Theory of metal-intercalated phenacenes: Why molecular valence 3 is special

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We develop a correlated-electron minimal model for the normal state of charged phenanthrene ions in the solid state, within the reduced space of the two lowest antibonding molecular orbitals of phenanthrene. Our model is general and can be easily extended to study the normal states of other polycyclic aromatic hydrocarbon superconductors. The main difference between our approach and previous correlated-electron theories of phenacenes is that our calculations are exact within the reduced basis space, albeit for finite clusters. The enhanced exchange of electron populations between these molecular orbitals, driven by Coulomb interactions over and above the bandwidth effects, gives a theoretical description of the phenanthrene trianions that is very different from previous predictions. Exact many-body finite cluster calculations show that while the systems with molecular charges of \(-1\) and \(-2\) are one- and two-band Mott-Hubbard semiconductors, respectively, molecular charge \(-3\) gives two nearly \(\downarrow\)-filled bands, rather than a completely filled lower band and a \(\downarrow\)-filled upper band. The carrier density per active molecular orbital is thus nearly the same in the normal state of the superconducting aromatics and organic charge-transfer solids, and may be the key to understanding unconventional superconductivity in these molecular superconductors.

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I. INTRODUCTION

Superconducting metal-intercalated polycyclic aromatic hydrocarbons (PAHs)\textsuperscript{1,\ldots,4}, discovered recently, constitute the third family of molecular carbon(C)-based superconductors, besides organic charge-transfer solids (CTS)\textsuperscript{5,6} and fullerides\textsuperscript{7,8}. Superconductivity (SC) has been detected from magnetic measurements in alkali metal (K, Rb)–intercalated picene, coronene, phenanthrene\textsuperscript{9} and dibenzopentacene (\(T_c > 30\) K)\textsuperscript{10}. Zero resistance has been confirmed in K\(_3\)-picene\textsuperscript{11}. Experiments in all cases reveal two rather remarkable observations, viz., (i) SC occurs in phenacenes (phenanthrene and picene) with “armchair” edges and PAHs with related structural motif, while it is absent in metal-intercalated acenes with linearly fused benzene rings, and, (ii) “doping” of nearly 3 electrons per PAH molecule is essential for SC. For example, in K-doped picene, hereafter K\(_x\)-picene, SC has been found both at “low \(T_c\)” of 7 K, and “high \(T_c\)” of 18 K in annealed samples. However, in samples produced from solutions only the 18 K superconductor is obtained with \(x\) lying within a narrow range of 2.9 – 3.1\textsuperscript{12}. Spectral shift measurements of molecular Raman modes have also indicated that the charge on the picene molecules at the superconducting compositions is nearly exactly \(-3\), independent of the nature of the metal ions. Very similar behavior is found in the metal-intercalated phenanthrenes\textsuperscript{13}. Observations of SC in nearly stoichiometric Ca\(_{1.5}\)-picene\textsuperscript{14}, Sr\(_{1.5}\) and Ba\(_{1.5}\) phenanthrene\textsuperscript{15} and, La- and Sm-phenanthrene\textsuperscript{16} have further confirmed the limitation of SC to ionic compounds with charges of \(-3\) on the PAH molecules. Raman spectral shifts in the doped phenanthrenes are independent of the metal ions, and again correspond to molecular charge \(-3\). Interestingly, the strong peaking of \(T_c\) at this particular doping is also shared by the fullerides\textsuperscript{17}.

The above observations place severe but obvious constraints on the correct theory of the normal states of charged phenacenes. Development of such a correct theory is the crucial first step to the future development of a theory of SC in these complex materials. There exist currently no theory of the normal state of the doped PAHs that explains both observations (i) and (ii) noted above. Doping of upto 3 electrons per molecule leads to occupancies of both the lowest unoccupied molecular orbital LUMO (L) and the next higher level LUMO+1 (L+1) by the doped electrons. A significant difference between acenes on the one hand, and phenacenes and coronene on the other, is that the single-particle energy gap between L and L+1, \(\Delta_{L,L+1}\), is much smaller in the second group of molecules (see Fig. 1 and Table I below), which immediately suggests that small \(\Delta_{L,L+1}\) is essential for SC. Indeed, density functional theory (DFT)-based band calculations for K\(_x\)-picene\textsuperscript{14,15,16} and K\(_x\)-phenanthrene\textsuperscript{18} find significant hybridization between the bands derived from the L and L+1 MOs; however, DFT calculations generally underestimate both \(\Delta_{L,L+1}\) and the gap \(\Delta_HL\) between the highest occupied molecular orbital, HOMO, and LUMO\textsuperscript{18}.

DFT-based band calculations have led to strong coupling BCS-based multi-band theories of SC for doped picene that emphasize band hybridization and, intermolecular\textsuperscript{19,20} and intramolecular\textsuperscript{21,22} electron-lattice vibration couplings. These theoretical formulations however do not give natural explanations for the absence of SC in the doped acenes; even in the absence of band overlap in these latter systems the same electron-phonon couplings should have driven SC, albeit at lower \(T_c\). Additionally, there is nothing unique about anions with charge \(-3\) within these theories. The observation of \(dT_c/dP > 0\) (where \(P\) = pressure) in high \(T_c\) K\(_x\)-picene\textsuperscript{18}, and in the superconducting phenanthrenes, with pressure coef-
efficient nearly independent of the cation in the lattice\textsuperscript{2,8,9}, also argues against the BCS approach.

Taken together, the above observations have led to the belief that PAH superconductors are unconventional, and SC may be driven by repulsive electron-electron (e-e) interactions. The interacting electron picture has received support from the observation of Mott-Hubbard semiconducting behavior in K\textsubscript{1}pentacene\textsuperscript{22}, in which \(\Delta_{L,L+1}\) is much larger than in the phenacenes (see Fig. 1 and Table I). Interacting electron theories that have been constructed for the doped acenes and phenacenes\textsuperscript{20–22,26}, however, still fail to explain the two crucial experimental observations completely. Taking the combined effects of the Hubbard \(U\) and nonzero \(\Delta_{L,L+1}\) into consideration, reference\textsuperscript{20} has concluded that K\textsubscript{3}picene in the normal state is a Mott-Hubbard semiconductor, with a completely filled L-band and a \(\frac{1}{2}\)-filled L+1-band. Very similar description is also obtained from calculations based on combined DFT and dynamical mean-field theory (DMFT), which have found antiferromagnetic semiconducting behavior for K\textsubscript{3}picene for all integer \(\pm 2\). These theories do not provide the correct starting point for any theory of SC in the trianions. Although mean field and DMFT calculations had found antiferromagnetic-to-SC transition within the frustrated \(\frac{1}{2}\)-filled Hubbard band model in the past\textsuperscript{23–26}, more recent numerically precise calculations, using a variety of techniques, have universally found absence of SC within this model\textsuperscript{27–32}. From an experimental perspective, the absence of SC in the Mott-Hubbard semiconductor K\textsubscript{1}pentacene\textsuperscript{29} confirms the theories that predict absence of SC within the \(\frac{1}{2}\)-filled band Hubbard model. \(\Delta_{L,L+1}\) approaching zero in picene, as has been recently suggested\textsuperscript{33}, does not provide a solution either, both because such tiny \(\Delta_{L,L+1}\) is improbable (see below), and also because this once again fails to explain the specific role of molecular charge of \(-3\).

To summarize, we are faced with a conundrum. Electron-phonon coupled models predict metallic behavior for all molecular charges, including \(-2\) which is known to exist experimentally, and therefore cannot explain the restriction of SC to molecular charge \(-3\). Models incorporating e-e interactions predict semiconducting behavior at all integer charges. There is thus an obvious need for the development of a correct theory of the normal state of the doped phenacenes and coronene, which can at least provide the starting point for a plausible theory of correlated-electron SC in these systems. In the present paper, we develop a correlated-electron minimal model for lattices of PAH anions that can explain both the crucial observations we have made in the above. Our approach is general and applicable to both phenacenes and acenes (see Appendix). For the specific case of phenanthrene ions we show from exact many-body cluster calculations that while crystals with molecular charges of \(-1\) and \(-2\) are indeed one- and two-band Mott-Hubbard semiconductors, in agreement with previous work\textsuperscript{1,22}, crystals of trianions consist of two nearly \(\frac{3}{4}\)-filled bands, even with realistic \(\Delta_{L,L+1} \geq 0.2\) eV. This specific band-filling is also characteristic of superconducting CTS\textsubscript{2}, as well as, a variety of apparently unrelated inorganic superconductors\textsuperscript{34–37}. One of us and colleagues have shown that precisely at this band-filling there is a strong tendency to form a correlated-electron spin singlet-paired semiconductor\textsuperscript{36–37}, which may undergo semiconductor-supercorner transition\textsuperscript{38}. While the theory of semiconductor-supercorner transition within the model constitutes ongoing research, examples of the spin-paired semiconductor already exist and our present results give additional credence to the theory.

In section II we present our theoretical model of PAH anions, starting from an atomic basis of \(\pi\) electrons on the carbon atoms of the molecules. We include the Hubbard repulsion between the \(\pi\)-electrons at the outset, and thus our approach is different from theories that “graft on” e-e interactions to band theoretical results. Starting from this fundamental atomic basis we derive an exact effective Hamiltonian in the reduced space of L and L+1 MOs. The effective Hamiltonian contains a term involving two-electron hops that has been ignored in previous correlated-electron models of phenacenes\textsuperscript{20–22,26}, but should not be ignored for small \(\Delta_{L,L+1}\), for the sake of completeness. However, as we demonstrate later, the effects of this off-diagonal Coulomb interaction on MO populations is weak compared to that due to diagonal density-density Coulomb terms. As is shown numerically in section III, the two-band \(\frac{3}{4}\)-filled nature of the trianion system is a consequence of co-operation between bandwidth and correlation-induced effects. Physical, intuitive reasonings that explain the mechanism of the electron population exchange between the MOs, and detailed understanding of the numerical results, are presented in the Appendix. In section IV, we summarize our conclusions and discuss a plausible (albeit incomplete) theory of correlated-electron SC in the PAH superconductors in the context of previous work\textsuperscript{1,36–38}. We also briefly discuss the antiferromagnetic-to-SC transition in Cs\textsubscript{3}C\textsubscript{60}\textsuperscript{39–41} from the perspective of the present results.

II. THEORETICAL MODEL: COMPLETE AND REDUCED BASIS SPACES.

We derive and study a model Hamiltonian describing the normal state of lattices of PAH or acene anions. The dopant metal ions are not included explicitly in the Hamiltonian. Justification for ignoring the metal ions comes from the nearly universal behavior of the intercalated phenanthrenes and picenes, independent of the metal ions\textsuperscript{1,2,8}. In particular, antiferromagnetic ordering of Sm\textsuperscript{3+} ions in Sm-phenanthrene at \(T_N \sim 15\) K, and the coexistence of SC with this antiferromagnetic ordering\textsuperscript{2} indicates the weak role of the metal ions. In agreement with the DFT calculation\textsuperscript{10,14} we assume that there occurs a homogeneous distribution of the ions in the actual materials, and in addition to donating electrons, they also enhance the intermolecular hoppings rel-
ative to the pristine systems by creating chemical pressure. We write the minimal many-body Hamiltonian for the organic ions in the solid state as

$$H = H_{\text{intra}}^{1e} + H_{\text{intra}}^{ee} + H_{\text{inter}}^{1e}$$  \hspace{1cm} (1)$$

where $H_{\text{intra}}^{1e}$ and $H_{\text{intra}}^{ee}$ are the one-electron and many-electron components of the intramolecular Hamiltonian, and $H_{\text{inter}}^{1e}$ is the intermolecular hopping. The individual terms are written as,

$$H_{\text{intra}}^{1e} = -\epsilon \sum_{\mu,i} n_{\mu,i} - t \sum_{\mu,(i)\sigma} c_{\mu,i,\sigma}^\dagger c_{\mu,j,\sigma}$$  \hspace{1cm} (2)$$

$$H_{\text{intra}}^{ee} = U \sum_{\mu,i} n_{\mu,i} n_{\mu,i}$$  \hspace{1cm} (3)$$

$$H_{\text{inter}} = \sum_{\mu\neq\nu,i,j} t_{\mu,\nu,i,j} c_{\mu,i,\sigma}^\dagger c_{\nu,j,\sigma}$$  \hspace{1cm} (4)$$

In the above $c_{\mu,i,\sigma}^\dagger$ creates a $\pi$-electron of spin $\sigma$ in the $p_z$ orbital of the $i$-th C-atom of the $\mu$-th molecular ion, $n_{\mu,i,\sigma} = c_{\mu,i,\sigma}^\dagger c_{\mu,i,\sigma}$, and $n_{\mu,i} = \sum_{\sigma} n_{\mu,i,\sigma}$; $t$ and $U$ are the nearest neighbor intramolecular hopping integral and effective repulsion between two electrons occupying the same $p_z$ orbital, respectively, and $t_{\mu,\nu,i,j}$ is the intermolecular hopping between C-atoms $i$ and $j$ of molecules $\mu$ and $\nu$. We have not included the interatomic Coulomb repulsions in $H_{\text{intra}}^{ee}$ and $H_{\text{intra}}^{ee}$. This does not lead to loss of generality. The effects due to the intramolecular interatomic interactions can be included in the effective onsite repulsion $U$, while the intermolecular interatomic interactions play a negligible role in what follows and can be incorporated at a later stage in the search for a theory of SC if so desired, without loss of generality. The primed sum in the site-energy dependent term in Eq. 2 is restricted to C-atoms without C-H bonds, accounting for their larger electronegativity relative to the other C-atoms.

The atomic basis space is complete, but the Hamiltonian is clearly unsolvable because of its very large dimension. We rewrite the Hamiltonian in the MO basis, from which we then derive a reduced Hamiltonian in the space of L and L+1 MOs of the phenacene ions. In this we use the standard approach of molecular exciton theory, and ignore one-electron as well as many-electron matrix elements involving widely separated MOs. Given the relatively small $\Delta_{L,L+1}$, however, Coulomb matrix elements involving two-electron hops between L and L+1 cannot be ignored, and this is where we differ from previous correlated-electron models of phenacenes.

The first step in constructing the effective Hamiltonian in the MO basis is to solve $H_{\text{intra}}^{1e}$ exactly,

$$H_{\text{intra}}^{1e} = \sum_{\mu,k,\sigma} E_k a_{\mu,k,\sigma}^\dagger a_{\mu,k,\sigma}$$  \hspace{1cm} (5)$$

Here $a_{\mu,k,\sigma}^\dagger$ corresponds to the $k$th MO of the $\mu$th molecule. In Fig. 1 we show the highest few bonding and lowest few antibonding MOs that are obtained as solutions to $H_{\text{intra}}^{1e}$ with $\epsilon = 0$ and the same $t$ for all the molecules included in the Figure. As mentioned above $\Delta_{L,L+1}$ in phenanthrene and picene are much smaller than those in anthracene and pentacene, respectively, $\Delta_{L,L+1} = 0$ in coronene, but is expected to be small but nonzero if the Jahn-Teller effect due to interactions of electrons with molecular vibrations are included. Correspondingly, $\Delta_{HL}$ in the phenacenes and coronene are much larger than in the acenes. Table 1 gives the numerical values of these gaps, along with the gap $\Delta_{L+1,L+2}$ between LUMO+1 and LUMO+2 in units of $|t|$, which we have taken to be 2.4 eV. Note however that $\Delta_{L,L+1}$ in phenanthrene (picene) is about 25% (50%) of that in anthracene (pentacene). Thus recent calculations that find tiny $\Delta_{L,L+1}$ (0.04 eV) for picene along with very large $\Delta_{L,L+1}$ for pentacene (1.26 eV) are unrealistic, and cannot be obtained within $H_{\text{intra}}^{1e}$ without assuming widely different $|t|$ for these molecules.

| Molecule       | $\Delta_{L,L}$ | $\Delta_{L,L+1}$ | $\Delta_{L+1,L+2}$ |
|----------------|----------------|-------------------|-------------------|
| Phenanthrene   | 1.210          | 0.164             | 0.373             |
| Anthracene     | 0.828          | 0.586             | 0.000             |
| Picene         | 1.004          | 0.178             | 0.179             |
| Pentacene      | 0.439          | 0.398             | 0.382             |
| Coronene       | 1.078          | 0.000             | 0.461             |

$H_{\text{intra}}^{ee}$ and $H_{\text{inter}}^{1e}$ are now expressed in terms of these
localized MOs $a_{\mu,k,\sigma}^\dagger$

$$H_{\text{intra}}^e = U \sum_{\mu,k,k',i} |\chi_{\mu,i,k}|^2 |\chi_{\mu,i,k'}|^2 N_{\mu,k,\uparrow} N_{\mu,k',\downarrow} +$$
$$\sum_{\mu,k_1 \neq k_2, k_3 \neq k_4, i} \left( \prod_{i=1}^4 \chi_{\mu,i,k_i} a_{\mu,k_1,\uparrow} a_{\mu,k_2,\uparrow} a_{\mu,k_3,\downarrow} a_{\mu,k_4,\downarrow} \right)$$

(6)

$$H_{\text{inter}}^e = \sum_{\mu \neq \nu, k_1, k_2, \sigma} \chi_{\mu,i,k_1} \chi_{\nu,j,k_2} t_{\mu,\nu,i,j} a_{\mu,k_1,\sigma} a_{\nu,k_2,\sigma}$$

(7)

Here the $\chi$ and $\psi$ matrices are inverses of one another, $N_{\mu,k,\sigma} = a_{\mu,k,\sigma}^\dagger a_{\mu,k,\sigma}$, and we define $t_{k_1,k_2} = \sum_{i,j} \chi_{\mu,i,k_1} \chi_{\nu,j,k_2} t_{\mu,\nu,i,j}$.

The above transformation is exact. We now note that the intermolecular hoppings are tiny relative to the HOMO-LUMO gaps of both acenes and phenacenes, and do not affect the occupations of the bonding MOs or the high energy antibonding MOs. The reduced Hamiltonian $H_{L,L+1}$ is therefore obtained by restricting the sums over the $k$'s in Eq. (6) and (7) to $L$ and $L+1$, with $E_{L+1} - E_L = \Delta_{L,L+1}$. In what follows, we will distinguish between the diagonal density-density dependent terms of $H_{\text{intra}}^e$ which we write as $H_{\text{intra}}^{ee}$, and the off-diagonal terms involving two-electron hops between MOs, which we write as $H_{\text{inter}}^{ee}$. $H_{\text{inter}}^{ee}$ consists of three distinct terms, $U_{L,L}$, $U_{L,L+1}$, and $U_{L+1,L+1}$, given by,

$$U_{L,L} = \sum i |\chi_{\mu,i,L}|^2 |\chi_{\mu,i,L}|^2$$

(8)

$$U_{L,L+1} = \sum i |\chi_{\mu,i,L+1}|^2 |\chi_{\mu,i,L+1}|^2$$

(9)

$$U_{L+1,L+1} = \sum i |\chi_{\mu,i,L}|^2 |\chi_{\mu,i,L}|^2$$

(10)

where $U_{L,L}$ and $U_{L+1,L+1}$ are the repulsions between two electrons occupying $L$ and $L+1$, respectively, and $U_{L,L+1}$ is the repulsion between electrons of opposite spins occupying different MOs of the same molecule. As shown in Fig. 2(d), $H_{\text{inter}}^{ee}$ consists of two kinds of terms, both proportional to $U_{L,L+1}$.

III. COMPUTATIONAL APPROACH AND RESULTS.

While our theoretical formulation in section II is general, we have performed numerical calculations explicitly for phenanthrene and anthracene ions only, as the computations quickly become unmanageably large and complex for the larger molecules. We discuss picene and coronene in the Appendix. In Fig. 2(b) we show the simplified two-dimensional (2D) herringbone structure of the doped phenanthrene crystal we consider. We retain intermolecular hoppings $t_{k_1,k_2} = t_{k_1,k_2}$ for $|\mu-\nu| = j = 1, 2$ and $k_1,k_2 = L, L+1$, labeled $t_1$ and $t_2$ in Fig. 2(b). The terms $t_{L,L+1}$ in Fig. 2(c) appear naturally in Eq. (7) and are responsible for the hybridization between $L$ and $L+1$-derived bands found in DFT calculations. Fig. 2(d) shows the effect of $H_{\text{intra}}^{ee}$ on many-electron configurations. Here $\Delta_{L,L+1} = 0.16|t|$ for phenanthrene for $\epsilon = 0$ and is even smaller for realistic $\epsilon > (21)$. In contrast, $\Delta_{L,L+1}$ in anthracene is much larger at 0.59|t| (see Table 1).

The parameters of the reduced Hamiltonian are the intramolecular $\Delta_{L,L+1}$ and e-e interactions, and the multiple intramolecular hopping integrals. The first two are obtained from molecular calculations, while we parameterize the intermolecular hoppings based on the existing literature on the CTS. Justification for the latter assumption comes from the comparable or even larger superconducting $T_c$ in the phenacenes than in the CTS. We then perform exact calculations within our reduced Hamiltonian for clusters of phenanthrene ions with charges of $-1$, $-2$ and $-3$, and show that there exists a realistic parameter range ($\Delta_{L,L+1} > 0.2$ eV) wherein crystals consisting of mono and dianions of phenanthrene are one- and two-band Mott-Hubbard semiconductors, while crystals of trianions are two-band systems with electron density per localized $L$ $(n_L)$ and $L+1$ $(n_{L+1})$ close to $\frac{3}{2}$. Restriction of the parameter range to realistic $\Delta_{L,L+1} > 0.2$ eV is necessary, since for smaller $L$-$L+1$ gap the difference between mono and trianions ceases to exist, and both mono and tri anions behave as two-band systems with $n_{L+1}/n_L \sim \frac{1}{2}$ and $\frac{3}{2}$, respectively.

Exact calculations with $U \neq 0$ are not possible for the 2D lattice of Fig. 2(b). Our 2D calculations are therefore for the $U = 0$ limit. We choose the standard intramolecular $|t|$ of 2.4 eV (22), for which $\Delta_{L,L+1} = 0.4$ eV at $\epsilon = 0$. Although complete band structure calculations are possible within Eqs. (5) and (7) for $U = 0$, we perform exact numerical calculations within the localized description because, (a) the $U \neq 0$ calculations in 1D reported below are based on the localized basis, and, (b) only by considering both zero and non-zero $U$.
FIG. 3: (Color online) Ratio of electron populations in L+1 and L, versus different hopping integrals, for a periodic 2D lattice of noninteracting electrons, with 20×20 sites (molecules), and ΔL,L+1 = 0.4 eV.

results together, the co-operative effects of intermolecular hopping and Coulomb interactions are fully revealed. We have calculated numerically exact nL and nL+1, the average L and L+1 occupations, respectively, for a periodic lattice of 20 × 20 molecules (40 × 40 MOs) for many different sets of tLk1,k2. In the absence of crystal structure information we did not attempt to determine the tLk1,k2 from first principles. Rather, our chosen values are comparable to known hopping integrals in the CTS35 as already mentioned. We report computational results for multiple sets of tLk1,k2, maximum values of which are, tL,L = 0.15 eV, tL+1,L = 0.05 eV, tL+1,L+1 = 0.10 eV; tL+1,L+1 = 1/2 tL,L, tL+1,L = 1/2 tL,L+1. For each (k1, k2) pair we vary the two tLk1,k2 simultaneously, keeping the four other hopping integrals fixed at their maximum values.

In Figs. 3(a)–(c) we report the computational results for all molecular charges −1, −2 and −3, respectively. The monanions continue to have all electrons in the LUMOs, independent of electron hoppings (except in the limit of tL → 0, where nonzero tL,L+1 promotes a few electrons from L to L+1). In both the di and the trianion, there is a strong enhancement of L+1 population. The different behavior of the monanions on the one hand, and di and trianions on the other, stem from the overlap between L- and L+1-derived bands, as demonstrated in the Appendix. As explained there, for all realistic Δ that is neither too small nor as large as in anthracene, this difference will persist.

We now demonstrate that e-e interactions further enhance the L+1-populations in the di and trianions, over and above the bandwidth-driven effect shown in Fig. 3. This is done in 1D. The 1D lattice we consider is shown superimposed on the 2D lattice in Fig. 3(a). Band structure calculations for K3picene using very similar 1D and 2D lattice motifs give essential features that are nearly the same34, justifying our choice of the 1D lattice. Our calculations are within the interacting electron Hamiltonian of Eqs. (6) and (7), for periodic 1D clusters of 6 and 8 molecules (12 and 16 MOs) for all three molecular charges, and 10 molecules (20 MOs) with molecular charges −1 and −3 only. The 10-molecule calculation with molecular charge −2 (20 electrons on 20 MOs) is beyond current computational capability. Numerical results for 8 and 10 molecules are identical for mono and trianions. The calculations are done again with parameterized hopping integrals. However, we evaluated the effective e-e interactions using Eq. (6), which gives ULL,L+1 ∼ 0.115U, ULL+1,L+1 = 0.114U and ULL,L+1 = 0.044U. For realistic atomic U = 8−10 eV32, ULL,L ∼ ULL+1,L+1 ∼ 1 eV, close to other estimates30.

Our calculations of the finite clusters at nonzero U are done using the many-body valence bond method of reference33. Calculations for all ionic charges were checked by comparing the results of the valence bond method at U = 0 against the simple tight binding approach. In Figs. (a) and (b) we show our numerical results for 10-molecule clusters of mono and trianions, and the 8-molecule cluster of dianions, for hopping parameters corresponding to the maximum values of Fig. 3. MO populations of the dianion change drastically with U, with equally populated L and L+1 MOs reached at large U. As is shown in the Appendix, this moderate to large enhancement (depletion) of L+1 (L) electron density is driven by Hee. In Fig. 3(a) there is no U-dependence of the MO populations for the monoanion and the trianion. However, electrons in the monanion again occupy only the L, while trianion is multi-band. Fig. 3(b) differs from 3(a) only in having ε = 0.65 eV (0.27|t|), which reduces ΔLL+1 to 0.3 eV. All other parameters are the same. Even with this very slight reduction in ΔLL+1, the consequences for the trianion are dramatic. Over and above the bandwidth-driven enhancement in nL+1 for U = 0, further enhancement is seen for nonzero U, with nL+1 approaching nL. As shown in the Appendix, this is a cooperative effect, driven both by the bandwidth and Hee.

We have found results similar to those in Figs. 3 and 4 for a wide range of hopping parameters (see Appendix, section C). The minimal requirement for nL ∼ nL+1 in the di and trianions appears to be tLL ∼ tL+1,L+1 ≥ 0.1 eV, with tL +1,L+1 about this value, and second neighbor hoppings close to half the nearest neighbor values. For too small ΔLL+1 the distinction between the mono and the trianion disappears (as noted in the Appendix, rigid bond calculations in such cases would be inappropriate). We emphasize that the parameter range we have considered is very close to those used previously, despite some seeming differences. Thus ΔLL+1 much smaller than ours10, as well as nearly the same as ours20, have been calculated for doped picene. In general, L-L+1 band gaps obtained from DFT calculations are smaller compared to our ΔLL+1. However, our intermolecular hopping parameters give an overall bandwidth that is
close to the upper value calculated for doped picene by Subedi and Boer.

Fig. 1 suggests that a lattice of phenanthrene monoanions is a one-band Mott-Hubbard semiconductor with the L (L+1) band \( \frac{1}{2} \)-filled (empty). The dianions behave as either weakly correlated one-band semiconductor or two-band Mott-Hubbard semiconductor. In contrast, a lattice of phenanthrene trianions is two-band, with filling close to \( \frac{1}{2} \) in each band for moderate \( \Delta_{L,L+1} \) and \( U \) [as in Fig. 1(b)]. It is interesting to note that in Reference 21 which had presented an effective \( \frac{1}{2} \)-filled band model \( (n_{L+1} = 1) \) for K$_3$picene, the authors had speculated that “a more accurate treatment of electron-electron correlations may revive” the possibility that K$_3$picene should be described as a “\( \frac{1}{2} \)-filled two-band system.”

We have calculated spin-spin correlation functions at large \( U \) for all three molecular charges. In Fig. 5 we show our results for the parameters of Fig. 1(b). Both the monoanion and the dianion show strong intraband intramolecular antiferromagnetic spin-spin correlations. Notice the ferromagnetic intramolecular correlations in the dianion. As shown in the Appendix, the intramolecular ferromagnetic correlations and the enhanced \( n_{L+1}/n_L \) in the dianion are intimately related.

The spin-spin correlations for the trianion, in contrast to the other cases, do not indicate any ordering, as is to be expected for the frustrated lattice with non-integral occupancies of the MOs.

The above calculations were repeated for clusters of anthracene ions, and as may be expected from the large \( \Delta_{L,L+1} \), both mono and trianions are Mott-Hubbard semiconductors now (see Appendix). The uniqueness of crystals of trianions of phenanthrene comes from their having \( n_L \sim n_{L+1} \sim \frac{3}{2} \), which must be a requirement for SC (see next section). This is a stronger criterion than having merely multi-band electronic structure, which is certainly reached at molecular charges \(-2\) and slightly greater values, where however SC is not observed.

IV. CONCLUSIONS AND DISCUSSIONS

We have derived an effective model for crystals of acene and phenacene ions within the reduced basis space of L and L+1 orbitals, and performed exact calculations within this basis space for clusters of mono, di and trianions, for both atomic \( U = 0 \) and nonzero \( U \). We find that clusters of trianions of phenanthrene are indeed spec-
cial, in agreement with what is observed experimentally. With realistic $\Delta_{L,L+1} > 0.2$ eV, the electronic population per antibonding MO per molecule in this case is $\sim \frac{3}{2}$.

Our determination that $n_L \simeq n_{L+1} \simeq \frac{3}{2}$ in the trianions of PAH suggests that the mechanism of SC in the PAH and the CTS are related. Although conducting CTS in general can have a wide range of carrier concentration $C$, concentration per antibonding MO per molecule in this case is $\sim \frac{3}{2}$.

The ambient pressure antiferromagnetism in this material is explained within a theory that incorporates both the Jahn-Teller electron-molecular vibration coupling and the Hubbard $U$. The Jahn-Teller distortion lifts the three-fold degeneracy of the $C_{60}$ LUMOs, which split into a lowest doubly occupied MO, a singly occupied MO at intermediate energy, and a vacant MO at the highest energy. Antiferromagnetism is described as the intermolecular spin-spin coupling between the unpaired electrons occupying the nondegenerate singly occupied MOs. Capone et al. have performed DMFT calculations within the $\frac{1}{2}$-filled band Jahn-Teller-Hubbard model, and have proposed that pressure-induced increased bandwidth leads to intramolecular pairing of electrons. This conclusion is in apparent disagreement with theoretical work showing the absence of SC within the $\frac{1}{2}$-filled band (the latter however do not include Jahn-Teller distortion). An alternate explanation of the antiferromagnetic-to-SC transition can be given within our approach, wherein the antiferromagnet at ambient pressure is indeed effective $\frac{1}{2}$-filled, but the pressure-induced increase in bandwidth leads to equalization of the electron population among the two lowest occupied MOs (as would occur in trianions of coronene within our theory, see Appendix). SC in this case would again be related to MO populations of $\frac{1}{2}$ in two different MOs, and the pairing is intermolecular. We are unaware of any experiment that would preclude our proposed mechanism.

To conclude, the trianions of phenacenes are indeed special, with LUMO and LUMO+1 electronic populations of nearly $\frac{3}{2}$ each. The asymmetry between the mono and the trianions is strongly dependent on the cooperative interaction between the bandwidth, $\Delta_{L,L+1}$ and $U$. For too large $\Delta_{L,L+1}$ (as in anthracene), as well as for unrealistically small $\Delta_{L,L+1}$, this asymmetry vanishes, and molecular charge $-3$ is no longer special. We have proposed that SC is a consequence of this specific carrier concentration per active MO. Although further work is necessary to actually demonstrate the transition to the superconducting state, the attractiveness of this proposal comes from its potential ability to explain SC in all three families of carbon-based superconductors within a single theoretical approach.

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VI. APPENDIX

A. Mechanism of the valence-dependent electron population exchanges

In the following we give physical, intuitive explanations of the different behavior of the three ionic charges, supported by additional numerical calculations. Although our discussions are general, we focus largely on the parameters of Fig. 4(b), for the sake of illustration only.
We discuss band effects \((U = 0)\) and effect of electron-electron interactions \((U \neq 0)\), separately.

**A.1. Band Effects \((U = 0)\):** We have calculated numerically the one-electron eigenspectra within \(H_{\text{inter}}^{1e}\) (Eq. 7) for lattices of 10 and 20×20 phenanthrene molecules. In Figs. (a) and (b) we show the L and L+1 characters of the resulting one-electron eigenstates. The one-electron energy levels have been numbered in increasing order of energy. For clarity, degenerate levels are given consecutive indices. The similarity of the plots in (a) and (b) indicates that beyond a threshold size (which has already been reached at 10 molecules in 1D), band effects in 1D and 2D are same. Each eigenstate has both L and L+1 character, the normalized relative weights of which depend on both \(\Delta_{L,L+1}\) and intermolecular hoppings. As indicated in the figures, for the parameters of Fig. (b), the eigenstates are either predominantly L or predominantly L+1. Importantly, while in the lowest energy region the bands are predominantly L-derived, at higher energies there is overlap between the L- and L+1-derived eigenstates. It is easily ascertained that by filling these levels sequentially, only the L-derived bands are occupied in the monoanions (the lowest 5 MOs accommodate all 10 electrons in the 10-molecule monoanion cluster and the lowest 200 accommodate all 400 electrons in the 20×20 lattice). Hence \(n_L = 1\) here, as calculated in Figs. 3 and 4(b). Switchings in the L- and L+1-characters occur at slightly higher energy, even as the bands retain their predominantly L- and L+1-characters. Sequential occupancy of the MOs in the di- and trianions involve filling of both the lowest L- and L+1-derived eigenstates, such that \(n_L < 2\) and \(n_{L+1} > 0\) (MOs up to the 10th and the 400th are occupied in the 1D and 2D lattices now). The same band overlap effect (as seen from Fig. 6) leads to \(n_L < 2\) and \(n_{L+1} > 1\) in the trianion. We emphasize that we have performed the 1D \(U = 0\) calculations using both the tight-binding approach and the valence bond approach we used for \(U \neq 0\), and in all cases the calculated \(n_L\) and \(n_{L+1}\) are identical. Thus, the band structure effects alone makes the monoanion different from the di- and trianions.

**A.2. Effect of e-e interactions \((U \neq 0)\):** For nonzero \(U\), our discussions will be in the localized representation which is more appropriate.

**Monoanion.** We have seen in the above that finite intermolecular hopping has no effect on the orbital occupancies in the monoanion for realistic \(\Delta_{L,L+1}\). The effect of nonzero \(U\) is merely to localize the electrons occupying the L orbitals. The system is a one-band Mott-Hubbard semiconductor as seen from spin-spin correlations in Fig. (a). For the other ionic charges, especially for the trianion, we will see that \(U\) enhances the bandwidth-induced population exchange in a highly cooperative fashion.

**Dianion.** In Fig. 6 we have given a schematic path in configuration space between the two extreme configurations, with \([n_L = 2, n_{L+1} = 0]\) and \([n_L = n_{L+1} = 1]\), for the case of four molecules, for illustration. Each step in the path constitutes one individual electron hop induced by \(H_{\text{inter}}\). Similar paths exist in the infinite solid, both in 1D and 2D. The band calculations in section A.1 indicate that even at \(U = 0\) the quantum mechanical wavefunction is not described by \(i\) alone, but has contributions from configurations \(\Pi\) and higher. The diagonal matrix elements of \(H_{L,L+1}\), shown in the Table, decrease from \(I\) through \(V\) for atomic \(U > 2\), as a consequence of which the ground state wavefunction gravitates further towards \(V\) with increasing \(U\). At \(U_{LL} \simeq U_{L+1,L+1} \sim \Delta_{L,L+1}\), the transition to \(V\) is complete, as seen in Figs. 4(a) and (b). We have performed analysis of the exact ground state wavefunction in Fig. 8 for the parameters of Fig. 4(b) to illustrate this. We write the ground state wavefunction of the phenanthrene di-anions as \(\Psi = \sum_{\nu,j} A_{\nu,j} |\phi_{\nu,j}\rangle\), where \(|\phi_{\nu,j}\rangle\) are the many-electron configurations and \(\sum_{\nu,j} |A_{\nu,j}|^2 = 1\). The index \(\nu = 1 - 4\) classifies \(|\phi_{\nu,j}\rangle\) into four classes based on their L and L+1 populations. \(\nu = 1\) and 2 refer to all configurations with integer \(\frac{n_L+n_{L+1}}{n_L} = 0\) and 1, respectively, while, \(\nu = 3\) and 4 correspond to configurations with fractional \(\frac{n_L+n_{L+1}}{n_L} < 1\) or \(> 1\), respectively. The total weight of configurations of each class in \(\Psi\) is defined as \(C_{\nu} = \sum_{j} |A_{\nu,j}|^2\). As seen in Fig. 8 the wavefunction is dominated by configurations with \(\nu = 3\) at small \(U\) including \(U = 0\), in agreement with the fractional \(\frac{n_L+n_{L+1}}{n_L}\) seen from the band calculations. A switching of the ground state occurs at the same \(U\) where the jump in \(\frac{n_L+n_{L+1}}{n_L}\) occurs in Fig. 4(b), indicating that the ground state is dominated by configurations of type \(V\).

**Trianion.** The case of the trianion is more subtle than either the monoanion or the dianion. We have repeated our exact calculations of Fig. 8(b) by (i) switching off the two-electron hops \(H^{ee}_g\) between the MOs but leaving \(H^{ee}_d\) and (ii) the exact opposite: switching off \(H^{ee}_d\)
but retaining $H_{od}^{f}$. We show the results of our calculations in Fig. 9(a). Surprisingly, the enhancement of $n_{L+1}$, seen in Fig. 9(b), appears to be driven almost entirely by the diagonal interactions $H_{d}^{f}$. The two-electron hop $H_{od}^{f}$ has a non-negligible but weaker effect when $H_{d}^{f} = 0$, and has no role when $H_{d}^{f} \neq 0$. We explain these apparently counterintuitive observations below.

Extending our discussion of the dianion in terms of many-electron configurations within the localized description, we have shown in Fig. 10 again for four molecules, the competing configurations with $n_{L} = 2, n_{L+1} = 1$] and $[n_{L} = n_{L+1} = 1.5]$. As in Fig. 9, we have given the diagonal matrix elements of $H_{L,L+1}$ for each configuration. Note that except for configuration $I$, all other configurations have identical matrix elements for the $e-e$ interaction terms, and are coupled through $H_{ee}^{t}$. Our band calculations (Figs. 3 and 6) show that the kinetic energy gain from the electron hopping already drives $2n_{L+1}$ to greater than 0.5. The important points now are the following: (i) the one-electron hops involving the L+1-electrons of $I$ necessarily create additional double occupancies and are suppressed by $U$. (ii) In contrast, even as one-electron hops that create additional double occupancies in $II - V$ are also suppressed at finite $U$, there also exist one-electron hops that conserve the number of double occupancies. These are suppressed only weakly by $H_{d}^{f}$, and can therefore still couple the set of configurations with $[n_{L} = n_{L+1} = 1.5]$, as shown in Fig. 10. The number of such double occupancy conserving hops are the largest when $n_{L} = n_{L+1}$, and hence the additional relative kinetic energy gain at nonzero $U$ drives the system towards this population ratio.

We demonstrate the validity of this argument from our exact calculation of the expectation values of the kinetic energies,

$$K_{L} = \sum_{\mu,\sigma} \left( t_{1}^{L,L}(a_{\mu,L,\sigma}^\dagger a_{\mu+1,L,\sigma} + \text{H.C.}) + t_{2}^{L,L}(a_{\mu+1,L,\sigma}^\dagger a_{\mu+2,L,\sigma} + \text{H.C.}) \right), \quad (11)$$

$$K_{L+1} = \sum_{\mu,\sigma} \left( t_{1}^{L+1,L+1}(a_{\mu,L+1,\sigma}^\dagger a_{\mu+1,L+1,\sigma} + \text{H.C.}) + t_{2}^{L+1,L+1}(a_{\mu,L+1,\sigma}^\dagger a_{\mu+2,L+1,\sigma} + \text{H.C.}) \right), \quad (12)$$

corresponding to the parameters of Fig. 4(b). We show
the results of these calculations in Fig. 8(b). There are two significant observations. First, while at $U = 0$, $K_{L+1}$ dominates over $K_L$, as is expected for $n_{L+1}$ only slightly larger than 0.5, for all $U \neq 0$, $K_{L+1} \simeq K_L$ in agreement with $n_L \simeq n_{L+1} \simeq 1.5$. Secondly, and more importantly, the sum $K_L + K_{L+1}$ not only shows a jump at small $U$ but is actually larger at all nonzero $U$ values in Fig. 8(b) than at $U = 0$, in precise agreement with our argument that the equal probability of $L$ and $L+1$ is given for the $\Delta_{L,L+1}$ expected in phenanthrene.

We now address the role of the $H_{ee}^{\sigma}$. In Fig. 11, we have constructed paths connecting the extreme configurations $n_L = 2$; $n_{L+1} = 1$ and $|n_L = n_{L+1} = 1.5|$, for the case of two molecules. The attached Table gives the diagonal matrix elements of $H_{L,L+1}$. Each step in the paths $I \rightarrow IIa \rightarrow IV$ and $I \rightarrow IIb \rightarrow IV$ again constitutes a single-electron hop, and the paths are equally probable at $H_{ee}^{\sigma} = 0$. From the Table, the energies of the intermediate and final configurations along both paths are larger by $\Delta_{L,L+1}$ at $U = 0$. The path $I \rightarrow IIb \rightarrow III \rightarrow IV$ involves two-electron hops and is relevant only for $H_{ee}^{\sigma} \neq 0$. Because of this additional channel, for $H_{ee}^{\sigma} = 0$ there can be enhancement in $\frac{n_L^{T}}{n_L^{L+1}}$ as seen in Fig. 9(a). The enhancement is however weak, for two reasons: (i) The competing paths not involving two-electron hops are shorter, and (ii) the diagonal energy of configuration $III$ is higher by $2\Delta_{L,L+1}$ at $U = 0$. Both (i) and (ii) make the path involving two-electron hops costly relative to the competing paths. Although our illustration is for the case of two molecules, the same difference between paths involving and not involving two-electron hops persist in larger systems. The role of $H_{ee}^{\sigma}$ in the limit of $H_{ee}^{\sigma} = 0$ is both relatively weak and complicated, and determined by the detailed values of hopping parameters, $\Delta_{L,L+1}$ and $U$. For $H_{ee}^{\sigma} \neq 0$ there is a new effect that makes channels involving two-electron hops even less competing. As seen from Fig. 11, the intermediate configuration $III$ is now at even higher diagonal energy because of the additional double occupancy. This explains why when both $H_{ee}^{\sigma}$ and $H_{ee}^{\sigma}$ are nonzero, $H_{ee}^{\sigma}$ has no effect on $\frac{n_L^{T}}{n_L^{L+1}}$. The weak role of $H_{ee}^{\sigma}$ is also true for the dianion, where we have already shown in Figs. 7 and 8 that $\frac{n_L^{T}}{n_L^{L+1}}$ is given by $H_{ee}^{\sigma}$ alone.

B. Application to coronene, picene and anthracene.

SC in metal-intercalated coronene and picene is also limited to trianions. MO occupancies in these systems are the same as that in phenanthrene: 3 doped electrons occupy the $L$ and $L+1$ orbitals (see Fig. 1). However, numerical calculations demonstrating two nearly filled filled bands in these cases would be far more involved. Here we give heuristic physical arguments why results similar to that for phenanthrene should be expected in these cases also.

Coronene. Coronene in the absence of electron-molecular vibration coupling has doubly degenerate LUMOs (see Fig. 1) and thus, the carrier densities per MO are expected to be equal, i.e., $n_{L_1} = n_{L_2} = \frac{3}{2}$ within a rigid bond model. Intramolecular Jahn-Teller distortion lifts this degeneracy, leading to a MO occupied by two electrons at lower single-particle energy, and a singly occupied MO at a slightly higher energy. The same bandwidth and correlation effects that tend to equalize MO populations in phenanthrene will bring back the densities close to $\frac{3}{2}$ here too. It is relevant in this context to recall that nonzero Hubbard $U$ reduces the stabilization of doubly occupied MOs due to Jahn-Teller distortion, but has no effect on the stabilization energy of singly occupied MOs. Thus, the Jahn-Teller induced energy gap between the MOs will be larger for the monoanion than for the trianion, and an asymmetry between the monoanion and the trianion is expected in coronene even without inclusion of intermolecular coupling.
Picene. The case of picene is more interesting, as solution of $H_{1\text{tra}}$ for $\epsilon = 0$ gives gaps between LUMO and LUMO+1, and, LUMO+1 and LUMO+2 that are equal, $\Delta_{L,L+1} = \Delta_{L+1,L+2} = 0.18|t|$ (see Table I). We have suggested in the text that $\epsilon \neq 0$ provides a more realistic scenario. As shown in Fig. 12, $\Delta_{L,L+1}$ decreases with $\epsilon$ while $\Delta_{L+1,L+2}$ increases. For $\epsilon \sim 0.65$ eV, as in Fig. 12b), $\Delta_{L,L+1}$ for picene and phenanthrene are nearly the same. $\Delta_{L+1,L+2}$ on the other hand is much larger. Even more importantly, the significant difference between the monoanion and the trianion in phenanthrene (see Figs. 3 and 4) indicates that the consequences of interband hopping between the singly occupied LUMO+1 and vacant LUMO+2 will be small. The very large separation between the LUMO and the LUMO+2 ($\Delta_{L,L+1} + \Delta_{L+1,L+2}$) with increasing $\epsilon$ will preclude significant hopping between them. We conclude therefore that the reason why trianions of picene are special is the same as in phenanthrene. Anthracene. $\Delta_{L,L+1}$ in anthracene is huge, 0.59$|t|$ at $\epsilon = 0$ (1.42 eV for $|t| = 2.4$ eV, see Table I). Even with nonzero $\epsilon$ this gap stays large. For the same lattice structure of Fig. 2b) we have calculated $n_L$ and $n_{L+1}$ for 20$\times$20 lattices, as in Fig. 8 for $\epsilon = 0$ and $\epsilon = 0.65$ eV. These results are shown in Fig. 13. The absence of SC in doped anthracene is understood within our theory. We predict Mott-Hubbard semiconducting behavior for all integer valence. It is emphasized that this same scenario is expected in intercalated pentacene, which has been found to be a Mott-Hubbard semiconductor\textsuperscript{19}. 

![Diagram of Paths linking the Mott-Hubbard configuration I, and the configuration IV with $n_L = n_{L+1}$, for the case of two molecules (see text). Two of the three paths involve only single electron hops. IIb to III involves a two-electron hop driven by $H_{od}$.](image)

![Graph showing one-electron energy gaps $\Delta_{L,L+1}$ and $\Delta_{L+1,L+2}$ for picene, calculated within Eq. 2 for $|t| = 2.4$ eV, versus $\epsilon$.](image)

C. Other parameter sets

As mentioned in the text, we have performed exact diagonalizations for many different parameter sets, for the clusters of Fig. 4. In Table II we have given additional parameter sets beyond those in the text for which calculations were done. These include hopping parameters both smaller and larger than those of Fig 4. Correspond-
FIG. 13: (Color online) $n_{L+1}/n_L$ versus different hopping integrals at $U = 0$, for $20 \times 20$ 2D lattice of anthracene ions with parameters of Fig. 3 (a)−(c), $\epsilon = 0$; (d)−(f), $\epsilon = 0.65$ eV.

FIG. 14: (Color online) $n_{L+1}/n_L$ versus $U$ for the trianion finite cluster of Fig. 2 for the hopping parameters of Table I. (a) $\epsilon = 0$; (b) $\epsilon = 0.65$ eV.

TABLE II: Representative parameter sets used in exact diagonalization studies

| Set | $t_{1}^{L,L}$ | $t_{1}^{L,L+1}$ | $t_{1}^{L+1,L}$ | $t_{1}^{L+1,L+1}$ | $t_{2}^{L,L}$ | $t_{2}^{L+1,L}$ | $t_{2}^{L+1,L+1}$ |
|-----|---------------|----------------|----------------|----------------|-------------|--------------|----------------|
| 1   | 0.109         | -0.059         | 0.059          | 0.143          | 0.05        | 0.0          | 0.0            |
| 2   | 0.125         | 0.025          | 0.025          | 0.075          | 0.05        | 0.0          | 0.0            |
| 3   | 0.15          | 0.05           | 0.05           | 0.1            | 0.075       | 0.025        | 0.025          |
| 4   | 0.175         | 0.075          | 0.075          | 0.125          | 0.1         | 0.05         | 0.05           |

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