or more lower than their corresponding singlets, so the Hückel model fails to provide even a correct qualitative picture for electronic excited states. Furthermore, since there is no explicit electron-electron interaction in the Hückel model, it provides no understanding of the role of electron correlation, which can change even the qualitative description of phenomena such as bond length alternation in conjugated polymers. These limitations can largely be overcome through use of the Hubbard model. Though largely unknown in the chemical community, in its simplest form it differs from the Hückel model only through the introduction of one additional type of interaction, an effective repulsion U_i^{eff} between two electrons, which occupy the same atomic orbital i .

The Hubbard model was introduced in the 1960s by Hubbard⁹ as the simplest model able to track the transition from independent electron (metallic) to correlated electron (localized atomic) behavior. It continues to play a prominent role in the physics literature as a model for strongly interacting fermions since, despite being one of the simplest many-body Hamiltonians, it exhibits a remarkably complex phase-space structure.¹⁰ In particular, it has been the model of choice for understanding high-temperature superconductivity¹¹ and is also widely employed in studies of conducting polymers¹² among many other applications. More recently, it has been combined with density functional theory (the so-called DFT+U method¹³) to study (anti-)ferromagnetic solids¹⁴ and molecular magnetism.¹⁵

The Hubbard model was first introduced into chemistry by Soos and co-workers¹⁶ as a model for donor/acceptor compounds. For such applications, it is reasonable to regard the formation of a chemical bond as a small perturbation compared to the separation between atomic energy states (large $|U_i^{\text{eff}}/t|$, see below), and most early uses of the model^{17,18} in chemistry proceed on this assumption. However, when applied to the π electrons in conjugated/aromatic hydrocarbons a much smaller ratio of $|U_i^{\text{eff}}/t|$ (see below) is appropriate, and a large U_i^{eff} perturbative solution is no longer completely adequate. Characteristics of the exact solution of the model were investigated by Klein and Trinajstić,¹⁹ Lee,²⁰ Schmalz,²¹ and in the context of high-spin hydrocarbons by Klein and co-workers.²² A wealth of information on the model and its applications by a variety of authors can be found in several books.^{23–25}

The Hubbard model can serve as an important conceptual tool in chemistry, as perhaps first emphasized by Matsen²⁶ and explained in a qualitative way in a nice series of papers by Fox and Matsen,²⁷ because it links two classic approaches to chemical bonding. It can be shown using perturbation theory,²⁸ or better using cluster expansion techniques,^{29,30} that in the large U_i^{eff} limit the spectrum of the Hubbard Hamiltonian can be mapped onto that of a Heisenberg spin Hamiltonian. At lowest order, the Heisenberg Hamiltonian is formally equivalent to the nearest-neighbor valence bond model as first derived by Pauling,³¹ starting from the Heitler-London approach to the hydrogen molecule. On the other hand, as developed in this paper, the Hubbard model represents an extension of the Hückel model, which goes to the Hückel limit

as the U_i^{eff} parameters become small. Thus the Hubbard model goes continuously from the molecular orbital to the valence bond limit as the strength of the effective electron-electron interaction is varied,²¹ and can be used to link and compare these two fundamental pictures of chemical bonding.

In Sec. II, we introduce the mathematical form of the models we consider and discuss the determination of the model parameters from accurate potential energy curves for a two-site fragment. We illustrate the procedure for the Hubbard model of the π electrons in conjugated hydrocarbons though the approach should be applicable to other uses of the models as well. Section III describes the *ab initio* methods used to produce accurate potential energy curves for ethene as a function of the carbon-carbon distance, which provide the inputs to the model. Section IV discusses the mathematical forms used to fit the model parameters to the *ab initio* data, and gives the numerical results for the parameters. In Sec. V, we validate the model by using it to predict both the ground state geometry and the low-lying excitation spectrum of several other conjugated molecules not used in the parameterization, and obtain agreement with results from much more expensive *ab initio* computations. Finally in Sec. VI, we summarize our main conclusions.

II. TWO-SITE PARAMETERIZATION OF THE EXTENDED HUBBARD MODEL

In second quantized form the simple Hubbard model Hamiltonian becomes

$$H^{\text{Hub}} = \sum_i t_{ii} E_{ii} + \sum_{ij} t_{ij} E_{ij} + \sum_i U_i^{\text{eff}} n_{i\alpha} n_{i\beta} + V_c, \quad (1)$$

where $E_{ij} = \sum_{\sigma=\alpha,\beta} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma})$, $n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$ is the number operator for electrons of spin σ on site i , and $a_{i\sigma}^\dagger$ ($a_{i\sigma}$) are creation (annihilation) operators for an electron of spin σ in orbital i . With the double sum limited to nearest-neighbor sites and the identification $t_{ii} = \alpha_i$, $t_{ij} = \beta_{ij}$, the first two terms of Eq. (1) are identical to the Hückel model Hamiltonian. As is well known, orbital eigenvalues for the Hückel Hamiltonian can be found by diagonalizing the t_{ij} matrix and, since the electrons do not interact, the total energy can be found as a sum of eigenvalues. The third term of Eq. (1) adds an effective repulsion U_i^{eff} for two electrons which occupy the same atomic orbital, leading to true many-electron eigenstates. Finally, we have added a potential V_c to account for the effects of the nuclei and core electrons not considered explicitly in the model. V_c may depend on the positions of the nuclei but is assumed to be independent of the distribution of electrons over the active orbitals of the model.

For systems in which all of the atoms are chemically identical (the only situation considered in this work), the first term of Eq. (1) simply adds a constant to the energy of all states at all geometries. Formally, it may be set to zero and incorporated into V_c , and we assume that this has been done in all of the following discussion. For systems containing heteroatoms, the α_i terms, which represent the electronegativities of the atoms, must be explicitly retained but we do not discuss them further. If the U_i^{eff} are also taken as identical for all sites, the Hartree-Fock self consistent field (HF-SCF) solution of the Hubbard model is trivial. The molecular orbitals are

unchanged from the Hückel model while the last term just adds a constant, $n_s U^{\text{eff}}/4$, to the ground state energy where n_s is the number of active sites. Already at the SCF-SCI (single configuration interaction) level, the degenerate singlet and triplet excitations, which for a two-electron system at the Hückel level are both equal to $2|\beta|$, are altered to $E_S = 2|\beta| + U/2$ and $E_T = 2|\beta| - U/2$, respectively. However, to take full advantage of the Hubbard model, including its ability to describe electron correlation, we are interested in the exact solution of the model, which can be found, among other ways, by a full configuration interaction treatment including all excited determinants generated from the one-orbital-per-site one-electron basis.

For a system consisting of just two identical sites and two electrons, the exact eigenenergies of the Hubbard Hamiltonian may be found analytically. The three lowest energy states are

$$E_G(R) = -\{[(U^{\text{eff}})^2 + 16t^2]^{1/2} - U^{\text{eff}}\}/2 + V_c(R), \quad (2a)$$

$$E_T(R) = V_c(R), \quad (2b)$$

$$E_S(R) = U^{\text{eff}} + V_c(R), \quad (2c)$$

where R is the internuclear distance, E_G is the ground state, and E_T and E_S are the lowest excited triplet and singlet states, and we have dropped the subscripts on t and U^{eff} since there is just one bond and one kind of site. Some years ago, Malrieu and co-workers³² noted that these relations could be used to determine the model quantities t , U^{eff} , and V_c as a function of distance from accurate potential energy curves for these three states. $V_c(R)$ and U^{eff} are given directly by $E_T(R)$ and $E_S(R) - E_T(R)$, respectively, and t can then be found from $E_T(R) - E_G(R)$. They illustrated the procedure for one particular application of the Hubbard model, the description of the π electrons in conjugated hydrocarbons. For that application the two-site two-electron system is an ethene molecule where each carbon atom is presumed to form three localized sigma bonds, whose energy is incorporated into V_c , and to possess one active $2p_\pi$ -type atomic orbital perpendicular to the molecular plane, which is treated by the Hubbard model.

The results of this treatment³² yielded the expected decrease of the t parameter with increasing bond length, and values of t in reasonable agreement with those usually chosen in semiempirical applications of the model. But the U parameter was somewhat smaller than the usual semiempirical values and also showed observable distance dependence. Superficially, this seems difficult to explain since U is apparently a one-center electron repulsion term. The distance dependence also complicates transferability of the model parameters to other systems where a carbon atom may have several neighbors at different distances. Here we propose to use a slight modification of the Hubbard model, which makes the situation clear. Rather than limiting electron-electron interactions to one center we add to the model an electron repulsion term V_{ij} for two electrons on nearest-neighbor sites. The Hamiltonian of Eq. (1) is modified to

$$H^{\text{ExtHub}} = \sum_i t_{ii} E_{ii} + \sum_{ij} t_{ij} E_{ij} + \sum_i U_i n_{i\alpha} n_{i\beta} + 1/2 \sum_{ij} V_{ij} (Z_i - n_i) (Z_j - n_j) + V_c, \quad (3)$$

with the double sums again limited to nearest-neighbors and Z_i , the core charges of the atoms. In the literature, this form of the model is sometimes referred to as the extended Hubbard model, but it is often simply called the Hubbard model.

The extended Hubbard model is also analytically solvable for a two-site two-electron system, giving in place of Eqs. (2), the expressions

$$E_G(R) = -\{[(U - V)^2 + 16t^2]^{1/2} - (U - V)\}/2 + V_c(R), \quad (4a)$$

$$E_T(R) = V_c(R), \quad (4b)$$

$$E_S(R) = (U - V) + V_c(R), \quad (4c)$$

in which we have again dropped the unneeded subscripts. Equations (4) are seen to be identical to Eqs. (2) except for the replacement everywhere of U^{eff} by $U - V$. This form of the model makes it clear that the proper interpretation of U^{eff} in the simple Hubbard model is not the repulsion energy of two electrons in the same atomic orbital, but rather the *excess* repulsion associated with the transfer of an electron from a singly occupied orbital to an adjacent site to form a doubly occupied orbital and an empty orbital.³³ The distance dependence of U^{eff} comes largely from V , which depends on the distance between the orbitals, while U can be taken as essentially an atomic property. The model can easily be applied to systems with differing bond lengths since each pair of atoms can be described by a distance-dependent V_{ij} . This analysis also makes it clear why U^{eff} in the simple Hubbard model must be assigned a value much smaller than a one-center Coulomb repulsion integral for the model to give realistic results.

In principle, all parameters of the extended Hubbard model can be extracted from the potential curves of the two-site system since U is given by the large- R limit of U^{eff} where V falls to zero, and $V(R)$ can then be found from the distance dependence of U^{eff} . But in practice, the simple three-state picture of the low energy spectrum breaks down long before V becomes small because the excited singlet dissociates to an excited state of the separated fragments, leading to crossings and avoided crossings with other high energy states. Thus, we have to depart slightly from our goal of parameterizing the model solely from the *ab initio* results. For applications to conjugated hydrocarbons, we have arbitrarily fixed U in the extended model at 5.0 eV and then extracted V as a function of R from the $E_S(R) - E_T(R)$ excited state potential curves. Fortunately, the performance of the model depends only weakly on the exact value chosen for U . In Sec. III, we describe the computation of the potential curves for stretched ethene which are used to obtain Hubbard parameters for hydrocarbons. However, we emphasize that Hubbard parameters for any application of the model could be obtained in this fashion as long as potential curves for a two-site fragment of whatever type of system is being modeled and are available.

III. COMPUTATION OF POTENTIAL ENERGY CURVES FOR STRETCHED ETHENE

The electronic spectrum of ethene is dominated by the intense and broad band $N-V$ $\pi \rightarrow \pi^*$ valence electronic

transition with the superimposed Rydberg excitation $\pi \rightarrow 3s$.³⁴ The maximum of this band occurs at 7.66 eV but does not correspond to the vertical transition.³⁵ Strong valence-Rydberg mixing is not common for the lower excited states of medium-sized systems but it frequently occurs for small molecules where the lowest valence electronic states fall in the same region as the onset of the first Rydberg series. Some accurate theoretical studies have led to a final estimate of about 8.0 eV for the vertical transition of the ethene V state.^{36–38} At the ground state geometry, the V state has a mixed valence-Rydberg character which strongly depends on the level of theory used to describe it.

The quantum-chemical multi-configurational methodology employed in the present work to compute the potential energy curves for ethene (D_{2h}) is the recently tested RASSCF/RASPT2 method.^{39,40} All multi-state RASPT2 calculations (hereafter MS-RASPT2) were performed with the MOLCAS-7 program.^{41–43} The large atomic natural orbital ANO-L basis set⁴⁴ contracted to $[6s5p4d2f]$ for carbon atoms and $[3s2p1d]$ for hydrogen atoms was employed. In order to describe the Rydberg states, a set of even-tempered $1s1p1d$ functions was added on carbon atoms. In the current MOLCAS code, the default IPEA shift⁴⁵ of 0.25 a.u. and Cholesky decomposition⁴¹ of the two-electron integrals set to the default threshold of 10^{-4} a.u. were used. The experimental gas-phase equilibrium geometry of the molecule was employed.⁴⁶

The MS-RASPT2 potential energy curves of the three lowest valence excited states of ethene were computed as function of the carbon-carbon distance keeping the carbon-hydrogen bond lengths and bond angles fixed at the experimental data. The total energies are collected in Table I and the corresponding potential energy curves are displayed graphically in Figure 1. The active space used is comprised by four σ orbitals placed in RAS1, six orbitals in RAS2 (the π and its correlating π^* orbital plus two more of b_{2g} symmetry, one of them being the $3d_{xz}$ Rydberg orbital, and the two (σ , σ^*) molecular orbitals (MOs) of the carbon-carbon bond), and a total of eight orbitals in RAS3 (corresponding to the antibonding counterparts of the four σ MOs plus extra correlating orbitals in order to minimize the appearance of intruder states resulting from the use of an extended basis set.).^{47,48} Twelve electrons are active and up to two holes/particles are allowed in RAS1/RAS3. Using the notation from a recent benchmark calibration,⁴⁰ the level of calculation of the present work is labelled as MS-RASPT2(12,2,2;4,6,8)(SD), where within parentheses the number of active electrons (12), number of holes (2) and particles (2), as well as the number of active orbitals 4, 6, and 8 for RAS1, RAS2, and RAS3, respectively, are specified.

The valence-Rydberg mixing problem involving the 1^1B_{1u} (V) and 2^1B_{1u} ($3d\pi$) states was treated by previous studies at the ground-state equilibrium geometry.^{49,50} In the present contribution, this problem is solved with a low cost of computation and without loss of accuracy. Thus, at the gas-phase equilibrium geometry,⁴⁶ 1^1B_{1u} (V) and 2^1B_{1u} ($3d\pi$) are computed vertically at 8.03 and 9.33 eV, respectively, in agreement with the best available results.^{36–38,49–51} The chosen strategy is based on the study of free base porphyrin,⁴⁰

TABLE I. Lowest potential energy curves of ethene (in a.u.) as a function of the carbon-carbon distance (in Angstrom). Carbon-hydrogen bond lengths and bond angles held fixed at their experimental values.⁴⁶ Level of calculation: RASSCF/MS-RASPT2(12,2,2;4,6,8)(SD) with IPEA = 0.25 a.u. and ANO-L $C[6s5p4d2f]/H[3s2p1d]$ basis set plus a set of even-tempered $1s1p1d$ functions on C atoms (see text).

Bond length	$E_G (1^1A_{1g})^a$	$E_S (1^1B_{1u})^b$	$E_T (1^3B_{1u})^a$	$E_{Ryd} (2^1B_{1u})^b$
1.320	-78.42577737	-78.12582852	-78.25564168	-78.07939698
1.330	-78.42607949	-78.12873705	-78.25957612	-78.08151255
1.331	-78.42609838	-78.12901005	-78.25995449	-78.08170362
1.332	-78.42611504	-78.12928390	-78.26032910	-78.08189706
1.333	-78.42612944	-78.12955827	-78.26070072	-78.08208673
1.334	-78.42614160	-78.12982816	-78.26107203	-78.08227557
1.335	-78.42615106	-78.13009667	-78.26144846	-78.08246226
1.336	-78.42615883	-78.13036351	-78.26181194	-78.08264667
1.337	-78.42616441	-78.13062884	-78.26217273	-78.08282904
1.338	-78.42616781	-78.13089324	-78.26253050	-78.08300975
1.339	-78.42617493	-78.13114542	-78.26287103	-78.08319364
1.340	-78.42616859	-78.13141650	-78.26323576	-78.08336350
1.360	-78.42572143	-78.13610363	-78.26973290	-78.08634672
1.380	-78.42453137	-78.13988689	-78.27523977	-78.08844161
1.400	-78.42267946	-78.14298161	-78.27985405	-78.08973344
1.410	-78.42153020	-78.14429051	-78.28184628	-78.09009860
1.420	-78.42024175	-78.14543133	-78.28364598	-78.09029556
1.430	-78.41882430	-78.14642244	-78.28526125	-78.09033005
1.440	-78.41728546	-78.14729292	-78.28670042	-78.09017369
1.460	-78.41387314	-78.14860915	-78.28908970	-78.08950266
1.480	-78.41006120	-78.14944533	-78.29083070	-78.08830144
1.490	-78.40802122	-78.14969863	-78.29148150	-78.08752510
1.495	-78.40697022	-78.14978665	-78.29175760	-78.08709519
1.500	-78.40589991	-78.14984989	-78.29199323	-78.08663793
1.505	-78.40481074	-78.14988896	-78.29219379	-78.08615494
1.510	-78.40370334	-78.14990468	-78.29236082	-78.08564651
1.511	-78.40347974	-78.14990509	-78.29239035	-78.08554182
1.512	-78.40325543	-78.14990460	-78.29241861	-78.08543616
1.513	-78.40303045	-78.14990321	-78.29243991	-78.08532951
1.514	-78.40280477	-78.14990093	-78.29247360	-78.08522188
1.515	-78.40257840	-78.14989777	-78.29249824	-78.08511329
1.520	-78.40143653	-78.14987036	-78.29259492	-78.08455657
1.530	-78.39910446	-78.14975023	-78.29272257	-78.08337227
1.531	-78.39886785	-78.14973375	-78.29272858	-78.08324886
1.532	-78.39863064	-78.14971654	-78.29273350	-78.08312448
1.533	-78.39839283	-78.14969848	-78.29273732	-78.08299931
1.534	-78.39815443	-78.14967965	-78.29274007	-78.08287325
1.535	-78.39791544	-78.14966004	-78.29274174	-78.08274633
1.536	-78.39767588	-78.14963966	-78.29274234	-78.08261854
1.537	-78.39743573	-78.14961852	-78.29274188	-78.08248987
1.538	-78.39719502	-78.14959662	-78.29274037	-78.08236035
1.539	-78.39695373	-78.14957397	-78.29273780	-78.08222998
1.600	-78.38133975	-78.14707055	-78.29079773	-78.07275563
1.700	-78.35340295	-78.13934063	-78.28184795	-78.05199995
1.900	-78.29715857	-78.11401145	-78.25310077	-78.00623821
2.100	-78.24840557	-78.08676065	-78.22132094	-77.96261699
2.300	-78.21054154	-78.06211363	-78.19337809	-77.92559587
2.500	-78.18365611	-78.04155697	-78.17210838	-77.89625527
2.700	-78.16617461	-78.02535432	-78.15804275	-77.87443906
2.900	-78.15557142	-78.01309791	-78.14991563	-77.85971989

^aRASPT2(12,2,2;4,6,8)(SD) single root calculations.

^bMS-RASPT2(12,2,2;4,6,8)(SD) of two 1^1B_{1u} roots calculations.

FIG. 1. Potential energy curves of ethene for the three lowest valence states and the lowest Rydberg state: 1^1A_{1g} (N) (in blue squares), 1^3B_{1u} (T) (in red diamonds), 1^1B_{1u} (V) (in green triangles), and 2^1B_{1u} ($3d\pi$) (in orange circles) performed with RASSCF/MS-RASPT2(12,2,2;4,6,8)(SD) using ANO-L $6s5p4d2f/3s2p1d$ basis set and a set of even-tempered $1s1p1d$ functions on C atoms and IPEA = 0.25 a.u.

where the most relevant orbitals are placed in RAS2 and up to doubly excited configurations are allowed in RAS1 and RAS3 subspaces. As the extended RASSCF method includes only a small fraction of the correlation energy, the ionic V state (in the valence bond sense) is placed higher in energy where it may come close to the singlet Rydberg state of the same symmetry, leading to erratic valence-Rydberg mixing as it occurs at the CASSCF level.⁵⁰ Normally, as discussed in detail elsewhere,⁴⁰ when both π and σ correlations are included in the CI reference space at the RASPT2(SD) level, the multi-state procedure is required in order to treat properly the valence-Rydberg mixing (see orbital extensions in the supplementary material⁷⁴).

The potential energies in Table I are not true geometry optimizations, since the C–H bond lengths and bond angles were held fixed at their experimental values. Both experimental analysis⁵² using the semitheoretical method and theoretical analysis⁵³ with extrapolation to the basis set and full configuration interaction limits yield $R_e = 1.3305$ Å for the carbon-carbon bond length in ethene, while a conventional MP2/cc-pVTZ calculation (2nd order Moeller-Plesset perturbation theory with a correlation-consistent polarized valence triple zeta basis)^{54,55} gives $R_e = 1.3320$ Å. By contrast, a fit of a quadratic to the ground state minimum calculated here gives a minimum energy of $E = -78.42617494$ a.u. at 1.3390 Å. Investigation shows that the position of the minimum changes only slightly when the locations of the hydrogen atoms are optimized, so the discrepancy is apparently due to the description of the carbon-carbon bond. The RASPT2 method is expected to give bond lengths, which converge (slowly) to the correct value from above.

The calculated vertical excitation energies at 1.339 Å of 4.44 eV to the triplet and 8.03 eV to the excited singlet state are in excellent agreement with the available experimental and theoretical data. Experimentally, the triplet is found

TABLE II. *Ab initio* derived Hubbard parameters (in eV).^a

R (Å)	t	U^{eff}	V^b	V_c^c
1.320	−3.073557	3.532390	1.467610	1.009559
1.330	−3.027331	3.560306	1.439694	0.902497
1.335	−3.004387	3.574258	1.425742	0.851548
1.339	−2.986420	3.584430	1.415570	0.812838
1.340	−2.981622	3.586978	1.413022	0.802914
1.360	−2.891871	3.636231	1.363769	0.626118
1.380	−2.804717	3.683133	1.316867	0.476268
1.400	−2.719363	3.724482	1.275518	0.350708
1.420	−2.636059	3.761006	1.238994	0.247524
1.440	−2.554715	3.793465	1.206535	0.164409
1.460	−2.475355	3.822664	1.177336	0.099393
1.480	−2.398358	3.847285	1.152715	0.052018
1.500	−2.323576	3.867911	1.132089	0.020384
1.520	−2.251352	3.883726	1.116274	0.004011
1.536	−2.195000	3.894015	1.105985	0.000000

^a27.211338386 eV = 1 a.u.

^bAssuming $U = 5.0$ eV.

^c $V_c(R) = E_T(R) - E_T(R_{\text{eq}})$.

at 4.36 eV from electron impact⁵⁶ and 4.60 eV from optical studies,⁵⁷ while a variety of accurate calculations fall near 4.50 eV.⁵⁸ As mentioned above, the position of the excited valence singlet is not well determined experimentally because of the strong mixing with the nearby Rydberg levels, but the value found here is in excellent agreement with other theoretical calculations.^{36–38}

IV. FITTING OF THE MODEL PARAMETERS

The values of the t , V , and V_c parameters of the extended Hubbard model, and of U^{eff} for the simple Hubbard model, derived from the computed energies in Table I, are shown in Table II. The t values found here are close to those found previously,³² but the U^{eff} values are somewhat larger. For transferability to other systems these must be fit to a reasonably simple yet accurate mathematical functional form.

A. The t parameter

Most semiempirical applications of the Hubbard model take t to be a linear function of bond length. While this is certainly valid over small enough regions, over the full range of bond lengths encountered in conjugated molecules, say 1.32 – 1.48 Å, there is a noticeable curvature, as shown in Figure 2. Accordingly, we have represented t initially as a power series expansion around the ground state minimum at 1.339 Å. In order to ensure that the model accurately reproduces the ground state minimum, we have held the constant term fixed at the *ab initio* t value for 1.339 Å, and determined the coefficients of higher powers in the expansion by a least squares fit to the t values at points spaced every 0.02 Å from 1.32 Å to 1.48 Å. The expansion was then reexpressed with respect to a more convenient reference point, $R_0 = 1.40$ Å, which is the approximate length of aromatic carbon-carbon bonds as well as the approximate average bond length in linear conjugated polyenes. The final formula, for t in eV and the bond length R

FIG. 2. The *ab initio* derived values of the Hubbard t parameter as a function of carbon-carbon bond length (in blue diamonds) and the *ab initio* derived values of the Hubbard U^{eff} parameter as a function of carbon-carbon bond length (in red squares).

in Å, is

$$t(R) = -2.719288 + 4.22019(R - 1.4) - 2.6072(R - 1.4)^2. \quad (5)$$

Equation (5) gives t values which differ from the *ab initio* values by no more than 0.0004 eV over the range of the fit.

There is another tradition for representing the bond length dependence of t , which stems from Hückel theory. In, for example, Hoffmann's Extended Hückel Theory⁴ β (i.e., t) for a bond is taken to be proportional to the overlap between atomic orbitals on the two bonded atoms. This incorporates the fundamental explanation of chemical bonding as resulting from overlap of atomic orbitals while automatically assuring the correct exponential decay of t to zero at large separation. In applications to planar hydrocarbons, the overlap is usually computed between Slater $2p_z$ atomic orbitals using the standard Slater exponent for carbon of 1.625 bohr^{-1} . We investigated this prescription for t but found that it does not accurately track the *ab initio* t values. However, quite a good fit of this form can be found by treating the orbital exponent as a variable parameter. $t(R)$ can be written as

$$t(R) = A \times S(R) = t_0 \times S(R)/S(R_0), \quad (6)$$

where $S(R)$, the overlap between $2p_z$ atomic orbitals, is given by

$$S(R) = e^{-z}[1 + z + 2z^2/5 + z^3/15], \quad z = \zeta R. \quad (7)$$

We find the best fit for $A = -9.858271 \text{ eV}$ and an orbital exponent of $\zeta = 1.540 \text{ bohr}^{-1}$, corresponding to $t_0 = -2.719577 \text{ eV}$ at the reference point $R_0 = 1.40 \text{ Å}$. The results from Eqs. (5) and (6) are compared in Table III and are remarkably similar. Since values of t are needed only over the range of bond lengths encountered in conjugated hydrocarbons, we have used the slightly more accurate expansion of Eq. (5) in the remainder of this paper.

The need for a more diffuse $2p_z$ orbital to fit t may not be too surprising in light of the observation⁵⁹ that in *ab initio* calculations on double bonds using double zeta quality basis

TABLE III. Comparison of fits of the t parameter. t values in eV and errors in meV.

R (Å)	t^{exact}	t (Eq. (5))	t error (Eq. (5))	t (Eq. (6))	t error (Eq. (6))
1.32	-3.073557	-3.073589	-0.032	-3.072902	+0.655
1.34	-2.981622	-2.981885	-0.263	-2.981562	+0.060
1.36	-2.891871	-2.892267	-0.396	-2.892232	-0.361
1.38	-2.804717	-2.804735	-0.018	-2.804907	-0.190
1.40	-2.719363	-2.719288	+0.075	-2.719577	-0.214
1.42	-2.636059	-2.635927	+0.132	-2.636230	-0.171
1.44	-2.554715	-2.554652	+0.063	-2.554855	-0.140
1.46	-2.475355	-2.475463	-0.108	-2.475435	-0.080
1.48	-2.398358	-2.398359	-0.001	-2.397952	+0.406

functions, the more compact function has greater weight in the σ bond orbital and the more diffuse function has greater weight in the π bond orbital. This presumably expresses the fact that the π electrons, being displaced from the internuclear axis, are on average farther away from the nuclei.

B. The V parameter

According to our interpretation of the extended Hubbard model, the distance dependence of V should be related to that of U^{eff} , shown graphically in Figure 2, by

$$V(R) = U - U^{\text{eff}}(R). \quad (8)$$

In semiempirical applications of the extended Hubbard model, V is often assumed to be related to the constant value U by either the Mataga-Nishimoto formula,⁶⁰

$$V^{\text{MN}}(R) = 1/(1/U + R), \quad (9)$$

or the Ohno formula,⁶¹

$$V^{\text{OHNO}}(R) = 1/(1/U^2 + R^2)^{1/2}. \quad (10)$$

In Eqs. (9) and (10), all quantities are in atomic units. These formulas are simply interpolation formulas between a one-center electron-electron repulsion integral and the asymptotic Coulombic form of a two-center electron-electron repulsion integral. They are in fact just two choices from a general family of the form

$$V^\eta(R) = 1/(1/U^\eta + R^\eta)^{1/\eta}. \quad (11)$$

We investigated both the Mataga-Nishimoto and Ohno forms for V and found that neither gives an acceptable fit to the *ab initio* results. Nor can the fit be improved by varying η . However, since U and V in the Hubbard model are both extensively renormalized to account for, among other things, the effects of neglected repulsions between electrons on non-nearest neighbor sites, there is no particular reason that they should be related in the same way as bare Coulomb integrals.

Accordingly, we have simply fit the *ab initio* values of U^{eff} on the same grid of points used for t to a power series expansion around $R_0 = 1.4 \text{ Å}$. Addition of a quartic term was found to give very little improvement, so the result is

$$U^{\text{eff}}(R) = 3.724017 + 1.95894(R - 1.4) - 5.3549(R - 1.4)^2 + 1.457(R - 1.4)^3, \quad (12)$$

which, assuming U is fixed at 5.0 eV, gives for V ,

$$V(R) = 1.275983 - 1.95894(R - 1.4) + 5.3549(R - 1.4)^2 - 1.457(R - 1.4)^3, \quad (13)$$

with again energy in eV and distance in Å. This expansion is not as accurate as that for t , but V has much less effect on the predictions of the model than t so it appears to be sufficient. We caution that Eq. (13) is an interpolation formula only, and should not be applied outside the range of nearest-neighbor bond lengths since it does not have the proper asymptotic decay to zero.

C. The V_c parameter

According to the Hubbard model interpretation, the π electrons make no contribution to the energy of the triplet state. Its energy is then just the energy of the underlying σ -bonded core. Thus $E_T(R)$ should represent the energy of the σ bond between the carbon atoms. In fact, it shows a minimum between 1.52 and 1.53 Å, which agrees well with the expected equilibrium bond length for a σ bond between two sp^2 carbon atoms.⁶² In comparison, the corresponding triplet state in the two-electron system of H_2 is purely repulsive since the underlying potential is just the repulsion between the bare nuclei. In semiempirical applications of the Hubbard model, the underlying bond potential is most often modeled as a spring, in other words as a harmonic expansion about a minimum. But it is clear that the σ bond potential must be significantly anharmonic since short (i.e., double) bonds are much stiffer than long (i.e., single) bonds. This increased stiffness of the double bond is not due to the π electrons since the second derivative of the π electron energy (as evaluated from the Hubbard model) is actually negative, serving to soften the bond. Thus, we model $V_c(R)$ as an anharmonic expansion about the minimum of the triplet state including both a cubic and a quartic anharmonicity.

A fit of a quadratic to the three *ab initio* points nearest the minimum gives a minimum energy of $E_{eq} = -78.29274234$ a.u. at $R_{eq} = 1.5361$ Å. $V_c(R)$ is then represented as

$$V_c(R) = E_{eq} + 1/2K(R - R_{eq})^2 + 1/6K'(R - R_{eq})^3 + 1/24K''(R - R_{eq})^4. \quad (14)$$

The three force constants K , K' , and K'' were determined by a least squares fit to *ab initio* points spaced at 0.02 Å intervals between 1.32 Å and 1.52 Å. The value of E_{eq} just shifts the energy of all states by a constant and has no influence on any of the predictions of the model. The result is

$$V_c(R) = E_{eq} + 1/2(31.0140)(R - 1.5361)^2 + 1/6(-117.885)(R - 1.5361)^3 + 1/24(955.08)(R - 1.5361)^4, \quad (15)$$

with again energies in eV and distances in Å. The harmonic force constant of about 31 eV/(Å)² is of just the value expected^{62,63} for a carbon-carbon single bond force constant, confirming the interpretation of E_T as essentially the energy of the σ bond in ethene.

V. TESTING AND VALIDATION OF THE MODEL

Equations (5), (13) and (15), along with the fixed value $U = 5.0$ eV, define the parameterization of the extended Hubbard model. By construction, they accurately model ethene, but of course a critical test of the soundness of the model is whether the parameters are transferable to other hydrocarbons. Accordingly, we have applied the model to three typical molecules, *trans*-1,3-butadiene which introduces conjugation, *trans*-1,3,5-hexatriene which introduces conjugation extending beyond nearest neighbors, and benzene which shows the much more dramatic effect of conjugation around a cycle of $4n+2$ atoms. For each molecule, we have determined the equilibrium carbon-carbon bond lengths and computed low-lying electronic excitation energies.

A. Bond lengths

Care must be taken in comparing theoretically calculated equilibrium bond lengths R_e (the lowest point on the potential energy curve) with experimentally measured bond lengths. Experiments never measure R_e directly,⁶⁴ and experimental bond lengths are often longer than R_e , sometimes by as much as 0.01 Å. For example, the conventionally quoted⁶⁵ carbon-carbon bond length in ethene of 1.339 Å, measured by microwave spectroscopy, is substantially longer than the accurately determined^{52,53} value of $R_e = 1.3305$ Å. For diatomic molecules, it is usually possible to determine R_e using only experimentally measured quantities, but for polyatomic molecules only a few accurate experimentally based R_e values are known.⁵² Accordingly, we have a choice of comparing Hubbard model bond length predictions either with those computed by conventional quantum chemical methods or with experimental measurements for the ground state.

In theoretical calculations, it is generally acknowledged that electron correlation must be included to obtain accurate bond lengths, but correlation at the MP2 level is usually regarded as sufficient. Geometry optimizations are often carried out at the MP2 level using a Pople-style 6-31G** basis,⁵⁹ but for carbon-carbon bond lengths, it appears that the cc-pVTZ basis may be more accurate.⁶⁶ On the other hand, since the MS-RASPT2 bond length for ethene agrees with the experimental ground state value, it may be more relevant to compare the Hubbard model bond lengths to experiment for other small molecules as well. In Table IV, we compare bond lengths found by minimizing the energy of the Hubbard model as a function of bond length to those obtained from MP2 calculations with both basis sets, and to experiment.

Inspection of Table IV shows a systematic difference between the two *ab initio* basis sets. The 6-31G** basis gives longer lengths for all bonds, especially single bonds, and this difference persists in longer polyenes.⁶⁶ The Hubbard model bond lengths are generally between the *ab initio* and the experimental values, with the exception of the end bond in hexatriene. We strongly suspect that the experimental determination of this bond length is in error because it is shorter than the double bond length of butadiene, and all theoretical calculations with which we are familiar predict a smooth progression in the length of the end-most double bond in ethene,

TABLE IV. Carbon-carbon bond lengths (in Angstrom) of ethene, *trans*-1,3-butadiene, *trans*-1,3,5-hexatriene, and benzene at the ground-state equilibrium geometry.

Bond	MP2/cc-pVTZ ^a	MP2/6-31G** ^a	Extended Hubbard model	Experiment ^b
C ₂ H ₄				
Double	1.332	1.335	1.339	1.339
C ₄ H ₆				
Double	1.340	1.343	1.350	1.349
Single	1.453	1.459	1.461	1.467
C ₆ H ₈				
End	1.342	1.345	1.352	1.337
Single	1.446	1.450	1.454	1.458
Middle	1.350	1.353	1.362	1.368
C ₆ H ₆				
Aromatic	1.394	1.396	1.397	1.399

^aCalculated with the GAUSSIAN 03 program package.⁶⁸^bReference 65.

butadiene, hexatriene, octatetraene, . . . , with the bond becoming longer as the chain becomes longer. With that exception, the agreement between the Hubbard model predictions and experimental bond lengths is quite good, with the largest remaining error just 0.006 Å. Agreement with *ab initio* bond lengths, particularly those calculated with the 6-31G** basis, is also quite reasonable, indicating that the model has indeed captured the most important factors determining molecular structure.

B. Excitation energies

Care must also be used when comparing theoretically calculated excitation energies to experiment since experiments measure transitions between specific vibrational states. Nevertheless, experimental excitation energies measured at the band maximum often agree well with theoretical vertical transition energies. In Table V, electronic transition energies to low-lying excited states computed from the Hubbard model are compared both to *ab initio* calculations using the extended RASPT2 method recently developed^{39,42} and tested elsewhere,^{40,67} and to experiment.⁵⁸ Two different results from the model are shown, one at the cc-pVTZ *ab initio* geometry and one at the model equilibrium geometry.

The MS-RASPT2 vertical transition energy calculations were carried out at the *ab initio* equilibrium geometry as described in a recent work,⁴⁰ including all (π , π^*) valence orbitals in RAS2 subspace and the nine $3s3p3d$ Rydberg orbitals in RAS3 subspace, allowing up to singly excited configurations into the latter, RASPT2($n,0,1;0,n,9$)(S) with n the number of π electrons, that is equivalent to the number of π MOs of the full valence space. As in Sec. III, the results for ethene were performed at the RASPT2(12,2,2;4,6,8)(SD) level, employing the $6s5p4d2f/3s2p1d + 1s1p1d$ basis set, the default IPEA shift,⁴⁵ and Cholesky decomposition⁴¹ to compute the vertical transition energies with the MOLCAS-7 program.^{41–43} An imaginary level shift of 0.1 a.u. was used throughout. Symmetry restrictions were imposed for the com-

TABLE V. Excitation energies (in eV) of the lowest valence singlet and triplet states of ethene, *trans*-1,3-butadiene, *trans*-1,3,5-hexatriene and benzene at the ground-state equilibrium geometry.

Molecule	Exp. ^a	MS-RASPT2 ^{b,c}	Ext. Hubbard model ^c	Ext. Hubbard model ^d
C ₂ H ₄				
1 ¹ B _{1u}	8.00 ^e	8.07	8.08	8.03
1 ³ B _{1u}	4.36, 4.60	4.51	4.51	4.44
C ₄ H ₆				
1 ¹ B _u	5.92	5.97	5.71 ^f	5.65 ^f
2 ¹ A _g	—	6.57	6.37	6.25
1 ³ B _u	3.20	3.33	3.23	3.15
1 ³ A _g	5.08	5.12	5.05	4.95
C ₆ H ₈				
1 ¹ B _u	5.13, 4.93	5.01	4.47 ^f	4.41 ^f
2 ¹ A _g	—	5.37	5.07	4.95
1 ³ B _u	2.61	2.68	2.56	2.49
1 ³ A _g	4.11	4.31	4.12	4.04
1 ³ A _g	4.11	4.31	4.12	4.04
C ₆ H ₆				
1 ¹ B _{2u}	4.90	4.91	5.02	4.99
1 ¹ B _{1u}	6.20	6.15	6.34	6.32
1 ¹ E _{1u}	6.94	6.86	7.02	7.00
1 ³ B _{1u}	3.94	4.09	4.21	4.18
1 ³ E _{1u}	4.76	4.70	4.98	4.95
1 ³ B _{2u}	5.60	5.40	6.10	6.08

^aFor original experimental references (see Ref. 58).^bPresent MS-RASPT2($n,0,1;0,n,9$)(S) with n the number of π electrons and (π , π^*) MOs of the full valence space. MS-RASPT2(12,2,2;4,6,8)(SD) for ethene.^cAt the MP2/cc-pVTZ geometry.^dAt the Hubbard model geometry.^eEstimated vertical excitation energy from earlier theoretical work (see Refs. 36–38 and references therein).^fCharge transfer states not expected to be well described by the Hubbard model.

puted energies in the four molecules, D_{2h} for ethene, C_{2h} for *trans*-1,3-butadiene and *trans*-1,3,5-hexatriene, and D_{6h} (D_{2h} in MOLCAS) for benzene. Ground-state geometry optimizations were performed at the MP2 level⁵⁴ with the polarized cc-pVTZ basis set⁵⁵ by using the GAUSSIAN 03 package.⁶⁸

As can be seen in Table V, MS-RASPT2 transition energies for ethene are in agreement with accurate multi-reference CI theoretical studies.^{36–38} The vertical energy for the lowest 1¹B_{1u} state is computed to be 8.07 eV which is consistent with previous results.^{36–38,40,50,51,58} For the triplet 1³B_{1u} state, the MS-RASPT2 vertical transition energy is found at 4.51 eV, falling in the region of the experimental data.^{56,57}

As in ethene, valence-Rydberg mixing is a common situation in relatively small organic molecules and it is also present in the next studied polyenes, *trans*-1,3-butadiene and *trans*-1,3,5-hexatriene. The well-known erratic 1¹B_u valence state is well described by MS-RASPT2 yielding transition energies of 5.97 eV and 5.01 eV for butadiene and hexatriene, respectively. For the 2¹A_g state, the MS-RASPT2 transition energies of both molecules are near to those obtained in previous studies.^{49,69} The two lowest triplet states 1³B_u and 1³A_g estimated at the MS-RASPT2 level for both butadiene and hexatriene are close to those obtained by Silva *et al.*⁴⁸ and experimental data.⁵⁸

As shown in the past,⁴⁷ benzene also has valence-Rydberg mixing like the polyenes discussed before. In this aromatic molecule, the erratic valence state is 1^1E_{1u} but MS-RASPT2 solved it properly as shown previously.⁴⁰ The three lowest singlet valence states 1^1B_{2u} , 1^1B_{1u} , and 1^1E_{1u} estimated at the MS-RASPT2 level seem to be in agreement with experimental data⁵⁸ but the results found from the above-mentioned benchmarks turn out to be somewhat overestimated (see supplementary material⁷⁴).^{48,58} For the lowest triplet states 1^3B_{1u} , 1^3E_{1u} , and 1^3B_{2u} , the MS-RASPT2 values are close to the experimental data⁵⁸ and results obtained from Ref. 48.

As can be seen from Table V, the MS-RASPT2 results are in agreement with the experimental values. When computed at the same geometry, the Hubbard model results for the lowest excitation of each spin are also in agreement, with two exceptions to be discussed shortly. Errors in higher excited states are somewhat larger, generally in the 0.2–0.3 eV range. The two states for which the Hubbard model gives large errors are the 1^1B_u states of butadiene and hexatriene. These are charge transfer states in which determinants with two π electrons on one end carbon and none on the other end play a significant role. They are not expected to be well described by any nearest-neighbor model, which neglects long range electron-electron repulsion, including the Hubbard model. The Hubbard model does agree with CASPT2 and most^{58,70} (but by no means all^{71,72}) *ab initio* calculations in placing the 1^1B_u charge transfer states below the 1^1A_g homopolar states in these molecules. The homopolar state is spectroscopically dark, but there is no doubt that it becomes the lowest-lying singlet excited state in longer polyenes,⁷³ with the crossover probably coming at octatetraene in which the two states are nearly degenerate.

Calculations using the Hubbard model at its own equilibrium geometry rather than the *ab initio* geometry show only small shifts of less than 0.1 eV. These shifts generally act to worsen agreement with experiment for butadiene and hexatriene, but to improve the agreement for benzene. Nevertheless, the predictions of the model are quite satisfactory, with all states in the correct order and with the differences with respect to the MS-RASPT2 results no larger than those produced by other *ab initio* methods.⁵⁸ Thus again it seems that the Hubbard model has identified the important interactions needed to understand electronic spectra.

VI. SUMMARY AND CONCLUSIONS

A simple extension of the Hückel model, adding the one-center electron-electron repulsion as described by the Hubbard Hamiltonian, leads to an attractive model of chemical bonding. It has been shown that the extended form of the Hubbard model, including also nearest-neighbor electron-electron interactions, can be parameterized in a readily transferable form from accurate potential curves for a two-site fragment. As an illustration, accurate potential energy curves for ethene have been calculated via the MS-RASPT2 method. A multi-reference method such as MS-RASPT2 is essential to account for valence-Rydberg mixing in the π - π^* excited states of ethene as well as many other small molecules. The resulting

potential curves have been used to extract parameters for the Hubbard model as a function of bond length which should be applicable to other conjugated and aromatic hydrocarbons as well as pure carbon species such as graphene.

In test calculations on butadiene, hexatriene, and benzene, the extended Hubbard model was found to give a reasonable description of carbon-carbon bond lengths, intermediate between equilibrium bond lengths calculated at the MP2 level, and experimental bond lengths. MS-RASPT2 calculations were carried out for these molecules and the Hubbard model was found generally to provide a very good description of low-lying electronic excitation energies. That the model does not accurately reproduce the 1^1B_u excited state in butadiene and hexatriene illustrates a limitation of all nearest-neighbor models. The simple Hubbard model is reliable only for covalent states,^{30,33} that is in neutral molecules states dominated by determinants with no vacant or doubly occupied orbitals. The extended form of the model used here should correctly describe ionic states provided that the charges are on adjacent sites, which is not the case in the 1^1B_u states of polyenes. To position them correctly longer-range Coulomb interactions such as those included in the PPP model are needed. This probably also explains the poor performance of the Hubbard model relative to the PPP model found in Ref. 2(a) since some of the states considered are likely to have important contributions from nonadjacent charge centers.

The good performance of the model argues that, within the limitation of the previous paragraph, the extended Hubbard model successfully includes the most important interactions required to understand chemical bonding. This model provides a more balanced description of π versus σ bonding energy, and is capable of simultaneously describing geometric structure and low-level electronic excitations. The much greater power of the Hubbard model suggests that it should play a larger role in how chemists think about bonding than it has hitherto. The extra computational effort to solve the Hubbard model at the SCF level is very small. Thus, there seems little justification for leaving out the electron-electron interaction in semiempirical studies, which are still frequently done using the Hückel approximation. But the full power of the model comes from the inclusion of electron correlation. For small molecules such as those considered in this work, exact (full configuration interaction) solutions are feasible, and for larger molecules any of the standard quantum chemical methods for including electron correlation can be applied but at much reduced cost compared to an *ab initio* calculation.

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