Modeling the Charge Transfer between Alkali Metals and Polycyclic Aromatic Hydrocarbons Using Electronic Structure Methods

Thomas A. Baker[†] and Martin Head-Gordon*[,†,‡]

Department of Chemistry, University of California, Berkeley, California 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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The interaction of alkali metals—specifically, lithium—with polycyclic aromatic hydrocarbons (PAHs) was studied using a variety of electronic structure methods. Electron transfer from lithium to a PAH depends on the size and structure of the PAH and the electronic structure method used. In some cases, we observe an artificial transfer when using density functional theory (DFT) due to the self-interaction error, whereas Hartree–Fock underestimates the amount of charge transfer due to overlocalization. Our results have interesting implications for the validity of DFT calculations on the alkali metal–PAH interaction in Li batteries, hydrogen storage devices, and alkali-metal-doped superconductors.

Introduction

The interaction of alkali metals with polycyclic aromatic hydrocarbons (PAHs) and other conjugated carbon structures is important to understand because of the many applications of this system: lithium-based batteries,[1] alkali-metal-doped hydrogen storage devices,[2–4] and alkali-metal-containing superconductors.[5,6] For example, a wide variety of aromatic hydrocarbon containing materials are used with Li in batteries, especially at the anode, because carbon-containing structures exhibit both higher specific charges and more negative redox potentials than most metal oxides and chalcogenides.[1] For hydrogen storage devices, past work suggests that the doping of sp^2 hybridized carbon nanostructures with alkali metals—specifically—Li, can increase the adsorption and capture of hydrogen.[2–4] Li and other alkali metals are better dopants than transition metals, since alkali metals are lighter, cheaper, and less reactive. Understanding the interaction of Li with these substrates is important in the future design of these materials.

In many of these systems, it is critical to understand the role of the valence *s* electron of the alkali metal. Alkali metals have a low ionization potential, allowing its one valence *s* electron to be easily donated to another fragment, resulting in an ionic interaction ($M^+PAH^{•-}$), as opposed to the other extreme, a nonionic complex ($M^•PAH$). In the case of lithium, which we will focus on for much of this report, the low ionization potential of 5.4 eV combined with the high electron affinities of the larger PAHs (see Figure 1)[7] and other aromatic hydrocarbons result in what is believed to be an ionic interaction (Li^+PAH^-) in the many applications of this system. In hydrogen storage devices, it is proposed that the alkali metal has to donate its *s* electron to the carbon structure for the system to be effective, thereby producing an alkali metal cation to which hydrogen molecules can bind.[8] In the case of alkali metal superconductors, it is believed that the alkali metal has donated its electron to the carbon-based material, thus providing a possible explanation for the superconducting properties of the material.[5,6] Many of these conclusions are supported by density functional theory
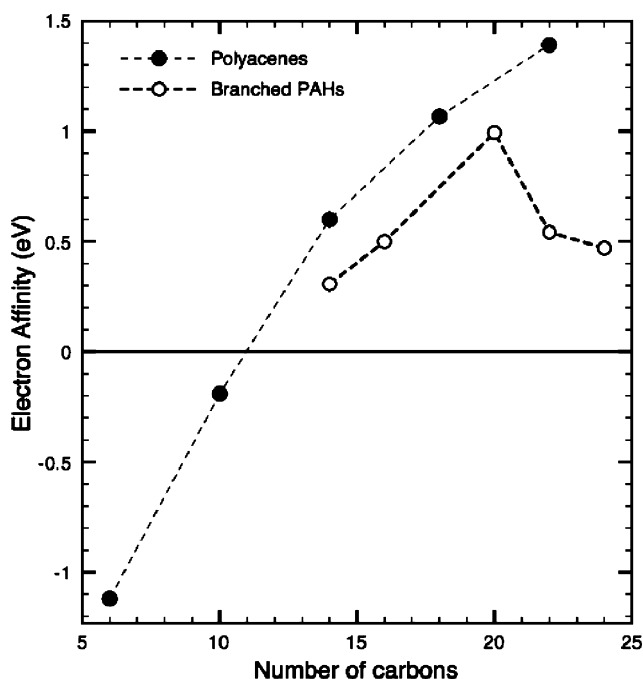

Figure 1. Experimental electron affinities for the PAHs studied in this report.[7]

(DFT) calculations. We will illustrate, however, that DFT can overestimate the amount of this charge transfer, which has important consequences on the calculated properties of these systems.

There is recent theoretical work that has investigated the interaction of alkali metals with PAHs. For example, Zhu et al. found charge transfer from Li, Na, and K to a variety of larger PAHs (containing at least 24 carbons) using DFT.[9] Vollmer et al. did not observe charge transfer between Li and benzene using second-order Møller–Plesset perturbation theory (MP2), but did find transfer from Li to a sandwich compound of Li between two benzene rings that both have a negative half charge.[10] There are several other papers that have looked at the interaction of Li with PAHs.[11–14] Some of these studies have focused on the charge transfer between Li and graphene. In one report, on the

* Corresponding author. E-mail: mhg@bastille.cchem.berkeley.edu.
† University of California, Berkeley.
‡ Lawrence Berkeley National Laboratory.

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basis of HF and MP2 calculations performed on coronene,[15] Ferre-Vilaplana concluded that charge transfer does not occur between Li and graphene. Martinez, et al. seemed to suggest that they found similar results with DFT calculations for the interaction of Li with coronene, but argued that coronene is too small a PAH to be used as a model of graphene, and they speculated that in the case of an infinite graphene sheet, charge transfer should occur.[16] Indeed, many periodic plane-wave DFT calculations have concluded that electron transfer occurs on an extended graphene sheet.[17−19]

We believe the evidence strongly suggests (at least for low concentrations) that Li and other alkali metals will donate their valence *s* electron to graphene. We are more interested in the case of charge transfer on smaller nonperiodic systems, in which the electron affinity is lower in energy (as compared with graphene's electron affinity, which is ~4.5 eV[20]). There have been a wide range of theoretical studies that have looked into the interaction of alkali metals with carbon nanostructures. DFT was used in most of these reports in which they found charge transfer between multiple Li atoms and the carbon-based substrate.[21−24]

We model the interaction of a single Li with several PAHs using a variety of electronic structure methods. The first class of methods, density functional theory (DFT), is a popular technique for modeling a wide range of systems due to its relatively good accuracy at a low computational cost.[25,26] Unfortunately, all common density functionals suffer, to varying degrees, from the self-interaction error that can cause an artificial delocalization of the electron density.[27] The Kohn−Sham equation has an explicit classical electron−electron repulsion potential, the Coulomb repulsion energy (J), which treats the charge distribution as a continuous classical charge:

$$J = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \qquad (1)$$

The total electron density $\rho(\mathbf{r})$, consists of all the electrons in the system, meaning that at each point in space, J contains an interaction between an electron and the total density, including an interaction with itself. The self-interaction is not exactly canceled by existing exchange functionals, leading to some residual error.

The self-interaction error is responsible for errors in a broad array of systems. The most simple and illustrative case is the bond breaking of H_2^+, which results in an erroneous stable configuration with partial half charges on each H, as compared with the correct result, H and H^+.[28] DFT calculations also produce spurious partial charges for the dissociation of alkali halide salts[29] and many other molecules[30,31] as the result of the self-interaction error. Furthermore, self-interaction is responsible for errors in the calculation of reactions barriers[32,33] and valence electronic structure[34] and is related to the incorrect asymptotic behavior of Kohn−Sham potentials.[35,36] The problem of electron delocalization and describing partial charges with DFT will potentially cause problems when applying this method to study alkali metal−PAH complexes.

The second class of methods we use are wave function approaches, which are typically self-interaction free. For instance, the problems of self-interaction do not exist for the HF method, since the energy is properly evaluated on the expectation value of the single determinant wave function. As a result, the exchange operator, K, in HF formalism exactly cancels what would be the self-interaction from J, which occurs when $i = j$ in the equation below:

$$J - K = \frac{1}{2} \sum_{ij} \iint |\psi_i(\mathbf{r})|^2\, |\mathbf{r} - \mathbf{r}'|^{-1}\, |\psi_j(\mathbf{r})'|^2\, d\mathbf{r}\, d\mathbf{r}' \ -$$
$$\iint \psi_i^*(\mathbf{r})\, \psi_j(\mathbf{r})\, |\mathbf{r} - \mathbf{r}'|^{-1}\, \psi_i^*(\mathbf{r}')\, \psi_j(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \quad (2)$$

However, HF has the opposite problem of DFT; there is an overlocalization of the electron density, since electron repulsion is smeared out as an effective mean potential. Cusp conditions are not treated correctly, and there is important dynamic correlation missing when two electrons approach each other, resulting in overlocalization. These problems can be remedied by adding accurate correlation corrections, such as coupled cluster theory to a HF reference, but doing so limits the size of a system that can be investigated due to the additional computational cost.

The problems of overlocalization and self-interaction can be especially troublesome for molecular fragments of a system that have an effective fractional number of electrons when the electron is delocalized over spatially separated fragments $(X^{\delta+}Y^{\delta-})$, as is the case in transition states or charge transfer processes. To correctly predict this behavior, it is necessary to correctly describe the energy of each fragment as a function of the fractional number of electrons in the system, N.[30] In agreement with the discussion above, DFT predicts highly nonlinear N dependence on E, producing energies that are too low,[37,38] whereas HF does the opposite: nonlinear N dependence that is too high.[39] Furthermore, the energy of adding an integer number of electrons is slightly too low for DFT and too high for HF. These trends are reflected in the calculation of barrier heights for chemical reactions; DFT predicts barriers that are typically too low, and HF tends to be too high.[30] We can also expect in calculations involving a possible charge transfer from a single atom to a much larger polycyclic aromatic hydrocarbon in which the charge can spread out, that DFT could artificially favor the partial or complete charge transfer, allowing the electron to delocalize on the PAH.

In this report, we illustrate that DFT will artificially delocalize an electron and favor charge transfer between Li and PAHs, but HF will do the opposite and overlocalize charge. Our results have important implications for smaller conjugated systems with lower electron affinities. We first summarize our results for calculations based on a wide range of PAHs, and then focus on a couple of interesting specific examples: first, the Li coronene system already mentioned, and second, a K-picene system related to a recently reported superconductor.[5]

Computational Details

Electronic structure calculations were used to study the electron transfer from a single Li to a set of differently sized PAHs, summarized in Figure 2. PAHs are split into two categories: (1) polyacenes, which are made up of linearly fused benzene rings; and (2) any other PAHs that are not linear, which we will refer to in the rest of the report as "branched" PAHs. A wide range of methods were compared, including unrestricted Hartree−Fock,[40] density functional theory,[25−27] and orbital optimized opposite spin MP2 (O2).[41] Density functional theory calculations were performed using three sets of exchange and correlation functions: (1) the popular hybrid functional B3LYP,[42] (2) Becke exchange[43] with Lee−Yang−Par correlation[44] (BLYP), and (3) the range separated hybrid functional ωB97.[45] Range-separated hybrids partition exchange into short- and long-range parts and evaluate the latter using the Kohn−Sham wave function. Thus, they are free of long-range self-interaction error.[46−49]
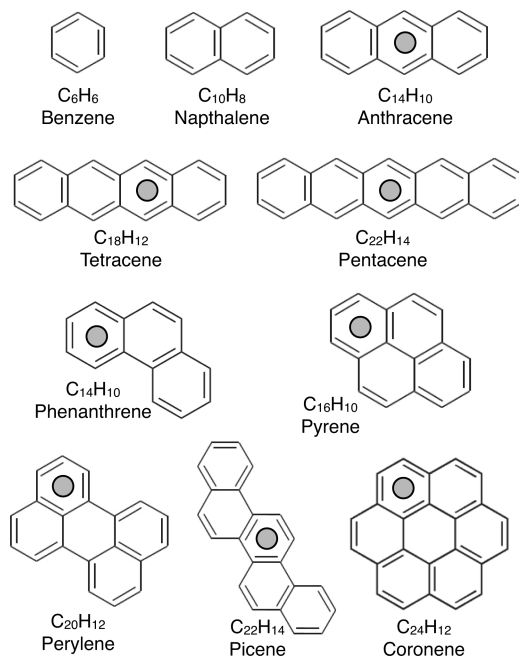
Figure 2. PAHs studied in this report. The top five PAHs are polyacenes; the bottom five will be referred to as "branched" PAHs. Gray circles represent the chosen biding site of Li.

Figure 3. Model of Li−benzene system: (a) a top view of both the ionic and nonionic configuration, (b) a side view of the ionic (Li^+ $C_6H_6^-$) configuration with C_{2v} symmetry as a result of Jahn−Teller distortion, and (c) the nonionic system (LiC_6H_6) with C_{6v} symmetry.

The accuracy of MP2 calculations can be significantly improved by semiempirically scaling the opposite spin correlation.[50,51] The O2 method introduces Brueckner orbitals that are optimized with the mean-field energy plus the scaled correlation energy taken from MP2.[41] We use the O2 method in this work because it yields substantial improvements for open-shell molecules, since problems of spin contamination and symmetry breaking associated with conventional MP2 are greatly reduced.[41,52] A scaling factor of 1.2 is used. Calculations were performed using the computational package Q-Chem 3.2[53] with a 6-311G(d,p) basis set.

We calculated the difference in energy between the ionic configuration in which the 2s electron of lithium has been transferred to the PAH (Li^+PAH^-) and the case in which the electron has not transferred, which we will refer to as the nonionic configuration (LiPAH). Interestingly, for most of the systems studied, it was possible to isolate separate solutions for both ionic and nonionic cases. Converging to each electronic solution (and then subsequently relaxing the geometry) depended on the initial electronic guess and starting geometry. To find the ionic solution, a small Li−PAH distance was used, and the initial electronic guess was found by first solving the electronic structure for the core Hamiltonian. To find the nonionic solution, a larger Li−PAH distance was used, and an initial guess was taken by combining the calculated electronic structure of the separate Li and PAH fragments.

The spin density on lithium was used as a measure of charge transfer. A spin density of ∼0 on lithium indicates that the unpaired 2s electron of lithium has been transferred to the PAH. We were able to find a purely ionic (a spin density on Li of ∼0) and nonionic (a spin density on Li of ∼1) configuration for nearly every combination of PAH and method. We will later discuss the few cases that we could not find a configuration with a complete electron transfer. A more complete discussion of the measure of charge along with a table showing the spin density on lithium for every system studied is found in the Supporting Information. There are a couple of cases in which the geometry relaxation convergence criteria needed to be
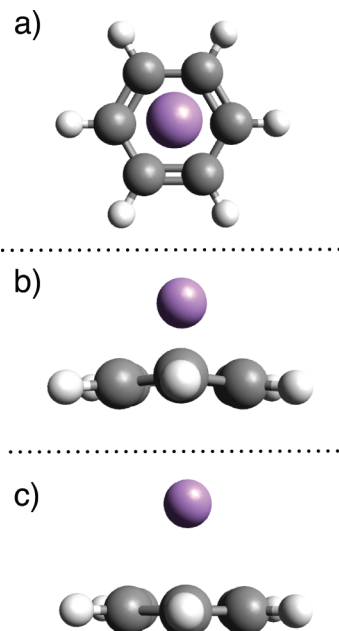
relaxed to find a metastable nonionic configuration. These are also discussed in more detail in the Supporting Information.

High-level multireference calculations have revealed that larger PAHs are polyradical in nature.[54−56] Methods that employ a single Slater determinant cannot capture the static correlation necessary to fully describe the polyradical behavior of these molecules.[57,58] We observe instabilities in some of our SCF solutions as a consequence of the polyradical nature of PAHs.[56] These instabilities are discussed in the Supporting Information.

Results and Discussion

Ionic versus Nonionic Interaction. The interaction of lithium with PAHs was calculated with a variety of electronic structure methods. We found two stable configurations at different Li−PAH distances: an ionic configuration (Li^+ PAH^-) in which the 2s valence electron of Li has been transferred to the PAH; and a nonionic (LiPAH) interaction, which is the result of no charge transfer. Figure 3 illustrates the two configurations for Li−benzene.

For every tested PAH, lithium prefers to bind above the PAH in the center of a ring, shown in Figure 3a. For the PAHs containing multiple rings, each symmetrically unique site was tested, and the configuration with the lowest energy is used, shown in Figure 2. The ionic configuration (Figure 3b) is characterized by a shorter (versus the nonionic configuration) Li−PAH distance and a Jahn−Teller distortion due to the charge transfer of the Li 2s electron to the benzene ring, which breaks the aromaticity of the PAH. In the case of benzene, this lifts two carbons on opposite sides of the ring out of the plane of the ring, reducing the symmetry of the total system from C_{6v} to C_{2v}. A similar effect occurs with larger PAHs, although it involves a buckling that is distributed over multiple rings of the PAH. Without charge transfer, the PAH remains planar, as in the case of the nonionic configuration (Figure 3c). At most Li−PAH distances, both electronic solutions (ionic and nonionic) can be found; however, the equilibrium distance for each configuration is very different and can also vary drastically with
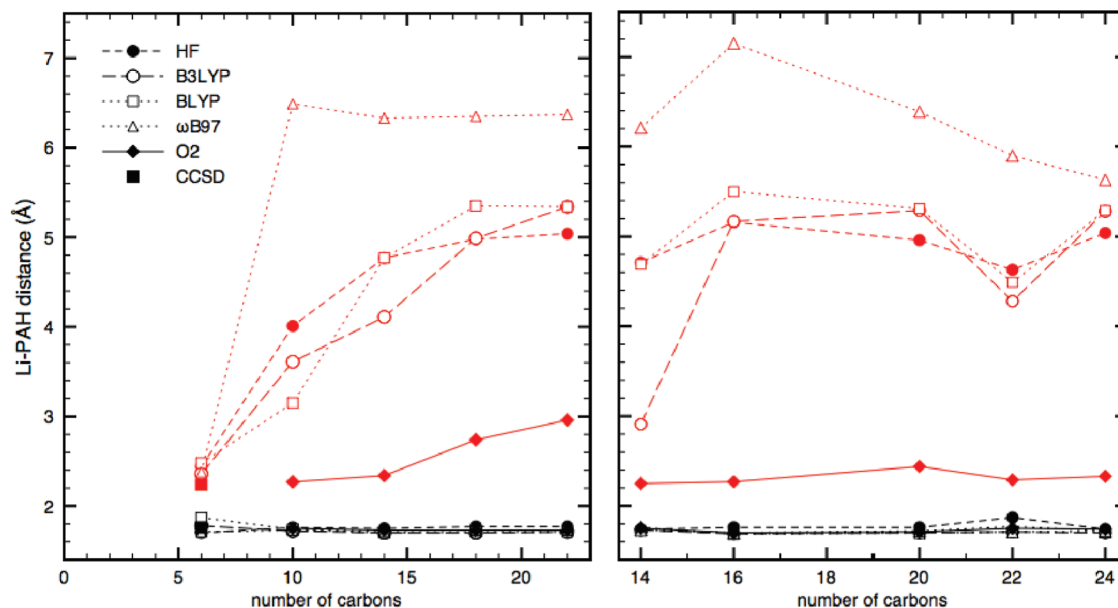
Figure 4. Distances between Li and center of 6-membered ring. The ionic and nonionic configuration are labeled black and red, respectively. The plot on the left and right contain the polyacenes and "branched" PAHs, respectively.

the method used, as shown in Figure 4. The nonionic configuration is characterized by a longer Li−PAH distance, which in the case of HF and DFT can be as long as 7 Å from Li to the center of the ring, while the ionic configuration is characterized by a short Li−PAH distance. In the case of the ionic configuration, the distance (∼1.7 Å) is nearly independent of the size of the PAH and the method used.

In contrast, the Li−PAH distance can drastically vary for the nonionic configuration, though the most extreme of these differences likely reflect limitations of some of the theoretical methods, as we shall discuss. This distance generally increases as the PAH becomes larger in size and as the nonionic configuration is energetically less preferred as compared with the ionic configuration. The very long distances observed with HF and DFT suggest a very weak interaction in these cases. Indeed, the nonionic interaction energy is nearly zero. A complete table of interaction energies is available in the Supporting Information. However, the Li−PAH distance in the nonionic configuration with larger PAHs is significantly reduced (by approximately half) when calculated with the O2 method. This is the result of a better description of dispersive interactions, which is missing from the HF and DFT methods. Therefore, the O2 energies are likely to be the most reliable reported here. However, because they are obtained without correction for basis set superposition error, they are likely to be shorter than would be obtained at the basis set limit.

We compare the energies of the two configurations to determine if charge transfer is energetically preferred. The energy difference between the nonionic and ionic configuration calculated with each method and PAH is shown in Figure 5. The plots are split into the polyacenes (left plot of Figure 5) and the "branched" PAHs (right plot of Figure 5). A negative (positive) energy difference indicates that the nonionic (ionic) configuration is energetically preferred. We could not find an ionic solution for Li−benzene using the O2 method. We replaced this data point on the plot with a coupled cluster singles and doubles calculation (CCSD).[59] Although the switch to a different method is unfortunate, the more accurate data point fits in correctly with the trends.

There are a couple of situations in which a complete ionic transfer of an electron was not found. This occurred for three

situations, all involving benzene, using the CCSD method, and with the B3LYP and BLYP density functional; the ionic solution produced partial charge transfers of 0.88, 0.69, and 0.46 electrons, respectively. Presumably, a complete charge transfer would be higher in energy, meaning that these points in the plot of Figure 5 should be slightly lower than indicated. This would not change our interpretation of the CCSD point; it would only slightly lower this point, since the energy difference is negative, but still indicating that charge transfer is not preferred. The slight electron transfer back to Li is the result of the singles excitations' lowering the energy. Indeed, when only doubles excitations are included (CCD), a complete transfer is observed. For DFT results, the energy difference is positive, meaning the configuration with the partial charge transfer is lower in energy than the nonionic configuration. Therefore, using the B3LYP and BLYP functional, the transfer of about half of an electron is expected, though this is likely to be a self-interaction artifact, as will be discussed in more detail below.

In general, the plots follow the expected trend in that they closely match the electron affinities of the PAHs (Figure 1). As the electron affinity of the PAHs increases, it should be easier for lithium to transfer an electron to the PAH. In the case of the polyacenes, the electron affinities steadily rise with the size of the PAH. The trend for the branched PAHs is slightly more complicated, but in general, the computational result qualitatively reproduces the trend in the electron affinities. Notably, the O2 curve most follows the trend, especially for the branched PAHs, confirming our suggestion that this curve is the most accurate.

It is more interesting and the purpose of this report to compare the results from different methods. We find that each method gives nearly the same curve (Figure 5), but offset to favor or discourage charge transfer. It is important to understand this offset, since in several cases, this offset straddles the zero on the plot, thus resulting in charge transfer with one method, but not with a different method. Starting with DFT, we find that it favors charge transfer, since its curve is offset to more positive energy differences. This is the direct result of the self-interaction error, causing the delocalization of the valence electron of lithium. HF, on the other hand, has the opposite effect: its curve is offset to lower energy differences, thus favoring nonionic
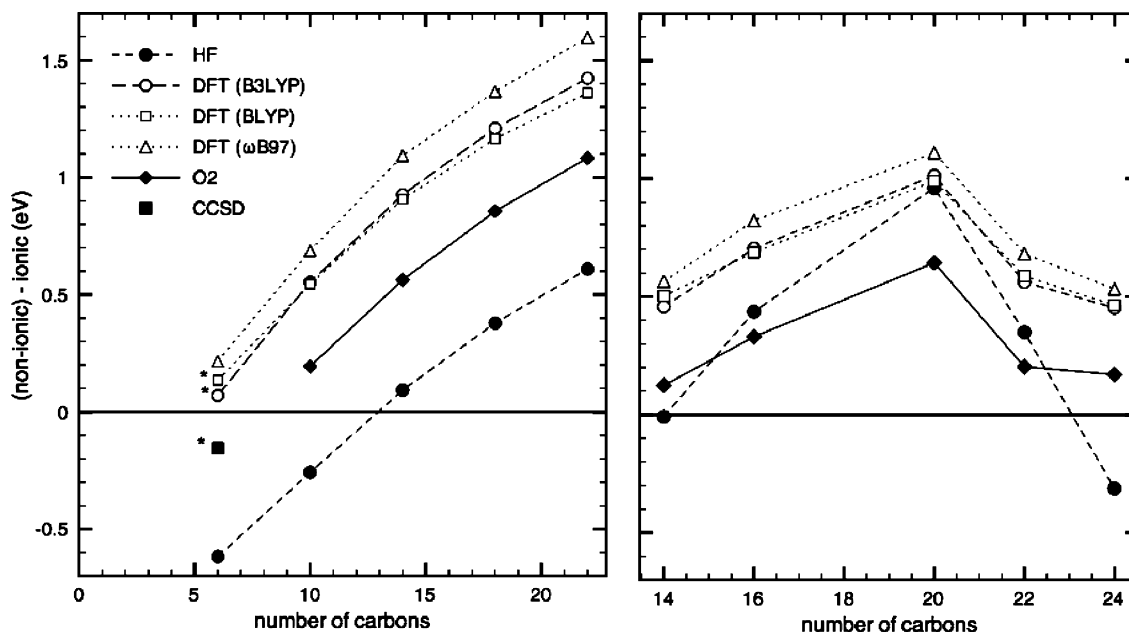
Figure 5. Difference in energy between the nonionic (LiPAH) and the ionic configuration (Li$^+$PAH$^-$). The data points marked with an asterisk had a partial charge for the ionic solution. The plots on the left and right contain the polyacenes and "branched" PAHs, respectively.

configurations due to overlocalization. The correct curve should be somewhere between HF and DFT, which is, indeed, where we find the O2 curve (and the CCSD point for benzene). We believe this to be a more accurate description of the LiPAH system, since O2 is a better description of electron correlation and can accurately treat open shell systems.[41]

Spin contamination is a problem when calculating the ionic configurations, especially for the larger branched PAHs in which the unpaired electron can delocalize over the entire PAH. As expected, spin contamination is especially bad with the HF method, whereas the O2 method does a proper job of removing spin contamination. One especially troubling case is the HF calculation of picene (Li$^+$picene$^-$), for which the calculated expectation value of S^2 is 2.82 a.u. (the correct value is 0.75 a.u., since the system is a doublet). This problem with spin contamination is likely the explanation for the strange HF calculated energy difference between the nonionic and ionic configuration of picene in which the difference is higher than the O2 result (Figure 5). The DFT results suffer from little spin contamination; values for $\langle S^2 \rangle$ are higher by no more than 0.15 au. The Supporting Information contains a complete table of $\langle S^2 \rangle$ for the ionic configurations calculated with each method.

Our results show that the calculated charge transfer from Li to PAHs is method-dependent. There are several examples in which we observed different qualitative results. Using density functional theory, at least some charge transfer is found with every PAH tested. However, the more accurate CCSD result suggests that charge transfer should not occur between Li and benzene. In contrast to DFT, HF predicts no charge transfer for benzene, napthalene, phenanthrene, and coronene. Importantly, our results generally show the problems of using electronic structure methods for calculating the charge transfer from an alkali−metal to an aromatic hydrocarbon. In the Introduction, we discussed important applications of these systems: Li ion batteries, alkali-metal-doped hydrogen storage devices, and alkali-metal-doped, carbon-containing superconductors. In many of these systems, a wide range of DFT calculations have been performed. Our results clearly show the implications of the self-interaction and delocalization errors favoring charge transfer in DFT calculations. Understanding these errors is vital to correctly

model the alkali metal−carbon interaction. We briefly discuss two implications of the errors below.

Coronene. In the Introduction, we discussed HF, MP2, and DFT results for the interaction of lithium with coronene and the possibility of using this PAH as a model for graphene. Our HF calculations match previous work, concluding that charge transfer does not occur between lithium and coronene.[15] However, our DFT results do not match those of Martinez.[16] We observe charge transfer with all the tested combinations of exchange and correlation, but Martinez writes that charge transfer does not occur. To directly compare our results with Martinez, we also performed DFT calculations with the XC functional employed in their work, the LSDA PW92 functional[60] and the GGA PBE functional.[61] With both of these functionals, we also found that charge transfer was energetically favorable.

Although coronene is a relatively large PAH, it is a poor choice as a model for graphene, since it has an electron affinity lower (0.47 eV) than other PAHs of similar size and far lower than graphene's electron affinity (4.5 eV). Using Hartree−Fock, we do not observe charge transfer, which is qualitatively different from the observed experimental and theoretical observations on graphene. Our best results for this system, using the O2 method, show that, in fact, the relative energy of the ionic and nonionic configurations are very delicately balanced, with just a slight preference for the ionic configuration. All density functionals yield a preference of ∼0.5 eV for the ionic configuration, ∼3 times larger than O2.

K-Picene Superconductors. We also discussed in the Introduction that a class of superconductors served as one of the important motivations for understanding the alkali metal−PAH interaction. A recent report has shown that certain alkali-metal-doped picene materials have superconducting properties.[5] It is found that a picene crystal interlaced with potassium (K$_{\sim3}$picene) has a superconducting transition around 18 K. It is believed that three electrons are transferred from the K to occupy the LUMO and half occupy the LUMO+1 of each picene, and this fact is at least partly responsible for the superconducting properties. DFT calculations have been performed on this system, although the authors did not comment on the possibility of a three-electron transfer per picene molecule.[62]

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TABLE 1: Difference in Energy between the Nonionic and Ionic Configuration for K-Picene[a]

method	(nonionic)/ionic energy (eV)
HF	−0.78
B3LYP	NA
BLYP	NA
ωB97	0.44
O2	−0.28

[a] In the case of B3LYP and BLYP, only one configuration could be found; it had a partial transfer of ∼0.6 electrons.

Given the results in our report, it seems unlikely that one picene could accept all three electrons from three potassiums. Although potassium has a lower ionization potential as compared with lithium (5.4 eV for Li, 4.4 eV for K), potassium is larger than lithium, and thus, an ionic interaction will be slightly weaker due to a larger distance between the two charged fragments. Our work has shown that using DFT to calculate the charge transfer in this type of system could be potentially dangerous, since it would overestimate the propensity for charge transfer. As a simple model for the superconductor, we replace lithium with potassium in our previous picene calculations and test this system with each method. We reduced the basis set to 6-31G(d,p) for the sake of computational efficiency, since the size of potassium is much larger than lithium. Our results are summarized in Table 1.

Interestingly, both HF and what is believed to be our most accurate method, O2, indicate that charge transfer does not occur between K and a single picene, whereas DFT results indicate that charge transfer is possible. We are unable to find both an ionic and nonionic configuration using the B3LYP and BLYP functional. Instead, every attempt to calculate this system resulted in a partial transfer of 0.6 electrons. Using the ωB97 function, we were able to find both the ionic and nonionic solution, with the ionic configuration preferred energetically by 0.44 eV.

The K-picene system follows the same trends as in the case of lithium: overlocalization of charge in HF causes the energy difference to be too low, delocalization inherent with DFT gives

too high an energy difference, and O2 is almost in the middle between the two energies and favors the nonionic configuration by −0.28 eV. These results suggest that one potassium may not be able to transfer one electron to picene, making the transfer of three electrons to one gas-phase picene highly unlikely. However, we need to be careful in the interpretation of our results and its application to the K-picene superconductor. We do not look at multiple K's around a picene nor a periodic crystal of piecene, which may favor an ionic interaction due to the multiple Coulombic interactions with neighboring molecules in adjacent unit cells. Our results, however, should serve as a guide as well as a caution on a heavy reliance on DFT for drawing conclusions for these types of systems.

Conclusions

We have used electronic structure calculations to study the charge transfer of alkali metals to polycyclic aromatic hydrocarbons. We have shown that different methods can produce qualitatively different results. For PAHs with a range of moderate electron affinities (between −0.5 and 0.5 eV; see Figure 6), HF will incorrectly predict no charge transfer due to overlocalization as a result of missing electron correlation. On the other hand, for PAHs with negative electron affinities (less than −0.5 eV), density functional theory will artificially predict charge transfer due to delocalization of charge. We believe the O2 method does a more reasonable job of describing the charge transfer between the two fragments.

The magnitude of the errors when using HF and DFT to study charge transfer is significant but not exceedingly large. The difference between HF and DFT results for the energy difference between the nonionic and ionic configuration is about 1 eV, and since the correct result (O2) is approximately in the middle, the error for each method is ∼0.5 eV in opposite directions. However, a drastically different qualitative result can be found, especially when the energy difference between the ionic and nonionic configuration is small.

Our results have important implications on a variety of systems, including Li ion batteries, alkali-metal-doped hydrogen storage devices, and alkali-metal-doped, carbon-containing
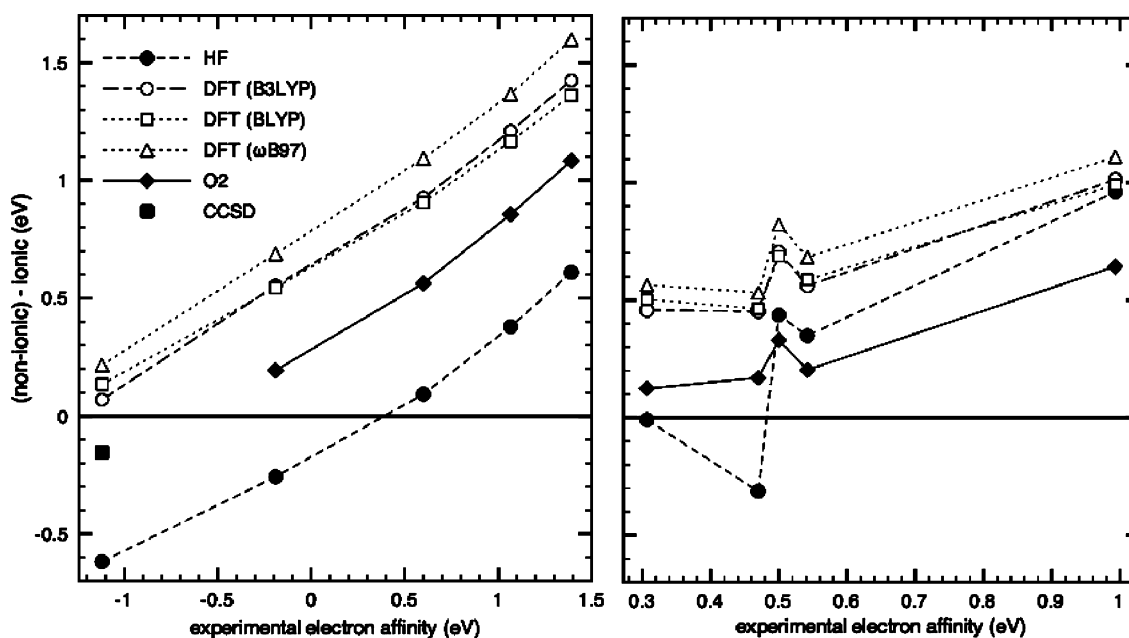

Figure 6. Difference in energy between the nonionic and ionic configuration as a function of the experimental electron affinity for each PAH. The plot on the left and right contain the polyacenes and "branched" PAHs, respectively.

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superconductors. Many of the past theoretical results on these systems have employed density functional theory and, as a result, may have overestimated the charge transfer. This is especially the case in systems that the carbon system accepting electrons has a small electron affinity or is accepting several electrons. This is especially troublesome, since many of the conclusions about these important systems have relied on the assumption that charge transfer occurred. Our work illustrates the need to reevaluate these previous conclusions and consider the inherent errors of DFT when investigating systems in which charge transfer occurs.

Our work also points out the need to look for two solutions (ionic and nonionic) when investigating the interaction of alkali metals with PAHs. In much of the previous work, only the ionic solution (especially when using DFT) is discussed, and it is not clear if the investigators found or even searched for both configurations. The investigation of only the ionic configuration is not as troublesome for the case of a single lithium interacting with PAHs other than benenze, since DFT agrees with the more accurate O2 method that charge transfer is energetically preferred. However, other single alkali metals could behave differently. We can expect, on the basis of the results from the interaction of potassium with picene, that the nonionic configuration will be energetically favored (depending on the method used) for several PAHs. In the case of Li, the nonionic configuration could play an important role when interacting more than one lithium with a PAH or other sp^2 carbon structure. For example, it has been proposed that C_{60} fullerene could be doped with Li to act as a hydrogen storage device. DFT calculations have predicted that charge transfer occurs between several Li's interacting with the same fullerene, resulting in a highly negatively charged fullerene.[23] The first electron affinity of C_{60} fullerene is very high (2.65 eV),[63] higher than the PAHs studied in this report, showing that electron transfer between at least one Li and the fullerene is not surprising. However, it has been calculated (B3LYP/6-311G*) that the second and third electron affinities are much lower: −0.79 and −3.76 eV, respectively.[64] If compared with the electron affinities of the PAHs in this report, this puts into serious question the transfer of many valence electrons from isolated lithiums to one C_{60} fullerene. Future work is planned to fully investigate these systems.

The alkali metal−PAH studied in this report serves as a model system. Although this work gives a general outline of the problems and how they may be solved, more work is needed to investigate the actual aromatic hydrocarbons that are used in the battery, hydrogen storage, and superconducting systems. For example, we have results suggesting that one gas phase picene molecule cannot accept the valence electron from potassium. This suggests that current interpretations of the K_3picene superconducting crystal may be wrong. This report does clearly indicate that additional calculations are needed (by accurate methods that do not suffer from problems of self-interaction and delocalization), before it can be concluded that all three valence electrons from potassium can be donated to a single picene in a superconducting material.

Supporting Information Available: The Supporting Information includes a table of the binding energies between Li and PAH for both the ionic and nonionic configuration, a discussion on measuring the Li charge, a table of spin densities on Li for the ionic configuration, a table of the S^2 expectation values for the ionic configuration, a comparison of other modern DFT functionals for benzene−Li, and a discussion on an approximation to the nonionic geometry and treatment of electronic stabilities. This material is available free of charge via the Internet at http://pubs.acs.org.

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