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PPP Hamiltonian for polar polycyclic aromatic hydrocarbons

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Abstract. Total energies of charged states and configurations of different spin multiplicity of two polar non-alternant polycyclic aromatic hdrocarbons (PAH), namely, pentaheptafulvalene and azulene, calculated by means of a Multi-Configurational (MCSCF) method which includes correlation only amongst π orbitals, have been fitted by exact solutions of the Pariser-Parr-Pople (PPP) and the Hubbard Hamiltonians for π electrons. As both molecules are planar, such an approach is in principle feasible. As found in our previous analysis of PAH, PPP fittings are significantly better than those attained with the Hubbard Hamiltonian. In addition, parameters for the Hubbard Hamiltonian are around twice those derived for the PPP model, indicating that parameters are not model independent. Fitted PPP parameters are close to those derived from a similar study of the PAH 2, 5, 8-trihydrogenated phenalene and those originally proposed by Pariser et al. providing further support to a wide applicability of the fitted parameters. Fittings obtained for a MCSCF method that also includes $\sigma\sigma$ and $\sigma\pi$ correlations (MCSCF/MP2) are slightly less accurate giving an on-site repulsion 10–15% smaller. The accuracy of the fittings further diminishes when parameters are derived from energies obtained by means of a DFT method (B3LYP) with an additional decrease in U of 5–25%. In the latter two cases, parameters have to be considered as *effective*, accounting for effects of σ orbitals not explicitly included in the model Hamiltonians. Electron affinities, ionization energies and dipole moments, calculated by means of the model Hamiltonians, are compared to those derived from DFT and ab initio methods and, whenever available, to experimental data.

1 Introduction

Model Hamiltonians are still throwing light on a variety of problems in Physics and Chemistry [1–26]. Illustrious examples in magnetism are the Ising and Heisenberg Hamiltonians [27]. The former has for long inspired a lot of studies in fields apparently as far from its original field of application as are sociology, economy, biology, etc. . Both are of great help in systems where local interactions amongst individuals are essential. More microscopic Hamiltonians which explicitly include the electron-electron interactions, the ultimate cause of magnetism, are those proposed by Hubbard and by Pariser-Parr-Pople (PPP). While the former restricts interactions to a local term (on-site Coulomb interaction), the latter includes, in addition, two-center Coulomb interactions. Despite the important simplifications inherent to both Hamiltonians, they can only be solved exactly in rather small sys-

tems [9,28][1]. Anyhow, as remarked above, both are being greatly useful in going beyond the highly successful DFT approaches [29–31]. This is a must when interactions are strong, an area in which many of the most interesting problems in Physics lie.

One of the most delicate issues when dealing with model Hamiltonians is the choice of an adequate set of model parameters [32–36]. In previous papers we have derived parameters of the Hubbard and PPP Hamiltonians for planar hydrocarbons [34–36]. The way we proceeded was to carry out non-linear fittings of the energies of sets of ionic and different multiplicity states calculated within the framework of DFT and ab initio (Configuration Interaction CI) methods, by means of exact solutions of model Hamiltonians. In a first attack to this problem and based upon fittings of Hubbard parameters to

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[1] The only exact solution for an infinite system was obtained by Lieb and Wu [28] for the Hubbard Hamiltonian in one dimension.

solely states with different spin multiplicity of dodecahy-drogenated coronene and anthracene (both polycyclic aromatic hydrocarbons, PAH) and 6H-corannulene (a non-alternant hydrocarbon) calculated by means of a DFT method, we concluded that the local repulsion parameter (usually referred to as U) was rather small, around 3.3 eV [34]. The derived set of parameters was however unable to give the energies of the ionic states of benzene [35]. In addition, while some improvement was obtained using PPP, the results were still highly unsatisfactory. A later and more systematic analysis modified to a great extent these conclusions [36]. The study was carried out on 2, 5, 8-trihydrogenated phenalene (a PAH molecule). The energies of ions (both cations and anions) and states of different spin multiplicity, calculated by DFT and Multi-Configurational (MCSCF) methods, were fitted by means of the Hubbard and PPP Hamiltonians. The main conclusions can be summarized as: (i) the best fit was attained for the PPP/MC combination (ii) fittings by means of the Hubbard Hamiltonian, although reasonably good, required excessively large values of the two model parameters, i.e., the hopping integral t and the local repulsion U, and (iii) instead, fittings by means of the PPP Hamiltonian led to $U = 10.51$ eV and $t = -2.63$ eV, both close to the values reported in the original papers on the PPP Hamiltonian (see Refs. [1,2] and discussion below) and to those currently used for graphene (see Ref. [36] and references quoted therein)[2]. These results led to the authors to suggest that this set of PPP parameters may have a largely universal character.

The purpose of the present work is to subject that proposal to a far more demanding test. In particular we will consider two non-alternant highly polar hydrocarbons, namely, pentaheptafulvalene and azulene. The energies of charged states and states of different spin multiplicity of these molecules, calculated by means of a MCSCF method [37,38], which includes correlation only amongst π orbitals, were fitted by exactly solving Pariser-Parr-Pople (PPP) and Hubbard models. The appealing result is that the fitted PPP model parameters only differ in 0.5–5% from those obtained from fittings of the electronic spectra of the PAH 2, 5, 8-trihydrogenated phenalene. Fittings of energies derived from an ab initio and a DFT method which also include $\sigma\sigma$ and $\sigma\pi$ correlations are, albeit still good, less accurate. In particular, fittings for a multi-reference perturbation theory method (MCSCF/MP2) [39,40] are slightly less accurate giving an on-site repulsion 10–15% smaller. Accuracy further decreases when energies derived from a DFT method (B3LYP) are fitted, with an additional decrease in U of 5–25%. In these two cases, parameters have to be considered as *effective*, accounting for effects of σ orbitals

not included in the model Hamiltonians. Electron affinities, ionization energies and dipole moments, calculated by means of the model Hamiltonians, are compared to those derived from ab initio methods and, whenever available, to experimental data. The two molecules investigated here show an interesting property shared with the broad family of annulenes [41,42], namely, annulenes which are aromatic [43–45][3] in their singlet ground states are anti-aromatic in their lowest triplet or quintet and vice versa. This property (revealed by the sign of the dipole moments) is duly reproduced by the model Hamiltonians.

The rest of the paper is organized as follows. Section 2.1 is devoted to describe the ab initio methods used in this work, highlighting the main features of the multi-configurational approaches we have followed. The Pariser-Parr-Pople Hamiltonian is described with some detail in Section 2.2, while the results of the fittings are discussed in Section 3. Finally, the main conclusions derived from the work presented here are summarized in Section 4.

2 Methods and numerical procedures

2.1 Ab initio calculations

Calculations of total energies of ionic and different spin multiplicity states of pentaheptafulvalene and azulene (see Fig. 1) were carried out using a DFT optimized PC2 basis set [46,47] and the cc-pVTZ basis set [48]. Both give similar results and guarantee sufficient precision, so only the PC2 results are shown. A total of 500 σ and π orbitals were included in the calculations carried out with multi-configurational (MC) SCF on the fully optimized set in the active space version [37,38]. The active space in the case of pentaheptafulvalene (azulene) was generated with a window constructed with the last six (five) occupied π-molecular orbitals and the first six (five) empty π-molecular orbitals, filled with 12 (10) electrons for the neutral system. The remaining 12 (10) core, 23 (19) valence and 500 (412) empty orbitals, were kept frozen in the MCSCF calculations. For all states, the molecular orbitals of the active space have been kept fixed and equal to those used for the ground state.

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[2] There is a general agreement on the value of the hopping integral that should be used in graphene $t = -2.71$ eV. However that is not the case for the on site repulsion U for which values within a rather wide range, $\approx$1.5–20 eV, are being currently used. It should be noted, however, that it may not make sense to transfer parameters from a given model Hamiltonian to another (see discussion in the results section).

[3] As the aromaticity of the two molecules herewith investigated could be questioned (none of the molecules is *bencenoid*), it is worth discussing current criteria to evaluate that property. As there is a charge transfer between the two rings, both molecules have an aromatic character according to the Huckel criterion, namely, when there are $4n + 2$ $(4n)$, n being an integer, electrons in each ring of the molecule, it can be considered aromatic (anti-aromatic). Nowadays, three additional criteria are most widely used. Energetic criteria: It deals with the stability of a molecule compared to its acyclic or cyclic conjugated unsaturated analogues. Geometrical criteria: the lesser the alternation of bond lengths the greater is the aromaticity. Magnetic criteria: molecules which exhibit significant exalted diamagnetic (paramagnetic) susceptibility are aromatic (anti-aromatic). There is a lot of information in the literature [44,45] which indicates that both molecules fulfill these criteria.
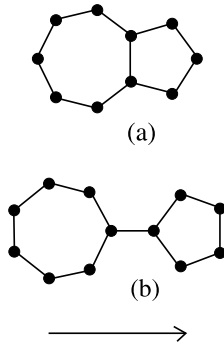
Fig. 1. Schematic view of the carbon network in azulene $C_{10}H_8$ (a) and pentaheptafulvalene $C_{12}H_{10}$ (b). The arrow indicates the direction of the positive x-axis (needed to correctly interpret the results for the dipole moments.

In order to check the relevance of molecular orbitals of σ symmetry, SCF calculations were also done by means of the hybrid density-functional B3LYP [49–51] and using a perturbation theory with the MCSCF reference wavefunction (MCSCF/MP2) [39,40]. In both cases, and in order to get well-defined total spin values, the restricted-open-shell variant was used. In the MCSCF/MP2 calculation, the 23 (19) valence orbitals and the 12 (10) π orbitals of the active space were included in the MCSCF calculation in first order, whereas the effects of the 500 (412) empty orbitals were taken into account in second order perturbation theory. In this case only the 12 (10) core orbitals remained fully frozen.

Geometries were optimized at the B3LYP level for the ground state, considering this geometry for all calculations of ionic and different spin multiplicity states. All quantum chemistry calculations were done using the GAMESS program [52].

2.2 Model Hamiltonians

The model Hamiltonians used in this work are those proposed by Pariser et al. (PPP model) [1,2] which includes on-site and two-center Coulomb interactions, and Hubbard [3] which only includes on-site Coulomb interactions. The Hubbard Hamiltonian is nothing but the local version of the PPP model and is being widely used in condensed matter physics as it is the simplest model describing the effects of electron-electron interaction. Both Hamiltonians incorporate a single orbital per atom, which in the present case we assume to represent the carbon unsaturated π orbital.

The PPP Hamiltonian contains a non-interacting part $\hat{H}_0$ and a term that incorporates the electron-electron interactions $\hat{H}_I$:

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

A core term has been included to account for the contribution of core electrons to the total energy. The non-interacting term is written as,

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

where the operator $\hat{c}^\dagger_{i\sigma}$ creates an electron at site i with spin σ, ϵ_0 is the energy of carbon π-orbital, N is the number of unsaturated C atoms and $t_{i,j}$ is the hopping between nearest neighbor pairs (i,j) (kinetic energy). In the present case, as the distance between neighbors $d_{i,j}$ may significantly differ from the graphene C-C distance $d_0 = 1.41$ Å, we use the following scaling adequate for π orbitals [53],

$$t_{i,j} = \left(\frac{d_0}{d_{i,j}}\right)^3 t_0. \quad (3)$$

where t_0 is a fitting parameter. The assumption in using this scaling law is that the C-C distance will always be around d_0 as it actually occurs in most molecules. The interacting part is in turn given by:

$$\hat{H}_I = U \sum_{i=1,N} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \frac{1}{2}\sum_{i\neq j} V_{|i-j|}(\hat{n}_i - 1)(\hat{n}_j - 1), \quad (4)$$

where U is the on-site Coulomb repulsion and $V_{|i-j|}$ is the inter-site Coulomb repulsion, while the density operator is

$$\hat{n}_{i\sigma} = \hat{c}^\dagger_{i\sigma}\hat{c}_{i\sigma}, \quad (5)$$

and the total electron density for site i is:

$$\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}. \quad (6)$$

Finally the core term is assumed here to be the fourth constant of the model,

$$\hat{H}_{\text{core}} = \Delta\hat{I}, \quad (7)$$

where $\hat{I}$ is the identity operator.

This Hamiltonian reduces to the Hubbard model if $V_{|i-j|}=0$. In incorporating the two-center Coulomb interaction $V_{|i-j|}$, we use Ohno interpolating formula [54] which reads,

$$V_{|i-j|} = U\left(1 + \left[\frac{U}{e^2/R_{i,j}}\right]^2\right)^{-1/2} \quad (8)$$

where $R_{i,j}$ is the distance between sites i and j and e is the electron charge. Using this interpolation scheme implies that no additional parameter is introduced and, consequently, U remains as the single parameter associated to interactions.

In calculating the ground states energies of PPP and Hubbard Hamiltonians for various ionic and different spin multiplicity states, we use a straightforward Lanczos transformation which, starting from a random ground state candidate (which guarantees to reach the complete Hilbert space), generates a small Hamiltonian matrix that can be diagonalized to get a better approximation for the

ground state. This process is iterated until convergence is reached (see Ref. [56] for details).

The four model parameters (ϵ_0, t_0, U and Δ) are obtained in a standard way by minimization of the root mean square (rms) deviation of the differences amongst ab initio and model Hamiltonian total energies for the whole set of molecular states. That is, a global minimum of

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

has to be searched for the N_{states} entering the fit. A version of the Nelder-Mead optimization (downhill simplex method) has been employed for this purpose.

It is worth noting that the PPP and Hubbard Hamiltonians were initially solved approximately [1–3]. Since then several numerical techniques have been developed that allow to find exact solution in cases where the number of orbitals involved in the calculation is small [9,55,56]. In particular, we mention the exact solutions of the PPP Hamiltonian for organic molecules reported in reference [55].

A key point in applying these model Hamiltonians to molecules is the choice of specific values for the model parameters. In the original work on the PPP Hamiltonian, values for U and t_0 were derived from experimental data [1,2]. In particular U was obtained from the ionization potential and the electron affinity of atomic carbon, obtaining $U = 10.53$ eV. Although this procedure is not fully justified its basis lies in the local character of U; however, as discussed below, using this value for U no matter the Hamiltonian may lead to serious problems. On the other hand the value of the hopping integral was chosen to give the experimental energy of the lowest singlet excited state, obtaining $t_0 = -2.39$ eV and –2.92 eV for benzene and ethylene, respectively. The so derived t_0 not only depends on the molecule but also on the Hamiltonian chosen to describe its properties and the method used to solve it. Despite of its possible flaws, this semi-empirical procedure is, in our opinion, the best founded of those being currently used (see also Ref. [57]). Recently, an alternative procedure is being widely used. It consists of deriving the parameters, particularly U, from DFT calculations. This is equivalent to truncate the DFT Hamiltonian, a procedure by no means justified.

The procedure adopted here allows to get deeper into the nature of model parameters and a more precise evaluation of their range of applicability. In particular: (i) fitting parameters for two model Hamiltonians using the same methodology allows to investigate, for instance, whether deriving U from atomic data is a reliable procedure that can be used no matter the Hamiltonian (ii) the completeness of the method is for sure substantially larger than those used up to now, allowing to evaluate, for instance, up to which extent σ orbitals, not included in the models, are important (iii) fitting the energies of both ionic states and spin configurations is a demanding test that allows to use the fitted model parameters in a wide variety of systems (note that including charged states requires to fit also the energy of the atomic orbital ϵ_0).

3 Results and discussion

A schematic view of the carbon network (π-orbitals) in the two molecules investigated here is shown in Figure 1. Both are non-alternant highly polar hydrocarbons [42] showing an essentially planar structure as present DFT structure optimization confirms (see also Ref. [42]). This feature justifies an analysis in terms of only π-electrons such as that discussed hereafter.

3.1 Fitting ab initio energies

Numerical values for the total energies of ionic and different spin multiplicity states of pentaheptafulvalene and azulene, as calculated by means of MCSCF method and through fittings of PPP and Hubbard model Hamiltonians, are reported in Tables 1 and 2, and graphically depicted in Figures 2 and 3. As these molecules can be positively charged rather easily but do not admit more than one electron in excess, the energies of ionic states with q from 1 up to 3 have been calculated, while $q = -3$ has not been considered. Altogether, the number of ionic and different spin multiplicity states of which the energy has been calculated is 33 and 28 for pentaheptafulvalene and azulene, respectively.

As regards fittings of MCSCF energies with the model Hamiltonians, we have explored several combinations concluding that the resulting parameters are not significantly dependent on the chosen set of states, provided that several ionic states are included. Actually, if the number of ionic states is low, the interaction parameter U is not clearly determined tending to be rather small. Accordingly, the following two sets of ab initio ionic and different spin multiplicity states have been chosen. The first one is that considered in our previous publication [36], namely, ground state (singlet) plus all spin multiplicities of the neutral molecule $q = 0$, and ground state plus two spin multiplicities of the molecule with $q = \pm 1$ and ± 2. In the second set we did not include ionic states with more than one electron in excess as they are very odd (see above) and their accurate description probably requires more orbitals than just the π orbitals included here. Thus, between 4 and 6 spin multiplicity states of each of the ionic states $q = 0$, ± 1, $+2$ and $+3$, were included in the second set. The states included in the fittings in each case are reported in Tables 1 and 2.

Ab initio energies versus the number of π electrons in the molecule are depicted in Figures 2 and 3 (only MCSCF and PPP results). A strong electron-hole asymmetry is clearly observed, which is satisfactorily reproduced by the model Hamiltonians. It is noted that the ground state of the charged molecule is always that having the lowest spin in each case, except for the dicationic state of pentaheptafulvalene.

Best fittings of ab initio total energies by means of the PPP and Hubbard Hamiltonians were obtained using the parameters reported in Table 3. The quality of the fittings is characterized by the root mean square rms deviation, also reported in the Table. It is noted that PPP fittings

Table 1. Ab initio MCSCF energies (in Hartrees) of ionic and different spin multiplicity states of pentaheptafulvalene $C_{12}H_{10}$ (see Fig. 1). The states are characterized by its charge q with respect to the 12 π-electrons of the molecule, and its multiplicity $2S + 1$, S being the spin. Model Hamiltonian energies obtained through fittings of ab initio energies of either 19 or 30 ionic and different spin multiplicity states (see text) by means of the Hubbard and PPP Hamiltonians with parameters shown in Table 3.

q	$2S+1$	MCSCF	PPP-1	Hu-1	PPP-2	Hu-2
−2	1	−460.2226	−460.2169	−460.2411		
−2	3	−460.2213	−460.2176	−460.2503		
−2	5	−460.0445	−460.0468	−460.0390		
−1	2	−460.4103	−460.4235	−460.4044	−460.4033	−460.4111
−1	4	−460.3325	−460.3401	−460.2976	−460.3210	−460.3080
−1	6	−460.1454	−460.1477	−460.1012	−460.1316	−460.1199
−1	8	−459.9240			−459.9127	−459.8991
−1	10	−459.6634			−459.6811	−459.6697
−1	12	−459.3525			−459.3941	−459.3990
0	1	−460.4501	−460.4528	−460.4892	−460.4455	−460.5069
0	3	−460.3773	−460.3829	−460.4030	−460.3764	−460.4241
0	5	−460.2623	−460.2487	−460.2665	−460.2442	−460.2935
0	7	−460.0726	−460.0560	−460.0757	−460.0552	−460.1118
0	9	−459.8417	−459.8269	−459.8449	−459.8304	−459.8922
0	11	−459.5735	−459.5713	−459.5831	−459.5797	−459.6429
0	13	−459.2590	−459.2780	−459.2764	−459.2920	−459.3514
1	2	−460.2096	−460.2223	−460.1984	−460.2265	−460.1793
1	4	−460.1229	−460.1266	−460.0834	−460.1318	−460.0688
1	6	−459.9884	−459.9693	−459.9199	−459.9770	−459.9125
1	8	−459.7683			−459.7617	−459.7025
1	10	−459.5134			−459.4995	−459.4431
1	12	−459.2201			−459.2101	−459.1536
2	1	−459.7958	−459.8072	−459.8316	−459.8218	−459.7759
2	3	−459.8028	−459.8049	−459.8363	−459.8201	−459.7808
2	5	−459.6676	−459.6598	−459.6573	−459.6772	−459.6087
2	7	−459.5438			−459.5283	−459.4723
2	9	−459.2874			−459.2796	−459.1948
2	11	−458.9977			−458.9739	−458.9112
3	2	−459.2064			−459.2279	−459.3222
3	4	−459.1573			−459.1766	−459.2629
3	6	−459.0247			−459.0377	−459.0931
3	8	−458.8869			−458.8668	−458.9296
3	10	−458.6132			−458.5860	−458.6287

are substantially better than Hubbard fittings, as their respective rms values indicate (a factor 2–3 smaller in PPP). A pictorial way to see the performance of the PPP fittings consists of plotting total energies derived from the model Hamiltonian versus those obtained in ab initio MCSCF calculations. Numerical results admit a linear fitting of slope close to 1, providing further support to the claimed goodness of the PPP fittings.

As regards the actual values of the PPP parameters reported in Table 3 we first note that they differ in all cases in less than 7% from those reported in reference [36]. Specifically, the values of the hopping integral are all within a 4% of –2.63 eV, the value reported in reference [36]. In the case of the interaction parameter U three of the values differ in less than 1% from 10.51 eV, while the fourth (9.94 eV) differs in around 6%. Finally, the results for the energy of the π orbital are in three cases within a 1% of –7.53 eV, but in one which differs in approximately 5%. As pointed out in our preceding work, these model parameters are very similar to those proposed in reference [58] for polyacetylene, namely, $t = -2.5$ eV and

$U = 10$ eV. On the other hand, the results for the on-site repulsion U derived from Hubbard fittings are around 30 eV, approximately a 25% higher than in our previous study [36]. This is a very high value which along with that of the hopping integral (greater than 5 eV) illustrates the oddness of the fittings and probably the inadequacy of the simple Hubbard Hamiltonian for describing these molecules. These results support one of the main conclusions of our previous analysis [36] in the sense that *actual values of model parameters are model dependent*. A more detailed discussion of this issue can be found in reference [36].

Parameters of the two model Hamiltonians were also derived from fittings of the energies of the same charged states and spin multiplicity states shown in Tables 1 and 2, obtained from ab initio methods that include correlation energies of σ orbitals. The results are also reported in Table 3. Fittings for a MC method (MCSCF/MP2) are slightly less accurate than those of MCSCF. In addition, the fitted on-site repulsion U is around 10–15% smaller. The accuracy of the fittings further decreases

Table 2. Ab initio MCSCF energies (in Hartrees) of ionic and different spin multiplicity states of azulene $C_{10}H_8$ (see Fig. 1). The states are characterized by its charge q with respect to the 10 π-electrons of the molecule, and its multiplicity $2S + 1$, S being the spin. Model Hamiltonian energies obtained through fittings of ab initio energies of either 18 or 25 ionic and different spin multiplicity states (see text) by means of the Hubbard and PPP Hamiltonians with parameters shown in Table 3.

q	$2S + 1$	MCSCF	PPP-1	Hu-1	PPP-2	Hu-2
-2	1	-383.2698	-383.2596	-383.2864		
-2	3	-383.2444	-383.2436	-383.2787		
-2	5	-383.0660	-383.0722	-383.0598		
-1	2	-383.4940	-383.4989	-383.4774	-383.4769	-383.4863
-1	4	-383.3916	-383.3948	-383.3582	-383.3745	-383.3710
-1	6	-383.1961	-383.1993	-383.1512	-383.1831	-383.1727
-1	8	-382.9056			-382.9200	-382.9021
-1	10	-382.6247			-382.6554	-382.6492
0	1	-383.5361	-383.5375	-383.5574	-383.5309	-383.5805
0	3	-383.4559	-383.4579	-383.4966	-383.4520	-383.5240
0	5	-383.3320	-383.3222	-383.3371	-383.3197	-383.3702
0	7	-383.0918	-383.0847	-383.1043	-383.0886	-383.1485
0	9	-382.8109	-382.8312	-382.8471	-382.8428	-382.9026
0	11	-382.5337	-382.5313	-382.5343	-382.5514	-382.6044
1	2	-383.3002	-383.3070	-383.2817	-383.3112	-383.2611
1	4	-383.1972	-383.1936	-383.1535	-383.1992	-383.1379
1	6	-383.0424	-383.0152	-382.9772	-383.0246	-382.9692
1	8	-382.7901			-382.7780	-382.7199
1	10	-382.4810			-382.4694	-382.3864
2	1	-382.8584	-382.87484	-382.8848	-382.8842	-382.8182
2	3	-382.8408	-382.8491	-382.8808	-382.8595	-382.8159
2	5	-382.7018	-382.6899	-382.6965	-382.7031	-382.6376
2	7	-382.5490			-382.5308	-382.4647
2	9	-382.2490			-382.2116	-382.1480
3	2	-382.2034			-382.2340	-382.3184
3	4	-382.1426			-382.1570	-382.2480
3	6	-382.0083			-382.0113	-382.0614
3	8	-381.8092			-381.7764	-381.8472

when parameters are derived from energies obtained by means of a DFT method (B3LYP), with an additional decrease in U of 5–25%. In these two cases, parameters have to be considered as *effective*, accounting for effects of σ orbitals not explicitly included in the model Hamiltonians.

It should be noted that the large differences between the values of the on-site Coulomb repulsion parameter U derived here for the PPP and Hubbard Hamiltonian cast serious doubts on the procedure which uses the value of U obtained from atomic properties. The fact that in the case of the PPP Hamiltonian for π electrons this procedure works rather accurately, may not at all have a general applicability.

3.2 Electron affinities, ionization energies and dipole moments

Results for electron afinities (EA) and ionization energies (IE) are reported in Table 4. The first thing to be noted is the good agreement between the results derived from the PPP Hamiltonian and those obtained with ab initio methods. This is consistent with the rather good accu-

racy of the fittings discussed above. Then we note that MCSCF give unphysical values of EA, surely due to the relevance of σ orbitals when empty orbitals play a relevant role, as is the case of EA. Actually, MCSCF and its fitted PPP counterpart, give poor results for both EA and IE, as the comparison with the experimental data for azulene indicates. Instead, MCSCF/MP2 and B3LYP give reasonable results for both magnitudes. Particularly good is the agreement with the experimental data for IE of azulene.

A final and important issue of the present study is the dipole inherent to both molecules in the singlet S_0 and quintet Q_1 states of their respective neutral states. In the case of model Hamiltonians the only possible way to calculate dipole moments is to approximate the charge on each C atom (each π orbital) by a point charge located at the atom site. This is a rough approximation that may likely lead to differences with ab initio dipole moments. We also note that no results obtained with MCSCF/MP2 are shown, as in this method only energy corrections to MCSCF are provided by the standard codes.

The results are reported in Table 5. We first note that all calculations reproduce the aromaticity of the singlet and the anti-aromaticity of the quintet characteristic of
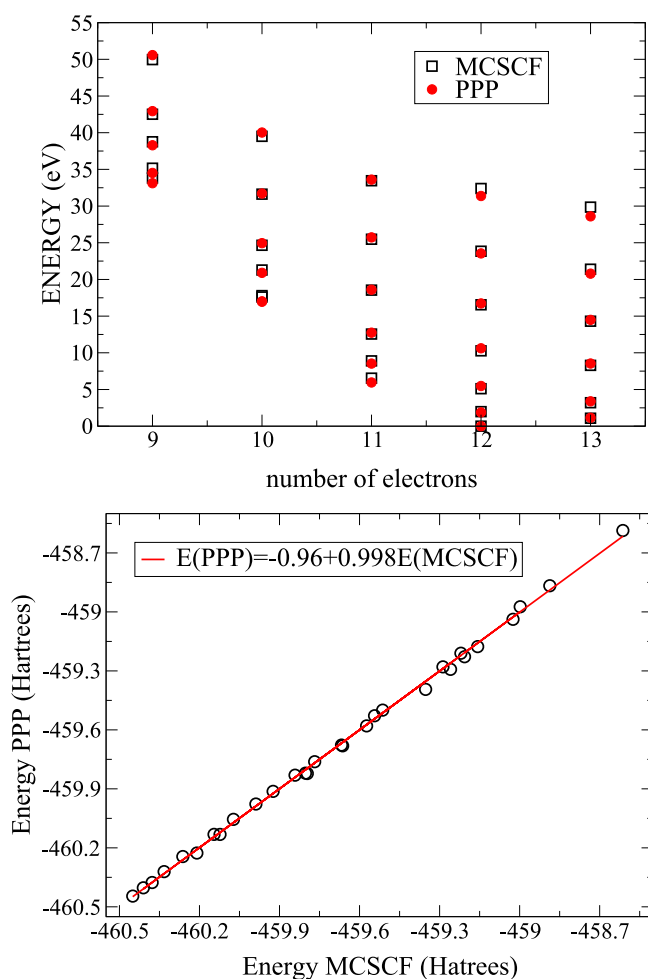
Fig. 2. (Color online) Upper: model Hamiltonian PPP energies and ab initio MCSCF energies (see text) versus charge, of ionic and different spin multiplicity states of pentaheptafulvalene $C_{12}H_{10}$ (see Fig. 1). Several results at constant charge correspond to different spin multiplicity states. Actual values of the energies are reported in Table 1, while parameters of the model Hamiltonian used in these calculations are given in Table 3. Lower: model Hamiltonian PPP energies versus ab initio MCSCF energies. The straight line is the best fit to the data.
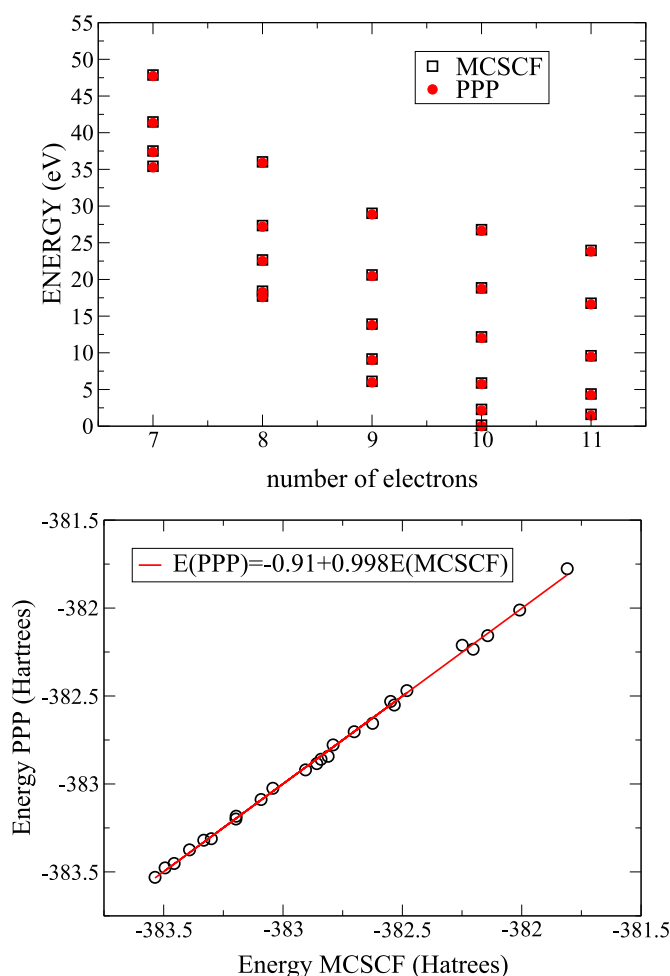
Fig. 3. (Color online) Upper: model Hamiltonian PPP energies and ab initio MCSCF energies (see text) versus charge, of ionic and different spin multiplicity states of azulene $C_{10}H_8$ (see Fig. 1). Several results at constant charge correspond to different spin multiplicity states. Actual numerical values of the energies are reported in Table 2, while parameters of the model Hamiltonian used in these calculations are given in Table 3. Lower: model Hamiltonian PPP energies versus ab initio MCSCF energies. The straight line is the best fit to the data.

both molecules [42] (note the opposite signs of the respective dipole moments). Concerning MCSCF calculations the most remarkable result is that in the case of a ferromagnetic spin arrangement, multiplicity 13 and 11 for $C_{12}H_{10}$ and $C_{10}H_8$, respectively, the dipole moments are small but not null, as one may have expected if the approximation of a single π orbital per C would have worked perfectly. In the case of $C_{12}H_{10}$ the dipole is much smaller than any other, whereas in azulene it is of the order or larger than the dipole moments of other spin states. This may indicate the existence of a non-negligible coupling of the π orbitals with other orbitals. In comparing the ab initio results with those of the model Hamiltonians, we first note that dipole moments calculated with the Hubbard Hamiltonian are substantially lower than MCSCF dipole moments, typically an order of magnitude smaller. The

cause of this behavior is the strong reduction of charge transfer between atoms that the high on-site interaction produces. As regards ab initio results it is noted that the DFT method gives dipole moments that are a factor of 2–3 higher in $C_{12}H_{10}$ as compared to MC results, a factor that is reduced to 1.5 in the case of azulene. In addition, while B3LYP gives a dipole for the singlet of azulene that is within the experimental range, the MC results is slightly lower. PPP results for the quintet of both molecules show a better agreement with MCSCF and B3LYP results than in the case of the singlet. Apart from the singlet of the $C_{12}H_{10}$ molecule, the differences between the PPP results and those derived from the MCSCF and B3LYP methods are very similar. Finally, PPP dipoles are a factor of two larger than the only experimental data available.

Table 3. Model parameters of PPP Hamiltonian either fitted to ab initio total energies of ionic and different spin multiplicity states of pentaheptafulvalene $C_{12}H_{10}$ and azulene $C_{10}H_8$ calculated by means of MCSCF (see text and Tabs. 1, 2) MCSCF/MP2 or B3LYP methods. The results should be compared with those derived from fittings to 1, 4, 7-trihydrogenated phenalene, namely, $t = -2.63$ eV, $U = 10.51$ eV and $\epsilon_0 = -7.53$ eV. The results of fittings by means of the Hubbard (Hu) Hamiltonian are also reported. The number of states whose energies were fitted are shown in parenthesis (the two set of parameters derived from those fittings are denoted as PPP-i, Hu-i, $i = 1, 2$). All parameters are given in eV, but the constant energy introduced to represent the core electrons Δ which is given in Hartrees. The root mean square rms is also given in eV.

Molecule	Fitting	t_0	U	ϵ_0	Δ	rms
$C_{12}H_{10}$ (19 states)						
MCSCF	PPP-1	−2.56	10.41	−7.86	−455.8121	0.29
	Hu-1	−4.99	24.20	−14.73	−452.7793	0.79
MCSCF/MP2	PPP-1	−2.61	9.33	−8.65	−457.1408	0.56
	Hu-1	−5.20	24.04	−15.98	−453.9127	1.07
B3LYP	PPP-1	−2.33	7.01	−7.44	−458.5774	1.01
	Hu-1	−4.73	20.44	−14.12	−455.6377	1.50
$C_{12}H_{10}$ (30 states)						
MCSCF	PPP-2	−2.54	10.59	−7.62	−455.9324	0.48
	Hu-2	−5.02	26.11	−16.04	−452.2783	1.63
MCSCF/MP2	PPP-2	−2.55	9.07	−8.47	−457.2375	0.63
	Hu-2	−5.16	25.16	−17.12	−453.4867	1.74
B3LYP	PPP-2	−2.39	8.64	−8.16	−458.3204	1.04
	Hu-2	−4.63	21.14	−15.62	−455.0705	2.06
$C_{10}H_8$ (18 states)						
MCSCF	PPP-1	−2.54	9.94	−7.54	−379.7598	0.29
	Hu-1	−5.12	24.91	−15.00	−377.0230	0.85
MCSCF/MP2	PPP-1	−2.59	9.18	−8.55	−380.7974	0.46
	Hu-1	−5.25	24.68	−16.26	−377.9673	0.98
B3LYP	PPP-1	−2.38	8.06	−7.99	−381.7945	0.53
	Hu-1	−4.98	23.23	−15.54	−379.0263	1.04
$C_{10}H_8$ (25 states)						
MCSCF	PPP-2	−2.56	10.55	−7.49	−379.7979	0.52
	Hu-2	−5.19	27.38	−16.63	−376.4939	1.75
MCSCF/MP2	PPP-2	−2.58	9.39	−8.56	−380.8071	0.51
	Hu-2	−5.32	26.65	−17.85	−377.4497	1.68
B3LYP	PPP-2	−2.36	8.60	−8.39	−381.6821	0.70
	Hu-2	−4.97	24.95	−17.30	−378.4621	1.88

Table 4. Electron affinities (EA) and ionization energies (IE), both in eV, of pentaheptafulvalene $C_{12}H_{10}$ and azulene $C_{10}H_8$ calculated by means of of either ab initio methods or model Hamiltonians (see Tabs. 1–3). Experimental data, if available, are also shown (references given in brackets).

Molecule	Method	EA		IE	
		Ab initio	PPP-2	Ab initio	PPP-2
	MCSCF	−1.083	−1.147	6.544	5.959
$C_{12}H_{10}$	MCSCF/MP2	0.662	0.671	7.367	7.376
	B3LYP	0.797	0.699	7.074	7.068
	MCSCF	−1.144	−1.467	6.418	5.976
$C_{10}H_8$	MCSCF/MP2	0.424	0.280	7.523	7.530
	B3LYP	0.422	0.686	7.249	7.578
	Experimental	0.79[4]		7.42[4]	

[4] National Institute of Standards and Technology (NIST), Material Measurement Laboratory, http://webbook.nist.gov/.

4 Concluding remarks

The present results reinforce the conclusion of our preceding work, concerning the universal character of the PPP model parameters derived here and in reference [36]. The fittings of the energies of several charged states and spin multiplicity states of alternant or non-alternant organic molecules carried out here and in the previous work are very satisfactory. The only limitations seem to be the planar character of the molecule and that the relevant electronic structure may be described by unsaturated π orbitals perpendicular to the molecule plane. On the other hand, fittings with the Hubbard model are poorer and lead to parameters (hopping integral and on-site repulsion) substantially higher than those being currently used in the literature. Parameters derived from fittings to ab initio

Table 5. Dipole moments (Debyes) of spin states of pentaheptafulvalene $C_{12}H_{10}$ and azulene $C_{10}H_8$ (see Fig. 1) calculated by means of either ab initio methods or model Hamiltonians (see Tabs. 1–3). Experimental data, if available, are also shown (references given in brackets).

Molecule	$C_{12}H_{10}$		$C_{10}H_8$	
$2S+1$	1	5	1	5
MCSCF	−1.25	2.6	−0.71	1.31
PPP-2	−3.30	3.52	−1.92	1.51
Hu-2	−0.28	0.21	−0.24	0.14
B3LYP	−3.56	5.28	−1.05	1.93
PPP-2	−4.24	4.76	−2.22	1.88
Hu-2	−0.54	0.44	−0.31	0.17
Experimental		−	−0.8 [59]	−
		−	−1.08 [60]	−

methods that include correlations associated to σ orbitals (MCSCF/MP2 and B3LYP) have to be considered as *effective*, accounting for effects of σ orbitals not explicitly included in the model Hamiltonians.

The large differences between the values of the on-site Coulomb repulsion parameter U derived here for the PPP and Hubbard Hamiltonians, cast serious doubts on the procedure which uses the value of U obtained from atomic properties. The excellent performance of this procedure in the case of the PPP Hamiltonian for π electrons may not have a general applicability.

The low rms deviation of the fittings guarantees the agreement beween the electron affinities and ionization energies derived from the model Hamiltonian with those obtained from the ab initio methods. Finally, dipole moments derived from PPP reproduce the aromatic character of the singlet ground state and the anti-aromaticity of the quintet excited state, characteristic of both molecules.

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