Lithium Adsorption on Polyacenes & Zig-zag-edge Graphene Strips

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Abstract

The behavior of electrons in a nano-ribbon with zig-zag edge is discussed, including resonance theoretical comments, and described then in terms of singly occupied edge-localized frontier molecular orbitals. The initial analysis is for classical chemical resonance theory, then we use a simple tight-binding (Hückel-theoretic) argumentation and finally we use the density functional theory (DFT).

1 Introduction

A very diverse range of intercalates\textsuperscript{1} in graphite (and charcoal) have long been known including those involving alkali metals. Now with the advent of single sheet of graphene\textsuperscript{2}, adsorption on such sheets is of interest, say as to how adsorbed alkali metals modify the exceptional electronic structure of graphene\textsuperscript{3, 4, 5}. Indeed not only the adsorption on graphene is interesting, but also on benzenoids, say the polyacenes, where there is an anticipated 0-band gap (in the high-polymer limit\textsuperscript{6}), much as for graphene. Here then we address alkali metal (especially lithium) adsorption on polyacenes, then on graphene strips with the same sort of boundaries as the polyacenes. Our approach is 3-fold:
• via classical chemical resonance theory
• via simple tight-binding (Hückel-theoretic) argumentation
• via modern DFT

This emphasizes some predicted commonalities, so that the predictions should be more reliable and also indicate what sorts of things can be adduced from the simple qualitative theories. Indeed, when it comes to electron pairing, including the weak pairing (or completely unpaired) limit, a qualitative resonance-theory approach seems to work quite well in view of the simplicity of the argumentation.

2 Li Adsorption on Finite Polyacenes

We consider each of these 3 approaches separately then compare the different predictions. The first two schemes are especially simple, and easily considered before computer calculations, and are hoped to prove to be qualitatively correct to aid in understanding what goes on in a variety of situations, up to Li adsorption on graphene. For the polyacenes we start from a standard geometry of a chain of regular hexagons, and address perturbations from this. Our smallest considered polyacene is that of 3 hexagonal rings (anthracene), with a network (graph) as indicated in figure 1. There is of course one attached (but unshown) H atom at each coordination 2 (degree-2) vertex.

![Figure 1: First line: Anthracene. Second line: The π-network for polyacene](image)

2.1 Chemical Resonance-Theoretic Argument

This follows Pauling’s [7] and Wheland’s [8] ideas. Here first for anthracene, with 1 or 2 Li atoms each with a low electronegativity, one can imagine that
they tend to lose their valence electrons to the anthracene. And granted electron addition to the anthracene pi-network it should be at the more reactive "radicaloid" sites, which can be anticipated to be the two sites located on a central reflection plane because the 2 end rings then manifest independent local benzene-like resonance, as indicated in figure 2, this is the p-orbitals on these central sites become doubly occupied (from transfer of an electron from the electropositive Li atom or atoms), then the double bonding to these sites becomes weakened and the two end rings can more readily independently accommodate alternating single and double bonds. This resonance is greater than if the 2 opposite sites in one of the end rings were to be removed from inter with just 3 resonance structures (usually) with single independent local benzene-like resonance patterns with just a single electron transferred into the anthracene $\pi$-network, so that besides a site with a doubly occupied p-orbital, there is also one with an unpaired electron, whence again a similar preferring for the location of this exceptional sites still occurs even with 2 Li atoms such single e-transferred structures are relevant. That is, the e-transferred from Li to anthracene should overall only the partial, with an effective sharing of electrons between these moieties, whence the favored position of Li atoms should be above and/or below the anthracene plane, so as to readier more favorable orbital.

When the polyacene becomes ever longer there is an even greater enhancement of resonance, with a preference for unpairing to appear at a ring at or near the center. (If for a polyacene of $n$ hexagons, the 2 unpaired sites are placed in the $m^{th}$ ring ($m \leq n$) then instead of 1 conjugated 6-cycle there arise 2, and instead of $n + 1$ neighbor-paired resonance structures, there occur $m(n - m + 1)$). The $\pi$-bond orders to the central charged C atoms should diminish and give longer bonds. Moreover, with negatively charged C atoms (participating less so in the rest of the $\pi$-system), one might anticipate $sp^3$ hybridization (with an accompanying bond angle distortion, so that the end rings of anthracene are no longer co-planar). This distortion might also reasonably arise from the attraction between the negatively charged C atoms and the positively charged Li atoms. For higher polyacenes, the interruption of the $\pi$-network then again facilitates resonance to the two separated pieces best when the added electrons are near the center.

### 2.2 Simple Tight-Binding Argument

The simple tight-binding (or Huckel) model for a polyacene of a general number H of hexagons is exactly soluble, as has long been realized [10]. In this case, the electron(s) from the Li atom(s) should be transferred into the
Figure 2: First line: Neighbor-paired resonance structures for (neutral) anthracene. Second line: resonance structures for Lithium coordinated anthracene. Benzene-like local conjugated 6-cycles are indicated with a small circle in the center of the associated ring.

Figure 3: The LUMO density for anthracene in the first line. And in the second line, the amplitude for a non-bonding MO of infinite polyacene. Different Colors represent different phases.
LUMO of neutral anthracene. Especially for longer polyacenes this LUMO has dominant density on the secondary C atoms (i.e., those at the "points" of the polyacene) concentrated more-so at these C atoms nearer the center - as indicated in the first line of Figure 3. For a very long polyacene, it is in fact readily seen that an orbital indicated in the second line of Figure 3 has a 0-energy contribution from electron transfer, and with the whole eigenspectrum (via the Coulson-Rushbrooke theorem [11]) being symmetric about this position, it is seen that such an MO must be non-bonding. The symmetric and antisymmetric combinations of the 2 such orbitals on the top and bottom edges then may be viewed as for a sufficient long polyacenes the HOMO and LUMO. Of course for a finite polyacene there is some modification to this MO but it is only reasonable that the LUMO have a density not too far from this. Thus for the polyacenes in general the excess unpaired (or weakly paired) electron density ends up in the same places as for the resonance-theoretic argument. The remaining discussion, including geometric bending in the central area still applies in somewhat the same way. The diminishment of the bond order for the more central C atoms (at the outer "points" of the hexagons) occurs because that is where the LUMO (and HOMO) tends to be localized. Again Li atoms are favored to lie above or below the anthracene plane so as to enhance orbital overlap between the Li 2s orbital and anthracene 2p orbitals. Thus qualitative predictions are pretty much the same as for resonance theory.

2.3 Ab initio DFT Computations

In a previous work[15] we used the software gaussian[12] for the DFT calculations with the B3LYP[13, 14] as the functional and basis set 6-311g* to obtain the configuration of the adsorption of two lithium atoms on opposite side of anthracene, the resultant geometrical configuration is shown in figure 4. We have made the similar calculations using the Möller Plesset [] perturbation theory (MP2) and basis set 6-311++g** from which we have obtained qualitatively similar results.

The excess electron densities near the carbon atoms indicated in our resonance and tight-binding MO coincide, while the charge on the Li atoms is 0.823 C for the lithium at the top and 0.868 C for the lithium at the bottom. Thus there is almost a complete electron transfer (on the average) and the simplicities of the qualitative resonance and Huckel-MO arguments plausible. The bending of the anthracene moiety can be anticipated, both from the resonance- or MO-theoretic- view points, with excess electron density transferred from the Li atoms more dominantly localized on the two cen-
Figure 4: Optimized configuration of two Li atoms adsorption on anthracene using the b3lyp/6-311gd functional and basis set correspondingly.

Table C atoms, as is shown in figure 5, these two atoms should tend toward (nonplanar) $sp^3$ hybridization, with contributions from a doubly occupied $sp^3$ lone pair. The location of the Li atoms and the qualitative aspects of the geometric distortions are borne out - thereby giving some confidence in our simple pictures.

3 Li Adsorption on Extended Benzenoid Species

After success with a simple qualitative understanding of Li adsorption on finite polyacenes, it is natural to try to understand how these ideas might work in application to extended systems: infinite polyacene; zig-zag boundary graphene strips; semi-infinite graphene with a zig-zag boundary; infinite graphene; and multi-layer graphite.

3.1 Infinite polyacene

If Li atoms are placed periodically along the strip, one obtains a system with a finite unit cell, though to leave some chance for resonance the Li atoms should skip at least one hexagone. In terms of the MO approach there are polyacene bands (from above and below the Fermi energy) going into the Fermi-energy $\varepsilon_F$ ($= 0$ for our simple MO model), so that the unoccupied band orbitals nearer this Fermi energy are preferably occupied by any additional electrons - that is, without occupancy of the whole band one imagines naively unsubstituted rings between the Li-perturbed ones. Our DFT computations reveal a favored structure as in figure 6[16], where a Peierls transition happens [17], with the results there again being consonant our qualitative resonance an MO-theoretic arguments.
Figure 5: Charge distribution. Left: One lithium atom adsorbed to anthracene. Right: Two lithium atoms adsorbed to anthracene. The lithium atom in the up-center corresponds to the Lithium at the top of anthracene and the lithium atom in the down-center corresponds to the lithium at the bottom of anthracene.

Figure 6: Periodic Calculations.
3.2 Semi-infinite Graphene with Zig-Zag Edges

Both the resonances and Huckel theoretic approaches seemingly become somewhat more involved, because of the extended size of the system [18]. Nevertheless each approach can be applied to yield much the same prediction, that unpaired (or nonbonding), electron density occurs localized along the zig-zag edge to the extent, that there is 1/3 of an unpaired (or slightly occupied MO) electron per unit cell on the edge. Moreover while all these unpaired electrons exhibit an exponential density of fall from the edge, the unpaired spin density for different electrons (for nonbonding MOs) have a range of penetration into the bulk of the graphene and thereby facilitate ferromagnetic coupling amongst this nominally unpaired spins. Indeed less complete observations of all of this were made by resonance-theoretical studies [19] and MO-theoretic [20, 21]. More comprehensive tight binding computations [22, 23, 24] and some experimental results [25, 26] further support this picture. The resonance theoretic arguments indeed lead to the general prediction that the number of unpaired electrons per unit cell of edge is

\[ u = \frac{|(n_{d1} + 2n_{d2}) - (n_{d1} + 2n_{d2})|}{3} \]

where \( n_{d1} \) and \( n_{d2} \) are the numbers of degree \( d \) "starred" or "unstarred" sites per unit cell of edge, respectively.

The overall result then is that there are edges-localized LUMOs near the edge to accept electrons donated from nearby Li atoms, again above or below the graphene plane. In addition to the edge-localized nonbonding MOs it is well known [18] that bulk graphene has bulk orbitals at and near the Fermi level, through a rather low density of then because of their localization at the apex of a Dirac cone. Thus Li atoms should stick to the bulk surface of graphene, albeit either less tightly if at the same inter-Li spacings as at the edge, or else at a lesser density (i.e. a larger inter-Li spacing) if at the same strength of binding as at the edge.

3.3 Zig-zag-boundary Graphene Strips

The picture is some like for semi-infinite graphene, so now with 2 edges at each of which one anticipates unpaired electron density

3.4 Infinite Graphene

Following our discussion of semi-infinite graphene, one can expects bulk adsorbant. To minimize Coulomb repulsion from (partially) ionic Li atoms one can anticipate the Li atoms preferably adsorb half on each side of the graphene sheet.
3.5 Graphite

Here one expects the Li atoms between 2 successive sheets to bind the sheets more strongly than in ordinary graphite. Successive Li atoms patterns should alternate between successive Li layers (to minimize Coulomb repulsion between ionic Li atoms).

4 Conclusion

A fairly comprehensive qualitative explication of Li adsorption on anthracene, general polyacenes, semi-infinite graphene with zigzag edge and more is obtained via a triple of arguments. The resonance theory is largely qualitative, while the simple thight binding (or Hückel) argument is also. For smaller or quasi-one dimensional infinite objects our DFT calculations give support to the formal arguments. Overall the consilience of the different aproaches provides confidence in the predictions of Li atoms above and below the molecule plane, specially strongly near a zig-zag edge. Presumably much of the argumentation and results extent to other alkali metals.
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