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Adsorption of Lithium on Finite Graphitic Clusters

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The apparent discrepancies between density functional (DFT) and Møller–Plesset (MP2) calculations for the interaction of lithium with graphene recently pointed out by Ferre-Vilaplana (*J. Phys. Chem. C* **2008**, *112*, 3998) are discussed. In his calculations, this author used a finite coronene cluster, $C_{24}H_{12}$, to simulate graphene. We show here that the DFT binding energies of Li to $C_{24}H_{12}$ are very weak, similar to those calculated by MP2. The weak binding energy is due to the large HOMO–LUMO gap of the coronene, which makes this cluster rather inert. So, the main reason for the earlier discrepancy is that the $C_{24}H_{12}$ cluster that Ferre-Vilaplana used to represent graphene is too small to properly account for the electronic structure of graphene. In contrast, graphene has zero gap, which allows for a strong interaction with partial ionic character between Li and graphene, as obtained previously in DFT calculations.

Materials with low weight and a large specific surface area that could adsorb and store a large amount of hydrogen could make reality the use of hydrogen as a fuel in the automotive industry. One of the proposed ways to store hydrogen is based on the adsorption of molecular hydrogen on porous carbon materials, such as activated carbons,¹ carbide-derived carbons,² and carbon nanotubes.³ Experiments^{4–8} and calculations^{8–20} have shown that doping those materials with alkaline impurities has a beneficial effect in enhancing the hydrogen adsorption and storage capacity of the material. A particularly interesting dopant is lithium because of its low atomic weight. Motivated by this purpose, several authors have studied the interaction between Li atoms and graphitic surfaces^{10,11,16,17,19–25} using the density functional formalism (DFT).

The general consensus from both experiment and theory is that for dispersed alkali adatoms, the bonding of the Li atom to graphene is mainly ionic,^{19,23,26} and the values of the charge transfer from the Li atom to the graphene surface calculated in the above works range between 0.4 and 1.0 e. The adsorption binding energies vary with the particular method used, but are close to 1 eV. However, Ferre-Vilaplana²⁷ has recently performed quantum chemical Møller–Plesset (MP2) and Hartree–Fock calculations of the interaction of a Li atom with the planar cluster $C_{24}H_{12}$, a small fragment of graphene with the borders saturated by hydrogen atoms, and proposed that his results challenge the established interpretation of the bonding of Li to graphene. In the MP2 calculations, he obtained a weak adsorption binding energy, 0.13 eV, a large equilibrium separation of 3.2 Å, and a very small charge transfer of 0.01 e toward the Li atom. This evidently corresponds to physisorption, very different from the accepted view. On the basis of this result, Ferre-Vilaplana criticizes the admitted interpretation of the enhancement of the binding energy of H_2 to the graphitic surface in Li-doped graphitic materials (the admitted interpretation is that the enhancement is due to the polarization of the hydrogen molecule by the nearby charged Li atom). In this Article, we

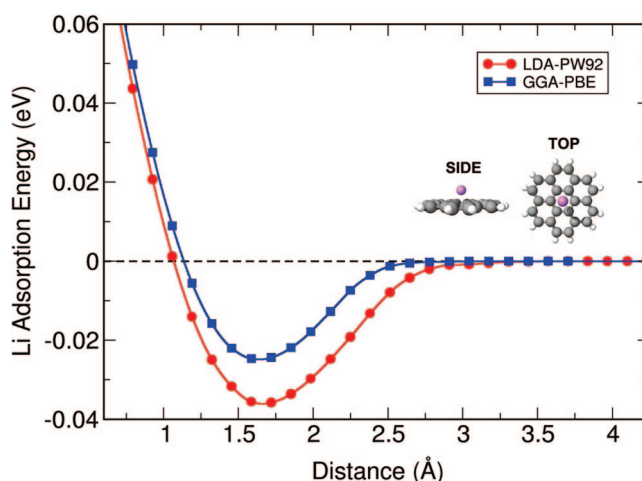


Figure 1. Potential energy curves for the interaction of a Li atom with the planar coronene $C_{24}H_{12}$ obtained using the LDA and the GGA approximations. The structure of the coronene with the Li atom adsorbed is given in the inset.

show that the interaction between a Li atom and the $C_{24}H_{12}$ coronene is very different from the interaction between Li and graphene. This is a typical size effect. $C_{24}H_{12}$ and graphene have very different electronic structures in the energy region around the Fermi level, and consequently the interaction of these two systems with atoms or molecules can be very different. This is the case of their interaction with Li. This touches the well-known question of the extent to which a finite cluster can simulate a macroscopic piece of material. The main conclusion from extensive experimental and theoretical work in the field of clusters is that only very large clusters can mimic the properties of the macroscopic material.²⁸

The structure of the planar coronene $C_{24}H_{12}$ is plotted as an inset in Figure 1. It is a finite piece of graphene; that is, the carbon atoms form a hexagonal network, and the edge all around the coronene is of the armchair type. The external atoms are saturated by hydrogen. We have performed density functional calculations of the interaction between Li and $C_{24}H_{12}$ using the

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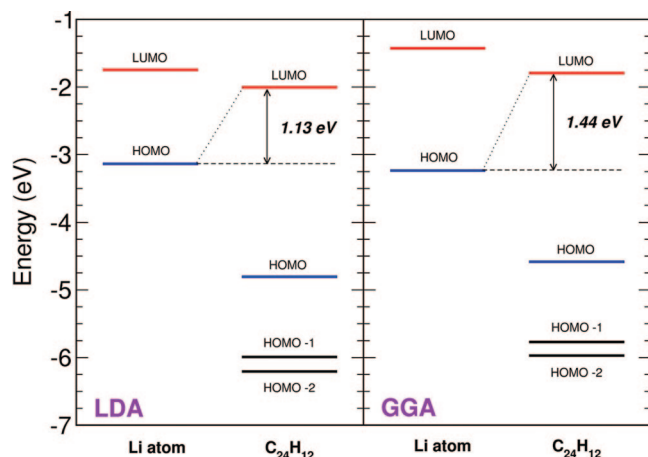


Figure 2. Electronic energy levels of the Li atom and the $C_{24}H_{12}$ coronene, obtained using the LDA (left panel) and the GGA (right panel) approximations.

ABINIT code,²⁹ which integrates the Kohn–Sham equations of DFT using Troullier–Martins ionic pseudopotentials³⁰ and a basis of plane waves to expand the wave functions. The code employs a supercell geometry, and we have used a supercell of size $30 \times 30 \times 30 \text{ au}^3$ and a single k point. The basis of plane waves used to expand the electronic wave functions has a kinetic-energy cutoff of 60 Ry. The supercell size and the kinetic-energy cutoff have been adjusted to achieve an accuracy in the total energy of 0.01 eV. For the exchange–correlation energy functional, we have adopted both the spin-polarized local density approximation (LDA)³¹ and the spin-polarized generalized gradient approximation (GGA).³²

The structure of the electronic levels of $C_{24}H_{12}$ near the Fermi energy is plotted in Figure 2. The electronic states are filled up to the HOMO (highest occupied molecular orbital). This is a doubly degenerate orbital state, so including spin the total electronic occupation is four. There is a large gap between the energy of the HOMO, $\epsilon(\text{HOMO})$, and the energy of the lowest unoccupied orbital, $\epsilon(\text{LUMO})$. The magnitude of the gap is 2.8 eV in the LDA, and 2.7 eV in the GGA. $C_{24}H_{12}$ is then a very stable closed-shell cluster. The chemical reactivity of a cluster can be measured by its hardness, which under reasonable approximations can be expressed as:³³

$$K = \frac{\epsilon(\text{LUMO}) - \epsilon(\text{HOMO})}{2} \quad (1)$$

That is, the chemical hardness K is controlled by the magnitude of the HOMO–LUMO gap. The large gap of $C_{24}H_{12}$ indicates that this cluster is rather unreactive, a feature common also to other H-saturated carbon clusters³⁴ like $C_{20}H_{10}$ or C_6H_6 . In contrast, graphene has a zero gap (and a vanishing density of states at the Fermi level). This means that the $C_{24}H_{12}$ and graphene will interact in a very different way with a lithium atom. Figure 2 also shows the energy of the HOMO and LUMO levels of the Li atom, that is, the energies of the occupied 2s orbital with spin up, and of the unoccupied 2s orbital with spin down. The occupied valence state of Li lies in the energy region inside the gap of $C_{24}H_{12}$, relatively far from both the HOMO and the LUMO levels of the coronene, and the hybridization interaction between the Li and the coronene orbitals is minimal. In particular, there is no charge transfer because the HOMO level of the coronene is fully occupied, and the LUMO is 1.13 eV above the valence level of the Li atom in the LDA (1.44 eV above in the GGA).

Figure 1 shows the calculated interaction energy:

$$E_{\text{int}} = E(C_{24}H_{12}) + E(\text{Li}) - E(\text{Li}-C_{24}H_{12}) \quad (2)$$

as a function of the perpendicular distance between the Li atom and the coronene plane. In this equation, $E(\text{Li}-C_{24}H_{12})$, $E(C_{24}H_{12})$, and $E(\text{Li})$ are the total energies of the system and of the two separated subsystems, respectively. The Li atom is placed on top of the central carbon hexagon of the coronene, which is the most stable position. At the equilibrium separation, the calculated LDA binding energy is 0.037 eV (0.025 eV in the GGA). These small values are consistent with the small MP2 binding energy calculated by Ferre-Vilaplana, 0.13 eV. In contrast to the above results, recent DFT calculations using the GGA for exchange and correlation^{23,24} obtained a binding energy of 1.10 eV between the Li atom and an infinite graphene layer, and LDA calculations^{16,21,25} give predictions similar to the GGA results. So, using DFT with the GGA for exchange and correlation, the results for the interaction between Li and graphene and between Li and the $C_{24}H_{12}$ are very different. The same conclusion is obtained using the LDA. Actually, the interaction with graphene is much stronger than the interaction with the coronene. The reason is that the coronene has a large gap and graphene, in contrast, is a system with zero electronic gap. Consequently, the finite $C_{24}H_{12}$ cluster does not represent at all the electronic structure of graphene in the region near the Fermi level. The case of the interaction with Li is particularly bad because the energy of the valence level of the Li atom lies in the middle of the large HOMO–LUMO gap of the coronene. The analysis of the charges of different atoms on the $C_{24}H_{12}\text{Li}$ cluster reveals that all of the atoms are very close to neutral, a fact that supports the very low interaction energy obtained in the calculation. The conclusion that the interaction between Li and $C_{24}H_{12}$ is very small because the coronene has a large HOMO–LUMO gap is robust and does not depend on the method of calculation, DFT or MP2.

A result observed in the MP2 calculations of Ferre-Vilaplana deserves a comment. For all Li–coronene distances, this author finds two different self-consistent solutions of the molecular problem. Those two solutions arise from two different ways of preparing the initial state of the system for the self-consistency cycle. The two solutions lead to interaction energy curves with different binding energies and equilibrium separations. In addition, the shape and relative positioning of those two interaction energy curves depend sensitively on the method of calculation, MP2 or Hartree–Fock (HF). Evidently, the lowest energy curve corresponds to the ground-state adsorption of Li and is the relevant one. The high energy curve, which might correspond either to a spurious solution of the self-consistent field procedure or to an electronic excited state, appears to be unbound with respect to the two separated subsystems. The minimum of the lowest energy curves obtained by Ferre-Vilaplana does not show a clear trend: the HF curve does not have a minimum, and the equilibrium distance changes between 2.5 and 3.2 Å, whether BSSE (basis set superposition error) corrections are included or not in the MP2 calculations.

On the other hand, previous DFT calculations of the interaction between Li and graphene, performed with different DFT codes, as well as our present work, have not encountered the problem of the dual solutions.^{10,11,16,17,19–25} To investigate in depth the possible existence of a second solution in a DFT context, we have carried out some additional tests. Those tests consisted of performing several calculations using different methods allowed in the code to construct the initial Kohn–Sham orbitals and density, and using also different density mixing schemes along the self-consistency cycle. (i) In a first method, the starting orbitals and density were constructed from the

atomic pseudo-orbitals used to generate the pseudopotentials. (ii) As an alternative method, the starting density was obtained from a previous self-consistent linear combination of atomic pseudo-orbitals (LCAO) calculation; that is, the code performs an initial diagonalization of the Kohn–Sham Hamiltonian in the subspace of those pseudo-orbitals. Next, for each of those cases, the densities at each iteration n in the self-consistent calculations were obtained by using three different mixing schemes. Two of them are based on a linear mixing of the densities from the iterations $n - 1$ and $n - 2$, with weights of 0.6 and 0.4, respectively, in one case, and weights 0.8 and 0.2, respectively, in the other case. A third mixing scheme used the Pulay algorithm.³⁵ All of these (2×3) tests gave consistent results for the interaction energy and the equilibrium distance, and we did not find any trace of a possible second solution for the potential energy curve.

In Figure 1, one can appreciate that the equilibrium distance between the Li atom and the coronene plane is about 1.7 Å. This separation, consistent with the values obtained in previous DFT calculations, is smaller than the distance obtained in the MP2 calculations of ref 27. So, it appears that the equilibrium separation is rather sensitive to the method, due to the shallowness of the attractive part of the interaction potential. However, all of the indications are that the DFT and the MP2 solutions correspond qualitatively to the same ground state of the $C_{24}H_{12}Li$ cluster. In a previous study³⁴ of the interaction between Cs and different H-saturated carbon clusters, C_6H_6 , $C_{20}H_{10}$, $C_{21}H_9$, and $C_{24}H_{12}$, we found that the equilibrium distances between the Cs atom and the clusters are very similar, independently of the strength of the binding (the binding energies span a large range, from 0.16 eV in benzene, a cluster with a large HOMO–LUMO gap, to 2.42 eV in $C_{21}H_9$, a case characterized by strong ionic binding). The reason is that the main factor determining the equilibrium distance is the repulsive wall of the effective interaction potential, and not the strength of the attractive interaction. In our case, the calculated Li–coronene equilibrium distance is close to that found by other workers for the interaction of Li with graphene,^{16,21,23,24} a fact that confirms the previous argument. Consequently, we have some confidence in our result for the equilibrium separation.

In summary, we have shown that the adsorption binding energies of a Li atom to $C_{24}H_{12}$ obtained in DFT calculations (both with the GGA and with the LDA exchange correlation functionals) are very small, in agreement with the MP2 results of Ferre-Vilaplana. The weak binding energy is due to the large electronic HOMO–LUMO gap of the coronene, which makes this cluster rather inert. Therefore, the discrepancies that this author noticed between his MP2 calculations and the DFT calculations of other workers for graphene have a simple interpretation: the $C_{24}H_{12}$ cluster that Ferre-Vilaplana used to represent graphene is too small to properly account for the electronic structure of graphene. In contrast, graphene is a system with zero gap and interacts relatively strongly with Li and other alkali atoms. The partly ionic nature of the binding between Li and graphene becomes confirmed by using the proper description of graphene. This also confirms the interpretation of the enhancement of the adsorption energy of molecular hydrogen to Li-doped graphene and carbons as an indirect effect due to the charge transfer from Li to the graphene surface. As another interesting, but less important, point for the present purposes, we have also pointed out that the discrepancies in the equilibrium distance between Li and the coronene

obtained with DFT and MP2 may be due to the shallowness of the attractive part of the interaction potential.

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