Spin alignment of extra electrons in K-phenanthrene clusters taken from the crystalline tripotassium-intercalated phenanthrene structure

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The appearance of ferromagnetic correlations among π electrons of phenanthrene ($C_{14}H_{10}$) molecules in the herringbone structure is proven for K doped clusters both by *ab initio* quantum-chemistry calculations and by the direct solution of the many-body Pariser-Parr-Pople Hamiltonian. Magnetic ground states are predicted for one or three additional electrons per phenanthrene molecule. These results are a consequence of the small overlap between the lowest unoccupied molecular orbitals (and lowest unoccupied molecular orbitals + 1) of neutral neighboring phenanthrene molecules, which makes the gain in energy by delocalization similar to the corresponding increase due to the Coulomb interaction.

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I. INTRODUCTION

There is an increasing interest in the study of the electronic structure of potassium doped polycyclic aromatic hydrocarbons (PAH) showing an "armchair" edge termination since the discovery of superconductivity in picene samples doped by K and Rb done in 2010 by Mitsuhashi *et al.*[1] A maximum critical temperature of 18 K has been obtained for K3picene. Although the precise structural information of the new compound is still not clear, several studies of the electronic structure of partially optimized structures have been published.[2–6] On the other hand, the interlayer K doping of another PAH (pentacene, as large as picene but showing "zigzag" edges) has also been investigated although no signs for superconductivity have been found.[7–9] The growing consensus is that potassium atoms ionize and populate lowest unoccupied molecular orbitals (LUMO) and LUMO + 1 of the corresponding PAH. The width of the partially occupied band is small since the overlap between distant molecular orbitals is minute. Therefore, the system is close to a metal-insulator transition and careful calculations are needed to decide the actual character of the system. Recently, the importance of electron-electron correlation has been emphasized by Giovannetti and Capone[10] and also by Kim *et al.*[6] who presented sophisticated band structure calculations aimed to improve the description of electronic correlation. In spite of the presumed importance of electron-electron correlation in these compounds, there are several independent electron calculations of the electron-phonon coupling that predict a transition temperature for the superconductivity transition that is close to the experimental value.[11–13] Furthermore, the possibility of superconductivity in other doped PAH has been investigated.[14,15] Following these experimental efforts, additional *ab initio* calculations of the band structure of the new class of superconductors have been undertaken.[16,17]

In this work, we study ground state manifestations of the strong correlations among doping electrons suggested by the narrow width of the conduction bands that has been obtained by previous band structure calculations. To this end, we isolate small clusters appearing in the crystalline structure and used either *state of the art* quantum chemistry methods for the whole interacting system or Lanczos methods applied to π electrons described by a realistic Pariser-Parr-Pople (PPP) model Hamiltonian.[18–20] For the second method, numerically exact solutions are obtained for the correlated π electrons of a phenanthrene molecule ($C_{14}H_{10}$, therefore, 14 sites) while very precise solutions are obtained for the π electrons of two molecules (28 sites) using a configuration interaction (CI) method that generates the relevant part of the whole Hilbert space starting from the Hartree-Fock many-body wave function of the system. We also use this method to study

four phenanthrene systems (56 sites) generating some hundred thousand configurations that provide a first approximation of the correlated ground state. Consistent results between both methods have been obtained that give us enough confidence in the fundamental result of our investigation, namely, that when phenanthrene molecules are populated by one or three extra electrons, each molecule contributes one electron to the resulting magnetic ground state. On the other hand, two electrons per phenanthrene molecule give ground states that are singlets.[21]

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. In particular, the multiconfigurational approach employed for the two and four phenanthrene systems is explained in Sec. II B. It is inspired in standard quantum chemistry CI methodology and can be used when interacting systems are described by huge Hilbert spaces. This methodology provides reliable solutions using only a small subset of states constructed in some appropriate way that will be later summarized. Section III gives our main results together with some discussion. Finally, our main conclusions are summarized in Sec. IV.

II. METHODS AND NUMERICAL PROCEDURES

To assess the emergence of magnetism for doped phenanthrene systems, we study doped clusters of phenanthrene molecules in the arrangement obtained from a previous band structure calculation of the crystalline system. We follow this approach for two reasons. First, we build upon our experience in the study of correlations in similar PAH molecules based in quantum chemistry calculations combined with the use of exact numerical solutions of the PPP model Hamiltonian.[22–24] In particular, we have shown the conditions for the existence of magnetic molecules based on the polycyclic aromatic hydrocarbon structure. Second, we have developed a new Lanczos procedure that follows standard methods of quantum chemistry to include electron-electron correlation taking advantage of a preliminary self-consistent field calculation (SCF) that is followed by configuration interaction (CI) within a wisely chosen subspace. While a Lanczos method based in the complete many-body space can typically deal with 14 sites, the new development is able to describe the major part of the correlation energy using some hundred thousand states obtained from a SCF Hartree-Fock (HF) state by the successive application of the many-body Hamiltonian to the initial many-body seed. In this way, we are able to study correlation effects among all the 28 C sites having a π orbital in a couple of phenanthrene molecules. The application of a Lanczos procedure to the solution of larger systems made of by four phenanthrene molecules is also possible but limited to a similar number of configurations (less than 10^6) which obviously represent a much smaller part of the whole Hilbert space. When studying 28 sites we are able to show how correlation energy converges to its precise value as the number of configurations taken into account increases. Instead, we are limited to a one-step procedure when solving the PPP model on 56 sites. Typically, one or two hundred thousand interacting configurations are considered in the last case, which produce a nonnegligible correlation energy of several electron volts.

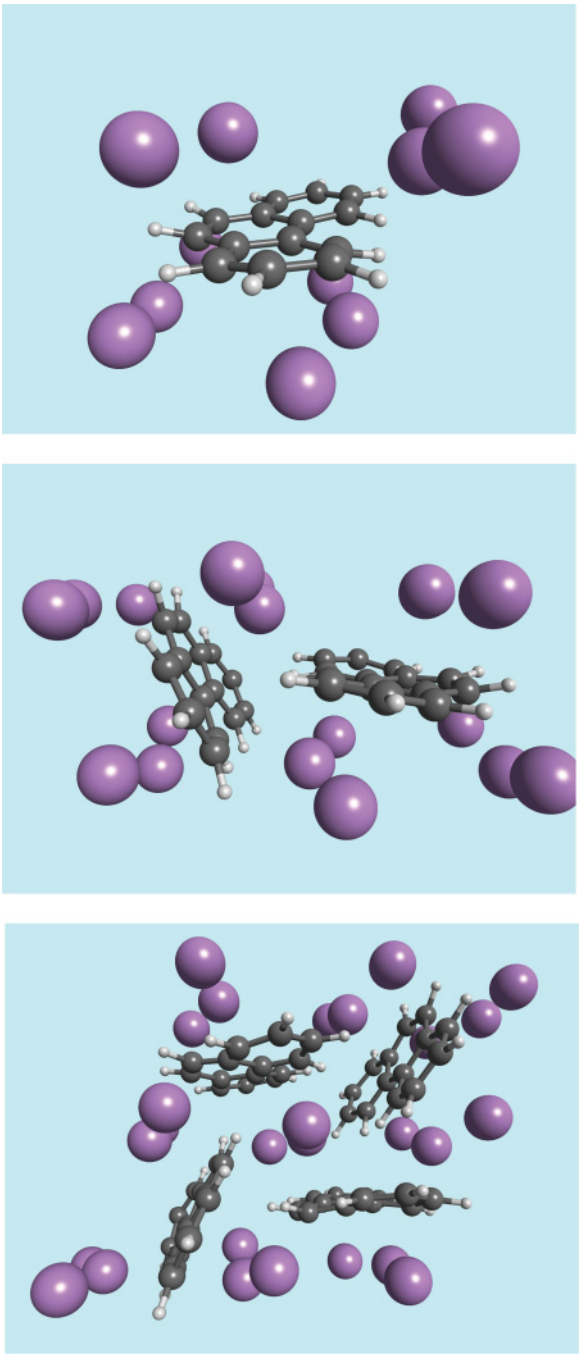

FIG. 1. (Color online) Main potassium-phenanthrene clusters studied in this work. Every phenanthrene molecule is surrounded by 12 K atoms that simulate the local crystalline ionic environment. All potassium atoms are ionized, therefore, all ejected 4*s* electrons populate phenanthrene LUMO and LUMO + 1 molecular orbitals. Three extra electrons per phenanthrene molecule are achieved after removing excess electrons from the calculation. Geometries correspond to ground states.

Some of the clusters studied in this paper are shown in Figs. 1 and 2.[25] They have been obtained from the optimized crystalline structure of tripotassium-intercalated phenanthrene,[17] which has been reported to show superconducting properties at 5K (Ref. 14). The number of K atoms included in the clusters is larger than the desired stoichiometry

because the ionic character of the compound makes the choice of a convenient cluster difficult. We have chosen clusters in which phenanthrene molecules are completely surrounded by potassium atoms to preserve the local symmetry as much as possible. Assuming that all K atoms are ionized, a feature that we have systematically checked, the number of extra electrons on phenanthrene molecules equals the number of K atoms of the cluster. To achieve the doping level of the compound, that is, three extra electrons per phenanthrene molecule for K_3phenanthrene crystal, excess electrons are removed from the cluster. In this way, all calculations correspond to three extra electrons per phenanthrene molecule. As said before, we have always checked the consistency of our approach confirming that doping electrons occupy molecular orbitals that correspond to slightly distorted LUMO and LUMO + 1 of the isolated PAH molecules.

The description of compounds of smaller potassium content follows a similar way. First, some K atoms are removed from the clusters shown in Fig. 1 to correctly describe the local crystalline environment of $K_n$phenanthrene. Second, some electrons are removed from the cluster to adjust the number of extra electrons per phenanthrene molecule to n. For example, Fig. 2 shows the clusters used to describe four phenanthrene molecules at doping levels one (one extra electron per molecule) and two (two extra electrons per phenanthrene).

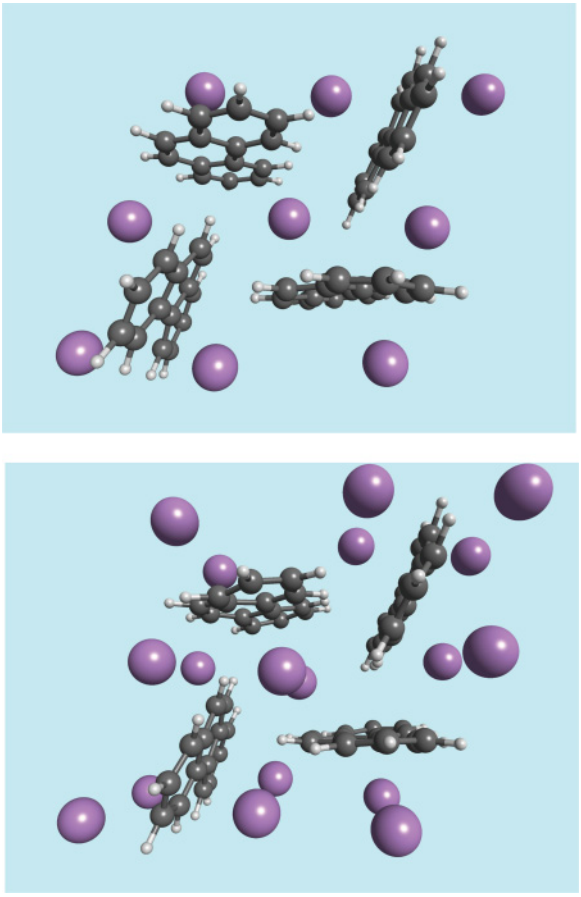

FIG. 2. (Color online) Four phenanthrene clusters used to describe compounds showing one extra electron per phenanthrene molecule (upper panel) and two extra electrons per molecule (lower panel). The atomic positions of PAH molecules have been optimized for any studied multiplet state keeping fixed the potassium positions.

Once the clusters are defined, the atomic coordinates of phenanthrene molecules have been relaxed to their equilibrium positions for any DFT state studied in this work. Actually, this is the hardest part of the job in terms of computational resources. Notice that geometry optimization should be done for fixed potassium positions to avoid the tendency of K atoms to desorb from the cluster.

A. Density functional theory

Results for the K-phenanthrene clusters studied in this work have been entirely obtained using the US GAMESS package for quantum chemistry computation.[26] Exchange and correlation are approximately included via DFT using the B3LYP functional.[27–29] This is a hybrid generalized gradient approximation (GGA) functional combining five functionals, in particular, HF exchange. It is quite popular in condensed matter physics and usually it gives a good description of magnetic states avoiding the tendency toward antiferromagnetism shown by pure HF. A large valence triple zeta plus polarization on all atoms (6-311G**) Gaussian basis has been chosen for H, C, and K atoms.[30,31]

B. Model Hamiltonian

The PPP model Hamiltonian has been chosen as a standard to describe electronic π-π correlations.[18,19] It is simple but realistic enough to reproduce some *ab initio* results. We use parameters recently obtained for similar molecules.[20] Although σ and π symmetries of electrons are only exact for isolated planar molecules, we trust that magnetic excitations of small energy *do* occur within the π-electron group that remains almost half-filled. The small overlap between phenanthrene molecules at the crystalline distance justifies this approach. Actually, the interaction among electrons in different molecules is exclusively Coulomb interaction in the model Hamiltonian.

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

$$\hat{H} = \hat{H}_0 + \hat{H}_I. \tag{1}$$

The noninteracting term is written as

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

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_{ij} is the hopping between nearest neighbor pairs $\langle ij\rangle$ (kinetic energy). Hopping is scaled by a power law[32]

$$t_{ij} = \left(\frac{d_0}{d_{ij}}\right)^3 t_0, \tag{3}$$

where d_{ij} is the C_i-C_j distance and $d_0 = 1.41$ Å. The interacting part is in turn given by

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

where U is the on-site Coulomb repulsion and V_{ij} is the C_i-C_j intersite Coulomb repulsion given by

$$V_{ij} = U\left(1 + \left[\frac{U}{e^2/d_{ij}}\right]^2\right)^{-1/2} \quad (5)$$

according to the Ohno interpolating formula.[33] The electronic density operator for spin σ is

$$\hat{n}_{i\sigma} = \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}, \quad (6)$$

and the total electron density for site i is

$$\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}. \quad (7)$$

We use $\epsilon_0 = -7.53$ eV, $t_0 = -2.63$ eV and $U = 10.51$ eV (Ref. 20).

The model Hamiltonian is solved using a Lanczos method which is numerically exact for 14 sites since the complete Hilbert space can be included in the diagonalization. We work in real space, that is, many-body states are defined giving the real space position (site) of every electron. This is the natural choice for a model Hamiltonian defined in real space [see Eqs. (2) and (4)]. When the number of sites increases up to 28 as it happens for 2P clusters (NP, meaning N phenanthrene molecules surrounded by a number of K atoms that produce the desired doping level), this procedure is useless as the number of real space configurations is huge (about 10^{15}). In this case, a CI procedure has been developed that starts from a SCF HF solution as in any currently available quantum chemistry package. Molecular orbitals of this mean field are obtained for the cluster and the whole Hamiltonian operator initially written in the local basis of creation operators $\hat{c}^{\dagger}_{i\sigma}$ transformed to the basis of extended molecular states. The simple physical interactions shown in Eq. (4) give way to a complete entanglement of the molecular orbitals due to interaction. When this rewritten Hamiltonian operator acts on the HF many-body solution $\Psi_{\rm HF}$, it produces many new configurations that are considered via Lanczos to improve electron-electron correlation. A similar procedure is well known in theoretical chemistry,[34] being the main innovation here the automatic selection of configurations that modern computers allow in the case of a model Hamiltonian.

Let us briefly summarize the numerical algorithms. The application of the full Hamiltonian operator $\hat{H}$ to the SCF HF state $\Psi_{\rm HF}$ produces an initial subspace of the whole Hilbert space (Full CI) that we use to get a better approximation for the correlated ground state. We have

$$\hat{H}\Psi_{\rm HF} = E_{\rm HF}\Psi_{\rm HF} + \sum_{\alpha} C_\alpha \Psi_\alpha \ , \quad (8)$$

where $E_{\rm HF}$ is the HF energy obtained in the SCF step. All configurations having a weight $|C_\alpha|^2$ larger than a convenient threshold are included in a first CI calculation. Usually, all configurations generated in this first step are considered. Next, Lanczos iteration is used to obtain a better ground state Ψ_1 of energy E_1 within this limited Hilbert subspace. Again, $\hat{H}$ is applied to Ψ_1 to generate further configurations that have to be included in the relevant Hilbert subspace

$$\hat{H}\Psi_1 = E_1\Psi_1 + \sum_{\beta} C_\beta \Psi_\beta \ , \quad (9)$$

and configurations of weight $|C_\beta|^2$ above the threshold are included in a further Lanczos diagonalization that gives an improved ground state Ψ_2 of energy E_2. This process is iterated until the number of relevant configurations is stabilized or is above our present computational capabilities. In some simple model Hamiltonians, as, for example, a local Hubbard term in a chain, it is possible to recover the whole interacting space describing the exact ground state. Nevertheless, the PPP model is highly coupled and only a large enough threshold limits the continuous increase of the basis. We would like to point out here to an obvious advantage of our selection of the CI space over other conventional choices like quadruple CI, multireference singles-doubles CI, and so on. Since the Hamiltonian operator is applied several times to the variational CI space, it is clear that states showing quite different occupation numbers can be automatically included if their weight in the ground state is considered relevant, that is, above threshold (which is just a matter of computer capabilities). Summarizing our Lanczos procedure in a few words, we can say that in a typical PPP calculation, the CI basis is enlarged as much as possible. Several hundred of thousands of configurations are finally included in our computations. A paradigmatic numerical result of our iterative procedure is shown in Fig. 3 for a two phenanthrene cluster doped with six extra electrons. Energy decreases monotonically as the

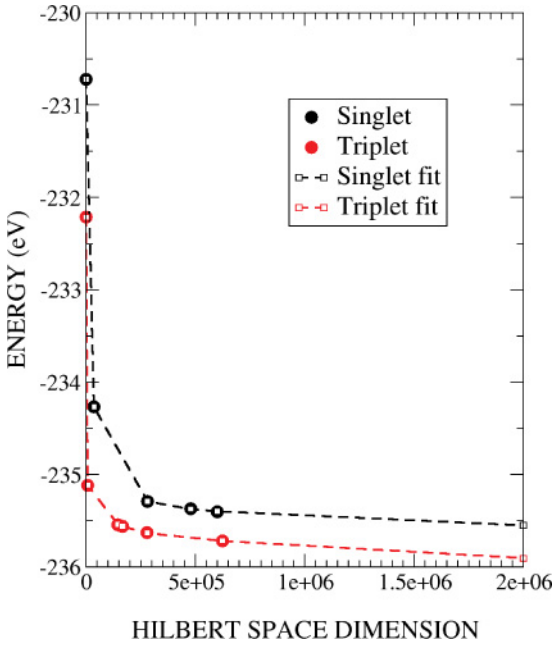

FIG. 3. (Color online) CI Lanczos energies of the two phenanthrene cluster as a function of the Hilbert space dimension. The fit predicts a singlet-triplet splitting of 0.36 eV in the asymptotic dimension limit.

TABLE I. Energy of the lower states of a phenanthrene molecule surrounded by potassium ions simulating a $K_n$phenanthrene crystal with n from 0 to 3 giving the number of electrons transferred to the organic molecule. We call doping the number of extra electrons per phenanthrene molecule, that is, the anionic charge of each phenanthrene molecule. The two last columns give the spin excitation energy first for the *ab initio* DFT calculation and second for the PPP model solved by Lanczos. Ground state energies are emphasized.

Doping	Singlet (H)	Doublet (H)	Triplet (H)	Quadruplet (H)	DFT spin excitation (eV)	Model spin excitation (eV)
0	**−539.3167**	–	−539.1947	–	3.32	3.44
1	–	**−2938.0773**	–	−2937.9683	2.97	3.79
2	**−5336.2298**	–	−5336.2189	–	0.30	0.17
3	–	**−7733.2310**	–	−7733.1938	1.01	1.02

number of configurations included in the CI is increased. In this particular case, 599 524 configurations were included to describe the singlet state and 623 762 were included for the triplet. A large energy drop is obtained in the first iteration step that considers 36 771 (8 277) configurations for the singlet (triplet) state. From this point onwards, energy is improved continuously but the limit is not reached. Fortunately, a nonlinear curve fitting using the model form

$$E = a_0 + a_1/\sqrt{N_{\mathrm{CI}}} + a_2/N_{\mathrm{CI}} + a_3/(N_{\mathrm{CI}}\sqrt{N_{\mathrm{CI}}}) \, ,$$

is very successful and provides a useful limit a_0 for the energy corresponding to the whole Hilbert space of dimension $N_{\mathrm{CI}} \sim \infty$.

As said in the Introduction, we are not able to analyze the convergence of our Lanzcos results for four phenanthrene systems (4P), that is, for correlated electrons moving on 56 sites. We just include configurations obtained by a first application of the Hamiltonian to the HF state. This means between one and two hundred thousand states entering CI. They give a noticeable stabilization of the Hartree-Fock energy and are able to change the ordering obtained for spin multiplets by the mean-field solution. This happens, for example, when eight electrons are added. 2An initial ground state showing large spin multiplicity (five) ends as an excitation after considering CI. In all studied cases, numerical values of the magnetic-nonmagnetic splitting are significantly modified from their mean-field values.

III. RESULTS AND DISCUSSION

The main results of our work are compiled in Tables I to III for increasing number of phenanthrene molecules forming the clusters. The first column gives the number of extra electrons per phenanthrene molecule that we call "doping" making a connection with the crystalline compound. Following columns give the energies obtained by DFT for the relevant states. Finally, the last two columns give the energy difference between the most stable magnetic state and the state of zero spin for the two approaches used in our work. A negative number means that the magnetic state is below the nonmagnetic one and is, therefore, the ground state.

Results in Table I, as expected, clearly preclude magnetism for isolated phenanthrene molecules. The consistency between DFT and Lanczos results for the PPP model is remarkable. In this case, Lanczos results are exact (14 sites) and correspond to a planar ideal phenanthrene molecule that is easily doped by a change in the total number of electrons. On the other side, different DFT doping levels are achieved changing the number of K atoms surrounding the phenanthrene molecule and optimizing its geometry for any calculated state. As Fig. 1 (upper panel) shows for doping level 3, the molecule is no longer plane but significantly distorted as it is in the crystal.[17] In any case, only the triplet state corresponding to the phenanthrene dianion (doping equal to 2) shows a small excitation energy of just some tenths of eV.

The results for 2P (two phenanthrene molecules surrounded by K atoms) collected in Table II show semiquantitative consistency between *ab initio* results and the interaction model. In both cases they point out to the existence of a magnetic ground state of spin 1 for doping with an odd number of electrons. The neutral system is quite stable (spin excitation is well above 3 eV) but the addition of one or three electrons per phenanthrene results in a magnetic state stabilized by some tenths of an electron volt. Larger doping results in a deeper magnetic state for the Lanczos calculation of 2P cluster whereas DFT points to an ideal smaller doping level of 1. The middle panel of Fig. 1 shows the cluster obtained for the triplet ground state corresponding to three anionic charges per phenanthrene molecule. Our results for 2P clusters can be interpreted in terms of population of LUMO and LUMO + 1

TABLE II. Energy of the lower states of a 2P cluster formed by two phenanthrene molecules surrounded by potassium ions simulating a $K_n$phenanthrene crystal with n from 0 to 3 giving the number of electrons transferred to the organic molecule. The two last columns give the spin excitation energy first for the *ab initio* DFT calculation and second for the PPP model solved by Lanczos. Ground state energies are emphasized.

Doping	Singlet (H)	Triplet (H)	DFT spin excitation (eV)	Model spin excitation (eV)
0	**−1078.6348**	−1078.5127	+3.32	+3.44
1	−4676.8273	**−4676.8416**	−0.39	−0.19
2	**−8274.0380**	−8274.0269	+0.30	+0.23
3	−11869.5978	**−11869.6034**	−0.15	−0.36

TABLE III. Energy of the lower states of a 4P cluster formed by four phenanthrene molecules surrounded by potassium ions simulating a $K_n$phenanthrene crystal with n from 0 to 3 giving the number of electrons transferred to the organic molecule. The two last columns give the spin excitation energy first for the *ab initio* DFT calculation and second for the PPP model solved by Lanczos. Ground state energies are emphasized.

Doping	Singlet (H)	Triplet (H)	Quintuplet	DFT spin excitation (eV)	Model spin excitation (eV)
0	**−2157.2727**	−2157.1508	–	+3.32	+3.44
1	−7554.7514	−7554.7661	**−7554.7788**	−0.75	−1.04
2	**−12950.9777**	−12950.9663	–	+0.31	+0.26
3	−18344.9536	−18344.9684	**−18344.9730**	−0.53	−0.44

provided by phenanthrene molecules. At doping level 1, the two extra electrons align ferromagnetically in separated molecular orbitals (MOs) instead of pairing in the bonding combination of both LUMOs, presumably because the gain in delocalization is not enough. Ultimately, we can point to an almost negligible overlap between LUMOs at different PAH molecules. When there are four extra electrons, they completely populate LUMOs of both molecules resulting in a singlet-triplet splitting of 0.30 eV that equals the result obtained for one molecule (Table I). Finally, with three extra electrons per phenanthrene, LUMOs remain fully occupied by four electrons and the last two electrons align parallel on different LUMO + 1s. Therefore, a triplet state is obtained as ground state.

Table III presents our results for the larger 4P clusters studied in this work. They are formed by four phenanthrene molecules in a herringbone configuration and a variable number of potassium atoms that depends on the crystalline compound being simulated. Figures 2 (upper panel) and 1 (lower panel) show the final geometries obtained for the quintuplet ground states obtained at doping levels 1 and 3. On the other hand, the final configuration for the singlet ground state obtained for an anionic charge of two per phenanthrene is shown in the lower panel of Fig. 2. In this case, quintuplet states are stabilized by a large energy of 0.75 and 0.53 eV for doping levels 1 and 3, respectively, in our DFT calculation. The values obtained via one-step CI show a nice consistency with DFT results. This fact points to the robustness of our main conclusion which is obtained via CI for pristine clusters of two or four planar phenanthrene clusters just by adding a convenient number of electrons.

The population argument given for the smaller clusters works equally well in this case but now four parallel electrons on four different LUMOs give rise to a quintuplet at doping level 1. For the double anions LUMOs are completely occupied resulting in a singlet ground state. Finally, the third doping electron goes to separated LUMO + 1s resulting again in a ground state showing fivefold spin degeneracy. Our reasoning is reinforced by the graphical representation of the spin density obtained for quintuplets. Figure 4 shows the electronic density corresponding to the unpaired electrons plotted using the WXMACMOLPLT graphical package.[25] It can be seen that total spin density corresponds to phenanthrene LUMO (LUMO + 1) states for doping 1 (3). It is also clear that the weight on K atoms is very small reinforcing the idea that the role of K is to dope the PAH molecules without forming strong bonds with them. Therefore, K atoms modify the overall electrostatic potential but do not actively participate in electronic correlations. If our results could be straightforwardly extrapolated to the crystalline case they would predict ferromagnetism for doping levels one and three. Electrons would enter parallel in the band corresponding to LUMOs when just one electron per phenanthrene dopes the material. Next electrons would further occupy the band reducing the spin polarization value. For just two electrons per phenanthrene the band would be completely occupied and nonmagnetic. Finally, the third electron would aligned spin parallel in the band formed by LUMO + 1s.

At this point it is important to remember that a zero-temperature transition from the nonmagnetic semimetal to an antiferromagnetic insulator was predicted for the Hubbard

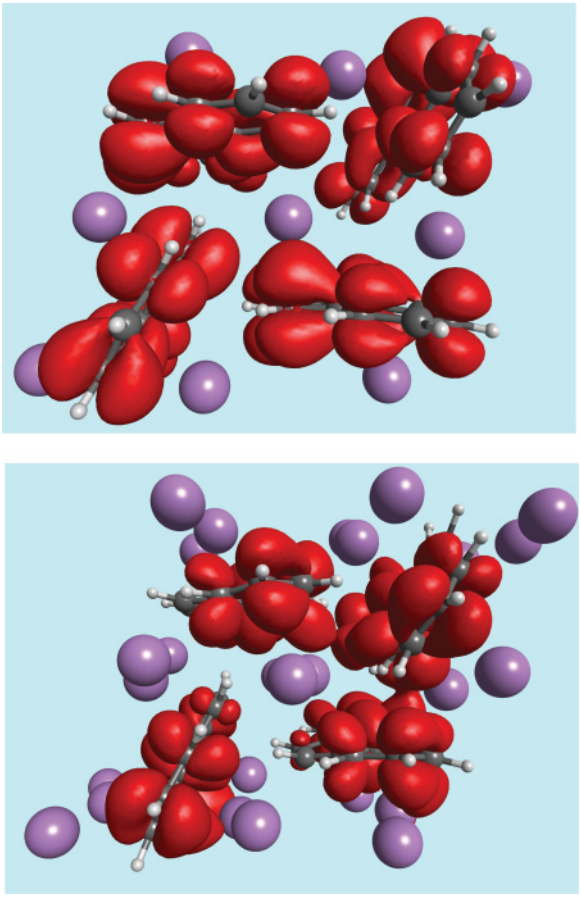

FIG. 4. (Color online) Total spin density for the quintuplet ground states of the four phenanthrene molecules clusters at doping levels 1 (upper panel) and 3 (lower panel). The contour level is 0.0008 $Å^{-3}$.

model on a honeycomb lattice by Sorella and Tosatti.[35] The transition occurs at half-filling for $U/t = 4.5 \pm 0.5$. In our case the value of U is large, $U/t = 4$, the lattice is bipartite, filling is somewhat above half-filling, and the PPP model Hamiltonian would reduce to the Hubbard one if intersite Coulomb repulsion were neglected. Nevertheless, our results have nothing to do with this transition since we are getting aligned spins on different molecules. Correlations among neighboring C sites are strongly antiferromagnetic but extra doping electrons add their spins. In fact, our results point to a ferromagnetic phase as the low temperature ground state of the extended system.

Let us finally comment on the previous study of correlation in crystalline K3picene by Giovannetti and Capone.[10] Certainly both systems share the same ingredients although picene molecules are sensibly larger than phenanthrene ones. Also DFT methods employed in both cases are quite similar. In their work, the authors compare the energies for several phases and conclude that antiferromagnetism is preferred although by a small energy advantage. We coincide with them in the importance of correlation for these systems, either molecular clusters or crystals but, based in our quantitative results, we favor ferromagnetism over antiferromagnetism.

IV. CONCLUDING REMARKS

Accurate calculations of doped potassium phenanthrene clusters obtained from the extended crystalline system show a clear tendency to align electronic spins in order to increase the spin multiplicity of their ground states when anionic charges are one or three per phenanthrene molecule. On the other hand, ground states corresponding to two extra electrons per phenanthrene do not show any tendency to spin alignment. A similar result was already reported in 2000 by Bock *et al.* for a tetrapotassium trianthracene crystal stabilized by THF (tetrahydrofuran).[37] A large calculated singlet-triplet splitting of 0.87 eV was obtained in this case.[38] Although it is a different system where cells interact very weakly, it shares with potassium intercalated phenanthrene the doping mechanism. In our opinion, it gives additional plausibility to our results. We have used an *ab initio* DFT method describing the whole system at the mean-field level and a new implementation of the Lanczos method applied to the PPP model that accurately describes the π-electron part of the system. Our numerical results show good consistency between these very different methods, pointing to a ferromagnetic phase of the crystal at $T = 0$ K for doping levels deviating from 2. Of course, a superconducting phase at low temperature cannot be excluded since a hypothetical formation of pairs by the simple electron-electron interaction has not yet been considered. Finally, electron-phonon interaction may play a role that we have not explored in this work, mostly focused on electron-electron effects.

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