

Fit of Pariser-Parr-Pople and Hubbard model Hamiltonians to charge and spin states of polycyclic aromatic hydrocarbons

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Total energies of charge and spin states of a specifically designed target molecule 2,5,8-trihydro-phenalenyl (3H-C₁₃H₉ from here on), calculated by means of multiconfigurational self-consistent-field (MCSCF) and density-functional-theory-B3LYP methods, have been fitted by means of interacting Pariser-Parr-Pople (PPP) (intrasite and intersite Coulomb interactions) and Hubbard Hamiltonians for π electrons. Numerically exact many-body solutions for these models were obtained by a variant of the Lanczos algorithm. Our calculation shows that the combination MCSCF-PPP with a hopping integral $t=-2.63$ eV and a local Coulomb repulsion $U=10.51$ eV produces the best results. Both model parameters are close to values frequently used in the literature, sometimes just for the Hubbard model. The fit of MCSCF energies by the Hubbard model is not as satisfactory (root-mean-square deviation is larger and $t=-4.83$ eV and $U=21.27$ eV parameters are far from common values). Neither of both models is able to accurately reproduce B3LYP energies. On the other hand, the value of the ratio $|U/t|$ is always close to 4 indicating the proximity to a magnetic phase transition in extended systems. Additionally, we find that Lieb's theorem for the Hubbard model on bipartite lattices applies to neutral 3H-C₁₃H₉ since all *ab initio* methods and model Hamiltonians predict a fivefold spin-degenerate ground state.

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I. INTRODUCTION

Despite the enormous success of density-functional-theory (DFT) calculations in many areas of Chemistry and Physics,¹⁻³ there is still a need of model Hamiltonians in cases where interactions are expected to play a crucial role,⁴⁻²⁸ and being very strong, perturbation theory fails even at a qualitative level. A key point when dealing with model Hamiltonians is to choose which interactions should be included as parameters and their actual values. For instance, the simplest Hamiltonian used in condensed matter to investigate the effects of the electron-electron interactions, namely, the Hubbard model,⁶ includes a single atomic orbital on each site, hopping between nearest-neighbor orbitals, and the on-site repulsion (intersite interactions are neglected). Describing properly the physics of some systems has required to incorporate more atomic orbitals and interactions between orbitals on the same or on different atoms.^{12,14,29} More recently, it has been suggested that the hopping integral may significantly depend on the charge state.³⁰ The important issue of the actual values of model parameters that have to be used to describe a particular physical system has been carefully addressed in Ref. 14 where a technique was proposed to derive the parameters of an extended Hubbard model for the cuprate La₂CuO₄. Many other works have focused on this question.¹⁵⁻¹⁸ Recently, present authors derived

the values of the parameters of an extended Hubbard model for the hydrogen molecule by a fitting procedure of *ab initio* energies of several charge and spin states of the H₂.²⁸

Particularly timely and relevant is the case of graphene for which the Hubbard Hamiltonian is being used to investigate a variety of problems. It is a widespread thought that a single set of model parameters will be valid when dealing with networks of carbon π orbitals whenever the C-C distance does not differ much from that found in graphene, namely, 1.41 Å. Unfortunately, actual values of the model parameters being used by researchers show a great consensus for the value of the nearest-neighbors hopping ($t \approx -2.71$ eV) but a really large dispersion for the on-site electron-electron interaction (U values range at least from 1.5 to 19.63 eV).³¹ This situation is especially worrisome since a magnetic transition is expected to appear close to $|U/t| \sim 4$. In this work, we carry out a detailed analysis of this issue. In particular, our aim is to determine whether *ab initio* total energies of charge and spin states of polycyclic aromatic hydrocarbons (PAH) can be fitted by means of either the Hubbard Hamiltonian⁶ or the more general Pariser-Parr-Pople (PPP) Hamiltonian^{4,5} that includes long-range Coulomb interaction. In both cases, accurate values of the model parameters will be obtained and their dependence on subtle details explained.

In order to produce a good database of *ab initio* molecular

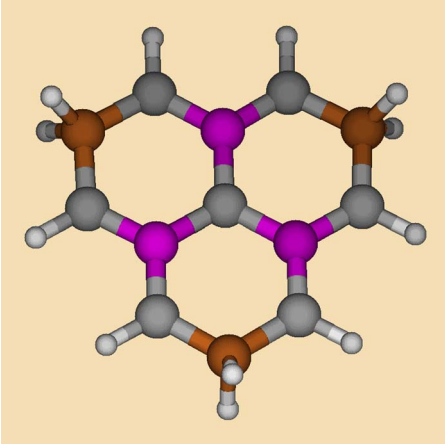


FIG. 1. (Color online) Schematic view of 2,5,8-trihydrophenalenyl ($3\text{H-C}_{13}\text{H}_9$). Phenalenyl system (C_{13}H_9) is an alternate uncompensated PAH radical appearing in three different charge states (neutral, cation, and anion) in some organic reactions (Ref. 32). Carbon atoms of one type (that is, belonging to one of the two sublattices) are depicted in gray and those of the other type in magenta and brown. Thus, there are seven C atoms of one type and six of the other. The artificial molecule investigated in our work is obtained by attaching an additional H atom to each peripheral carbon of the minority type (brown C), leading to an even higher uncompensated π orbital network: seven sites of one type (gray C) and only three of the other type (magenta C).

states to start our analysis, we choose a molecule that has not yet been synthesized but shows a particular topology serving perfectly to our purposes. It is derived from phenalenyl system³² by triple symmetric hydrogenation in the way that stronger affects alternation. We end with 2,5,8-trihydrophenalenyl (schematically represented in Fig. 1) which we consider very appropriate for our goals by several reasons: (i) this molecule shows a network of only ten π electrons allowing both extensive multiconfigurational calculations and exact solution of interacting model Hamiltonians, (ii) it maintains a planar structure and, thus, it is reasonable to expect that the results could be applicable to other planar PAH and particularly to graphene, (iii) its ground state shows robust spin degeneracy reinforcing thus our previous conclusions on other molecules hydrogenated in a similar way just to produce spin radicals^{33,34} and, (iv) model parameters can be immediately used to calculate properties of the similar well-known 1H-phenalene molecule in order to improve confidence in our procedure (for example, singlet-triplet splitting provides a satisfactory test).

The rest of the paper is organized as follows. Section II is devoted to give some details of the methods and procedures used in this work. The main features of the multiconfigurational approach that has been followed are highlighted in Sec. II A while the specific form of Pariser-Parr-Pople and Hubbard Hamiltonians that has been used in this work is described with some detail in Sec. II B. *Ab initio* quantum-chemistry results and their fitting by model Hamiltonians are given and discussed in Sec. III. Finally, the main conclusions derived from our work are summarized in Sec. IV.

II. METHODS AND NUMERICAL PROCEDURES

A. *Ab initio* calculations

Calculation of total energies of charge and spin states of $3\text{H-C}_{13}\text{H}_9$ were carried out using the triple zeta, polarized, and DFT-optimized PC2 basis set,^{35,36} which guarantees a sufficient precision. self-consistent-field (SCF) calculations were done at the restricted-Hartree-Fock level and by means of the hybrid density-functional RB3LYP.^{37–39} In both cases, and in order to get well-defined total spin values, the restricted-open-shell variant was used.⁴⁰ Aiming to check the accuracy of the description of the correlation energy of partially filled π shells, multiconfigurational wave-functions calculations were also performed. Configuration Interaction with single and double excitations calculations⁴¹ and multiconfigurational SCF (MCSCF) on the fully optimized set in the active space version,^{42,43} were carried out. The active space was generated with a window constructed with the last five occupied π -molecular orbitals and the first five empty π -molecular orbitals, filled with ten electrons for the neutral system. Geometries were optimized at the SCF (RB3LYP) level for the ground state, holding fixed this geometry for the calculations of excited and charged states. All quantum-chemistry calculations were done using the GAMESS suite of programs.⁴⁴

B. Model Hamiltonians

The model Hamiltonian utilized in this work is that proposed by PPP model^{4,5} which includes the local on-site interaction plus Coulomb intersite interactions. The local version of the PPP model is known in condensed matter physics as the Hubbard Hamiltonian⁶ and is the simplest model used to investigate the effects of electron-electron interaction. The PPP Hamiltonian contains an one-electron part \hat{H}_0 and a term that incorporates the electron-electron interactions \hat{H}_I

$$\hat{H} = \hat{H}_0 + \hat{H}_I + \hat{H}_{\text{core}}. \quad (1)$$

Notice that an extra core term has been added to account for the energy contribution of the electrons that are not explicitly included in the model (core plus σ -bonding electrons). The noninteracting term is written as

$$\hat{H}_0 = \epsilon_0 \sum_{i=1, N; \sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} + t \sum_{\langle ij \rangle; \sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}, \quad (2)$$

where the operator $\hat{c}_{i\sigma}^\dagger$ creates an electron at site i with spin σ , ϵ_0 is the energy of carbon π orbital, and t is the hopping between nearest-neighbor pairs (kinetic energy). N is the number of unsaturated C atoms. The interacting part is in turn given by

$$\hat{H}_I = U \sum_{i=1, N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} V_{|i-j|} (\hat{n}_i - 1)(\hat{n}_j - 1), \quad (3)$$

where U is the on-site Coulomb repulsion, $V_{|i-j|}$ is the intersite Coulomb repulsion, the electronic-density operator for a particular σ spin is given by

$$\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \quad (4)$$

and the total electron density for site i is

$$\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}. \quad (5)$$

Finally, the constant core term includes the fourth parameter of the model

$$\hat{H}_{\text{core}} = \Delta \hat{I}. \quad (6)$$

We use Ohno interpolating formula⁴⁵ to incorporate intersite Coulomb interaction $V_{|i-j|}$

$$V_{|i-j|} = U \left(1 + \left[\frac{U}{e^2/R_{ij}} \right]^2 \right)^{-1/2} \quad (7)$$

being R_{ij} the distance between i and j sites.

The advantage of using this interpolation scheme is that no additional parameters are needed and, therefore, U remains as the single parameter associated to interactions. Although Ohno's formula was originally devised for π orbitals, we have checked its performance on molecular hydrogen with a more than reasonable success.⁴⁶ PPP Hamiltonian reduces to the Hubbard model if intersite Coulomb interaction is neglected, that is, $V_{|i-j|}=0$ for all pairs.

Exact many-body wave functions of PPP and Hubbard Hamiltonians for the desired charge and spin states have been obtained by a Lanczos algorithm used within the complete many-body Hubbard space. Starting from a randomly generated state precursor, a straightforward Lanczos transformation is used to generate a small Hamiltonian matrix containing a better approximation for the desired state. Diagonalizing of this matrix ends a cycle that has to be iterated until convergence is reached, that is, until further application of the Hamiltonian operator to the state does not change it (details of the procedure can be found in Ref. 47). Model parameters are obtained in a standard way by minimization of the root-mean square (rms) of the differences among *ab initio* and model Hamiltonian total energies for the whole set of molecular states. That is, a global minimum of

$$\text{rms} = \sqrt{\frac{1}{18} \sum_{\alpha=1,18} (E_{\alpha}^{\text{ab initio}} - E_{\alpha}^{\text{fitted}})^2}$$

has to be searched. A version of the Nelder-Mead optimization (downhill simplex method) has been employed for this purpose.

III. RESULTS AND DISCUSSION

The molecule that has been specifically designed for this investigation is schematically shown in Fig. 1. It is based on phenalenyl system which is an alternate uncompensated PAH. Carbon atoms of one type (or sublattice, in a different nomenclature) are depicted in gray color and those of the other type magenta and brown. Thus, phenalenyl is formed by seven C atoms of one type and six of the other type. 2,5,8-trihydro-phenalenyl (3H-C₁₃H₉ in a simpler form) is obtained by attaching an additional H to peripheral carbons of the minority type (brown C), leading to an even more uncompensated π orbital network (seven gray C sites and three magenta). Thus, if Lieb's theorem⁴⁸ for the Hubbard model on bipartite lattices were applicable to this system, it would predict a ground state having spin $S=2$. Although not

the primordial objective of our work, the confirmation or not of this prediction is one important challenge for precise quantum-mechanics calculations.

Numerical values for the total energies of 18 charge and spin states of 3H-C₁₃H₉ as obtained by means of MCSCF and DFT-B3LYP *ab initio* methods are reported in Tables I and II. The energies resulting from a fit by PPP and Hubbard model Hamiltonians are also given followed by their absolute deviation. Six spin-excited states for the neutral molecule, three spin states for the corresponding anion and cation and also three spin excitations for doubly charged positive and negative ions form the whole set of analyzed state energies. A graphical version of Tables I and II (Fig. 2) shows the good description that PPP makes from the 18 *ab initio* energies (circles in upper panel are almost inside squares) while the other combinations give a qualitative but not precise description. Calculated root-mean-square deviations given in Table III for the four cases confirm the conclusion obtained by visual inspection of Fig. 2.⁴⁹

The first feature of these results worth of comment is that the ground state of the neutral molecule is a spin quintuplet no matter which *ab initio* method is used. It lies 0.34 or 0.30 eV below the triplet (1.02 or 2.37 eV below the singlet) for MCSCF and DFT-B3LYP calculations, respectively. Although differences between *ab initio* results for the singlet are important, the spin degeneracy predicted by Lieb's theorem⁴⁸ is confirmed in any case. Therefore, 3H-C₁₃H₉ molecule is a further example on how to get a ground state with a large spin multiplicity just by hydrogenation of some carefully selected C atoms at the molecule perimeter.³³

Some more features can be commented for the energies versus the number of occupied π electrons plot shown in Fig. 2. A strong electron-hole asymmetry is clearly observed in both panels although the effect is strongly enhanced for DFT results. This characteristic will later explain why models fitted to DFT-B3LYP energies better describe the anions of PAH. Notice also that the ground state of the ± 1 ionic states of the molecule always shows the lowest possible spin degeneracy, i.e., incipient magnetism of the molecule disappears for its charged states. Nevertheless, energy differences between doublet and quadruplet are quite small (in fact almost invisible at the energy scale of the figure). We get 0.04 eV (0.07 eV) and 0.02 eV (0.003 eV) for cation and anion, respectively, according to MCSCF (B3LYP) results.

Table III gives the main result of our work, namely, the model parameters giving the best fit of *ab initio* results. The obtained rms deviation is given in the last column. Let us further insist that based both on rms numerical value and the visual impression obtained from Fig. 2, it is clear that the best fit corresponds to the MCSCF-PPP combination, that is, a full configuration interaction calculation within the Hilbert space spanned by π orbitals modeled by a PPP model solved exactly by a Lanczos algorithm. Perhaps the fact that Hilbert spaces are almost equivalent in these cases can explain the coincidence but it is still a good news that a model Hamiltonian with just four parameters is quantitatively reproducing the results of a full state-of-the-art quantum-chemistry calculation. On the other hand, mean-field energies derived from DFT-B3LYP formalism are not correctly described by a model including the main part of the electron-electron correlation within the π -orbitals sector.

TABLE I. *Ab initio* MCSCF energies (in Hartree) of 18 charge and spin states of 3H-C₁₃H₉ (schematically depicted in Fig. 1). The states are characterized by total charge q and spin multiplicity $2S+1$, S being the spin. The energies obtained through fitting of the states by means of PPP and Hubbard model Hamiltonians with parameters given in Table III are also reported. Deviations of the model energies relative to *ab initio* values are given in eV.

q	$2S+1$	MCSCF (H)	PPP (H)	δ (eV)	Hubbard (H)	δ (eV)
+2	1	-498.7914	-498.7934	-0.06	-498.7988	-0.20
+2	3	-498.7831	-498.7917	-0.23	-498.7918	-0.23
+2	5	-498.6980	-498.6875	0.28	-498.7115	-0.37
+1	2	-499.1705	-499.1706	-0.01	-499.1504	0.55
+1	4	-499.1689	-499.1689	0.00	-499.1444	0.67
+1	6	-499.0566	-499.0595	-0.08	-499.0352	0.58
0	1	-499.3511	-499.3517	-0.02	-499.3556	-0.12
0	3	-499.3761	-499.3725	0.10	-499.3954	-0.52
0	5	-499.3885	-499.3815	0.19	-499.4132	-0.67
0	7	-499.1674	-499.1664	0.02	-499.1908	-0.64
0	9	-498.9533	-498.9485	0.13	-498.9594	-0.17
0	11	-498.6292	-498.6302	-0.03	-498.6157	0.37
-1	2	-499.3358	-499.3377	-0.05	-499.3175	0.50
-1	4	-499.3349	-499.3360	-0.03	-499.3115	0.64
-1	6	-499.2096	-499.2266	-0.46	-499.2023	0.20
-2	1	-499.1347	-499.1276	0.19	-499.1330	0.05
-2	3	-499.1328	-499.1259	0.19	-499.1260	0.19
-2	5	-499.0160	-499.0217	-0.16	-499.0457	-0.81

A somewhat complementary way of looking to the quality of the fits is obtained representing total energies derived from model Hamiltonians versus those obtained from *ab initio* calculations. This is actually done in Fig. 3. Squares of the upper panel closely follow the straight line while the circles corresponding to the Hubbard model values are scattered at both sides. The lower panel shows that neither model is capable to describe B3LYP results. Consider the importance of this last result, apparently negative, that shows that significant low-energy excitations cannot be assigned exclusively to the π electrons. Just because a hybrid functional method takes into account in an approximate way all the correlations of electrons close to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy region, it can better predict those important properties that need the inclusion of σ bonds in the formalism. This happens, for example, when the electron affinity is calculated.⁵⁰

As regards the actual values of the model Hamiltonian parameters reported in Table III, we first note that those for the combination MCSCF-PPP are close to classical Pariser and Parr values ($U=10.53$ eV and $t=-2.39$ eV and -2.92 eV for benzene and ethylene, respectively)⁴ and also to those proposed for polyacetylene, namely, $t=-2.5$ eV and $U=10$ eV, several years ago.⁵¹ They are also very close to the values used for an exact PPP model calculation of anthracene focusing on vertical singlet excitations relevant to its optical spectrum ($t=-2.4$ eV, $U=11.26$ eV, and Ohno interpolation for long-range Coulomb interaction)⁵² and for a

more general application of PPP Hamiltonian to the calculation of linear optical absorption and low-lying excited states of polyacenes ($t=-2.4$ eV and $U=11.13$ eV together with a standard Ohno interpolation, or $U=8$ eV in conjunction with a screened version of the same interpolation scheme).⁵³ Even in present material science, the use of $t=-2.8$ eV and $U \approx 10$ eV is suggested for a correct description of the electronic properties of graphene.⁵⁴ This is a remarkable result that may suggest the universality of these values for all PAH provided that C-C distances do not change much. However one should be cautious in deriving conclusions from this coincidence as in Refs. 51 and 54 no long-range Coulomb interactions are considered. Actually, if Coulomb repulsion is restricted to its on-site value as Hubbard model does, our fit to many-body eigenstates shows that both t and U increase to almost twice as large values (see Table III). We assign this result to the inclusion of ionic states in our database (12 from a total of 18 states are ionic). The value of U strongly increases as an indirect way of describing electronic repulsion for states well beyond local charge neutrality. Consequently, the results obtained in the present analysis reinforce the logical fact that *actual values of model parameters are not independent of the proposed model Hamiltonian* and, thus, one should be careful when comparing results reported in the literature.

Further analysis of results compiled in Table III shows that although model fits of DFT-B3LYP energies are of sensible lower quality, model parameters of both PPP and Hubbard theoretical Hamiltonians are similar (just 5–15 %

TABLE II. *Ab initio* B3LYP energies (in Hartree) of 18 charge and spin states of 3H-C₁₃H₉ (schematically depicted in Fig. 1). The states are characterized by total charge q and spin multiplicity $2S+1$, S being the spin. The energies obtained through fitting of the states by means of PPP and Hubbard model Hamiltonians with parameters given in Table III are also reported. Deviations of the model energies relative to *ab initio* values are given in eV.

q	$2S+1$	B3LYP (H)	PPP (H)	δ (eV)	Hubbard (H)	δ (eV)
+2	1	-501.6772	-501.6993	-0.60	-501.7027	-0.69
+2	3	-501.7010	-501.6924	0.23	-501.6963	0.13
+2	5	-501.5952	-501.5882	0.19	-501.6174	-0.60
+1	2	-502.0885	-502.0763	0.33	-502.0589	0.81
+1	4	-502.0861	-502.0751	0.30	-502.0534	0.89
+1	6	-501.9863	-501.9697	0.45	-501.9489	1.02
0	1	-502.2347	-502.2880	-1.45	-502.2828	-1.31
0	3	-502.3108	-502.3037	0.19	-502.3204	-0.26
0	5	-502.3219	-502.3106	0.31	-502.3371	-0.41
0	7	-502.0924	-502.1021	-0.26	-502.1219	-0.80
0	9	-501.8774	-501.8918	-0.39	-501.8985	-0.57
0	11	-501.5775	-501.5823	-0.13	-501.5652	0.33
-1	2	-502.3285	-502.3310	-0.07	-502.3136	0.41
-1	4	-502.3284	-502.3298	-0.04	-502.3081	0.55
-1	6	-502.2628	-502.2244	1.04	-502.2036	1.61
-2	1	-502.1608	-502.2087	-1.30	-502.2121	-1.40
-2	3	-502.1915	-502.2018	-0.28	-502.2057	-0.39
-2	5	-502.1520	-502.0976	1.48	-502.1268	0.69

smaller) to those given in the first two rows. This feature proves the robustness of our parametrization fit once a model Hamiltonian is selected. Even more stable is the value of the $|U/t|$ ratio always around 4, a value that suggests the proximity of a magnetic phase transition for the extended system.⁵⁵

Let us further comment on the transferability of model parameters to other similar systems. We will first point to electron affinity and spin-triplet splitting of anthracene, the largest PAH for which exact many-body results are amenable by our Lanczos technique (the Hilbert space for the neutral molecule consists of 11 778 624 states, a figure that is very close to the limit of our computational possibilities). We will use PPP model both by its better performance adjusting *ab initio* results and by the more consistent values of the parameters obtained. Electron affinity is predicted to be -1.34 eV using MCSCF parameters and 0.25 eV for B3LYP parameters (PPP rows of Table III). The experimental value is 0.53 eV that should be compared with the value given by a hybrid functional theory: 0.38 eV for the PC2 basis used in our work or 0.40 eV given by a better converged PC3 basis. The agreement is well within the statistical error in the last case but not for our preferred model. Fortunately, we know the reasons for the failure. As commented previously, model Hamiltonians are restricted to π -orbitals space but we know that σ states strongly contribute to the space of lower unoccupied states. Therefore, while a B3LYP calculation correctly describes electron affinity and parameters based in this values somewhat include the effect of σ states, a MCSCF de-

signed to ignore explicitly any σ -state contribution is unable to give a reasonable value of the electron affinity. On the other hand, spin-triplet splitting is predicted to be 2.04 eV which is satisfactorily compared with the value of 2.23 eV given by a basis converged B3LYP calculation.

The theoretical model can also be used to get some basic properties of the stable 1H-phenalene (C₁₃H₁₀) molecule. Although some C-C distances slightly differ from the bond distances of the fitted molecule, no scaling of the hopping parameter has been tried. PPP model adjusted to B3LYP values gives 2.36, 7.02, and -0.08 eV for singlet-triplet splitting, ionization energy, and electron affinity, respectively, which compare satisfactorily with reliable theoretical values (2.65, 7.14, and -0.11 eV, respectively) obtained for a fully converged DFT-B3LYP *ab initio* calculation.

A final use of the adjusted PPP model can be done for calculating electron affinity (EA) and ionization energy (IE) of neutral phenalenyl, the radical on which the molecule studied in this work is based. Converged PCn values at the B3LYP level for these magnitudes are 1.30 and 6.15 eV, respectively. One experimental value for the EA is available, 1.07 eV.⁵⁶ The corresponding exact values obtained by Lanczos are 1.20 and 5.73 eV for EA and IE, respectively, well within the error bar of the model when used to fit B3LYP-DFT energies (see Table III).

IV. CONCLUDING REMARKS

In this work, we have explored the possibility of fitting *ab initio* multiconfigurational and B3LYP total energies of

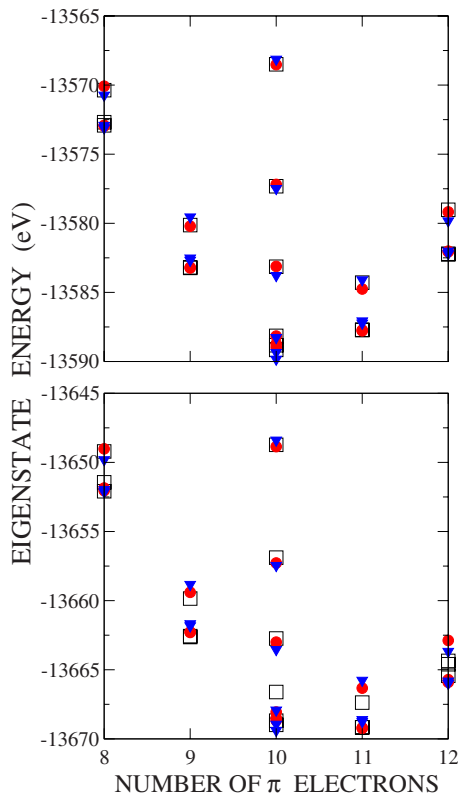


FIG. 2. (Color online) *Ab initio* MCSCF (upper panel) and B3LYP (lower panel) and model Hamiltonian energies of spin and charge states of 2,5,8-trihydro-phenalenyl (sketched in Fig. 1): squares give *ab initio* values while circles and triangles represent the results of the fit by PPP and Hubbard models, respectively. Actual numerical values of all energies are reported in Table I (MCSCF) and Table II (B3LYP) while parameters of the model Hamiltonians used in these calculations are given in Table III.

charge and spin states of polycyclic aromatic hydrocarbon by means of two Hamiltonians widely used in chemistry and physics, namely, the Pariser-Parr-Pople and the Hubbard models, respectively. In particular, we have focused on 2,5,8-trihydro-phenalenyl, a molecule that has been theoretically designed to show a neutral ground state of large spin (five-fold spin multiplicity). This feature that can be inferred from a *naive* application of a theorem proved by Lieb for the Hubbard Hamiltonian on bipartite lattices, is reproduced by both model and *ab initio* calculations. PPP model precisely repro-

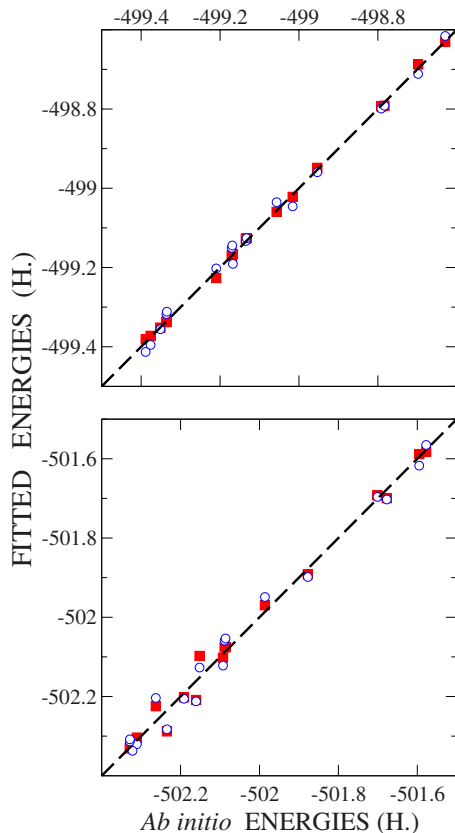


FIG. 3. (Color online) Model Hamiltonian energies versus *ab initio* MCSCF (upper panel) and B3LYP (lower panel) energies of spin and charge states of 2,5,8-trihydro-phenalenyl (sketched in Fig. 1). Squares give the energies obtained from PPP model while circles describe Hubbard results. The straight line signalizes a perfect fit ($y=x$). All numerical energies correspond to the values given in Tables I and II for model parameters compiled in Table III.

duces MCSCF energies obtained by full CI within the π -orbital Hilbert space but not B3LYP energies including additional correlations with σ orbitals that lie near HOMO-LUMO energies. On the other hand, Hubbard model shows a lower performance mainly due to the exclusion of long-range Coulomb interaction. Model parameters that are necessary to give the total electronic energy of the molecule include a constant energy due to electrons that are not explicitly described by the model and the absolute energy level of the π orbital. While PPP parameters agree with other values given

TABLE III. Model parameters of PPP and Hubbard (Hu) model Hamiltonians fitted to *ab initio* final energies of charge and spin states of $3\text{H-C}_{13}\text{H}_9$ calculated by means of MCSCF and B3LYP (see text and Tables I and II). All parameters are given in eV but the constant energy introduced to represent the core electrons Δ which is given in Hartree for a better comparison with state energies usually written in Hartree by computational packages. The root-mean-square deviation rms is also given in eV.

<i>Ab initio</i>	Model	Δ	ϵ_0	t	U	$ U/t $	rms
MCSCF	PPP	-495.8642	-7.53	-2.63	10.51	4.00	0.17
	Hu	-493.8714	-12.91	-4.83	21.27	4.40	0.47
B3LYP	PPP	-498.7853	-7.61	-2.34	8.29	3.54	0.68
	Hu	-496.9232	-12.63	-4.46	18.33	4.11	0.82

in the literature, values of t and U parameters for Hubbard model are about twice as large as usually assumed. This is actually the only way that Hubbard model has to describe the curvature of the energy versus charge function. In any case, we get $|U/t| \sim 4$ in all studied cases. The predictive character of the PPP model fitted to reproduce B3LYP total energies has been tested by obtaining some properties of anthracene, 1H-phenalene and phenalenyl radical. Therefore, we believe that the values provided for the parameters of the PPP model can show a rather wide applicability.

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