Defying Coulomb's law: A lattice-induced attraction between lithium ions

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ABSTRACT

Normally ions with the same charge repel each other, but in very rare cases an intervening medium can produce an apparent attraction. We have studied the adsorption of Li-ions on semiconducting carbon nanotubes by density functional theory, one ion being inside, the other outside. The tube shields the direct Coulomb interaction between the ions, but the presence of the ion inside facilitates the adsorption of the ion outside, thus producing an apparent attraction. We give a quantitative explanation based on the electronic band structure of the tube, and surmise, that the same effect will hold on other carbon materials. Our results may explain the apparent attraction of Li-ions that has been observed in Li-batteries.

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1. Introduction

One of the basic laws of electrostatics states that in the vacuum two charges of equal sign repel each other. An apparent attraction between two particles of equal sign caused by an intervening medium is extremely rare. To the best of our knowledge the only clear case occurs in superconductivity, where the interaction between two electrons is overscreened by the ionic lattice of the metal [1]. We note in passing that the overscreening [2] observed at electrodes in contact with a liquid salt is a related effect, but it would be far fetched to say it was caused by an effective attraction between like charges.

Here we want to report on DFT calculations which show a clear attractive effect between two lithium ions that are placed inside and outside of a narrow carbon nanotube. Although this effect was unexpected for us, there is in fact experimental evidence that a lattice of carbon atoms can induce an apparent attraction between Li-ions. In a recent article Leiva et al. [3] could explain entropy changes in the charging of graphite with Li-ions only by assuming an attractive interaction between these ions. Further they observed, that earlier experimental works of Levi and Aurbach [4] showed clear evidence for this effect: cyclic voltammograms for lithium intercalation in graphite exhibited narrow peaks indicative of an attractive interaction between Li-ions.

2. Results and discussion

We started our investigation with the question: Is there any interaction between an ion inside a single-walled nanotube and an ion outside? Clearly, if the tube behaves like a perfect conductor, the answer is no. Indeed, we verified that in the case of a gold nanotube there is no interaction. The chances of seeing an interaction are better for a semiconducting tube, therefore we chose an (8,0) carbon nanotube (CNT) for our studies.

The technical details of our calculations are the same as in Ref. [5]; in order to make this article self-contained, we summarize them in the appendix. The total system was always neutral; initially we placed Li-atoms into the systems, they ionized spontaneously when the program performed the optimization.

We first placed one lithium atom inside of the nanotube and optimized its position, obtaining the same result as in previous studies [5]: The preferred position is above a C-C bond, but the positions above a C-atom or above the center of a ring have almost the same energy, the difference being less than 0.1 eV.

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Subsequently the position of this ion was kept fixed, while a second ion was placed outside the tube at a given value of the z-coordinate, which is along the axis of the tube (see Fig. 1). During the optimization the ion outside was allowed to move in the xy plane perpendicular to the axis of the tube. Also the atoms of the nanotube could move freely.

The adsorption energy of the ion outside in the presence of the ion inside was calculated from the equation:

$$\Delta E_2 = E_{(CNT+Li_{ins}+Li_{out})} - E_{Li} - E_{(CNT+Li_{ins})} \quad (1)$$

where $E_{(CNT+Li_{ins}+Li_{out})}$ is the energy of the nanotube with a lithium ion inside and another lithium ion outside, E_{Li} is the lithium atom energy, and $E_{(CNT+Li_{ins})}$ is the energy of CNT with just one lithium ion placed inside in its optimal geometry.

To separate the interaction between the lithium ion outside from the interaction between the lithium ion inside the nanotube, we studied the same systems but without the lithium ion inside. The lithium outside was kept fixed at a given z-coordinate but the remaining coordinates were optimized. The adsorption energy in this case is defined as:

$$\Delta E_1 = E_{(CNT+Li_{out})} - E_{Li} - E_{CNT} \quad (2)$$

Both in the absence and the presence of the Li$^+$ inside, the xy position of the ion outside was the same. The most favorable position for the outside ion is above the center of a carbon ring, and if it is forced to cross a carbon bond it does so at the center of the bond. This can be seen in Fig. 2, which shows the energy ΔE of adsorption of the outside ion as a function of the relative z coordinate. The adsorption energy always obtains a local minimum when the ion is above the center of a carbon ring, and a local maximum when it crosses the carbon bonds.

When $\Delta E_2 < \Delta E_1$, the presence of the ion inside makes the adsorption of the outside ion more favorable, and we speak of a lattice-induced attraction between the ions. There is another, more symmetric way of viewing the same effect. We first calculate the energies of adsorption for a single Li$^+$ ion inside and a single Li$^+$ ion outside:

$$\Delta e_{in} = E_{(CNT+Li_{in})} - E_{Li} - E_{CNT}, \quad \Delta e_{out} \equiv \Delta E_1$$
$$= E_{(CNT+Li_{out})} - E_{Li} - E_{CNT} \quad (3)$$

Next we calculate the energy of adsorption for the pair, one ion inside, the other outside:

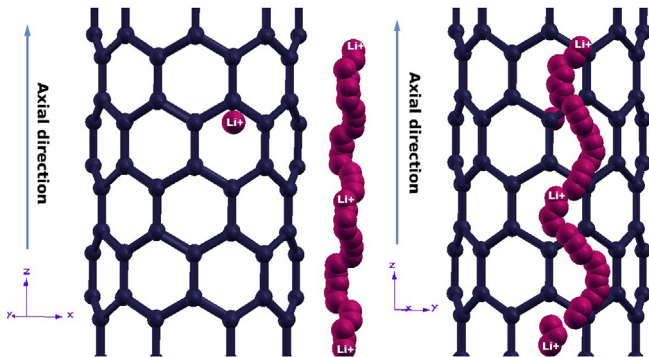$$\Delta E_{pair} = E_{(CNT+Li_{ins}+Li_{out})} - 2E_{Li} - E_{CNT} \quad (4)$$

Fig. 1. Lateral and front view of (8,0) CNT with 2 lithium ions, one inside and one outside, showing the optimal path of the ion outside as its z-coordinate was varied. (A colour version of this figure can be viewed online.)
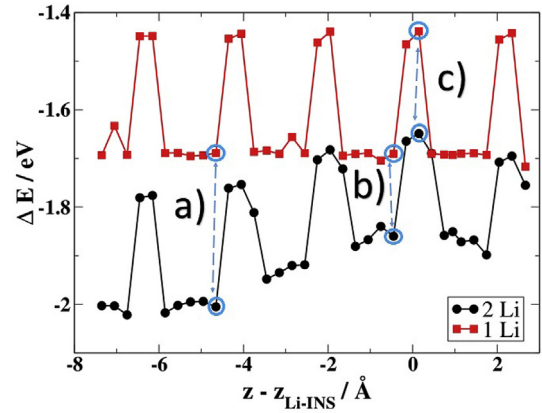

Fig. 2. Adsorption energy ($\Delta E_1, \Delta E_2$) versus axial component of Li-Li distance (z-$z_{Li\text{-}INS}$). The black and red curves were obtained using equations (1) and (2), respectively. Thus the lower black curve is the adsorption energy of the outside ion in the presence of the ion inside, while the upper red curve is the adsorption energy for the outer ion in the absence of the ion inside. $z - z_{Li-INS}$ is the difference in the z coordinate between the ion outside and the ion inside. (A colour version of this figure can be viewed online.)

Obviously, when $\Delta E_{pair} < \Delta e_{in} + \Delta e_{out}$, the two ions effectively attract each other. A simple calculation shows that this condition is equivalent to $\Delta E_2 < \Delta E_1$.

As can be seen in Fig. 2, in the presence of the Li-ion inside of the tube the energy of the ion outside is consistently lower by a few tenths of an electron Volt., i.e. $\Delta E_2 < \Delta E_1$. Over the limited range of distances which we could explore within our system with cyclic boundary conditions, the difference increases when the difference in the z position between the two ions becomes larger. At still larger distances, the difference must become less and finally disappear, but this range lies outside our present investigations, which aim at establishing the attractive effect.

The two ions have passed one electron each to the CNT, which appears on the latter as an image or polarization charge [6,7]. The distribution of this charge is shown in Fig. 3 for the three positions labelled a), b) and c) in Fig. 2. It is defined as:

$$\Delta \rho = \rho_{(CNT+Li_{ins}+Li_{out})} - \rho_{CNT} - \rho_{Li_{out}} - \rho_{Li_{ins}} \quad (5)$$

where ρ is the electronic density of the indicated systems. The induced charge is on the walls of the tube where the two ions are situated. In position a), when the ions are further apart, this charge is spread over a wider area — in other words, the image charges induced by the two ions overlap less.

When two Li-ions are both inside a nanotube or on the same side of a graphene layer, they are known to repel each other by a screened Coulomb Interaction [5,8,9]. So why do they seem to attract each other, when they are on opposite sides of the carbon wall? We shall first give a qualitative argument, which will then be substantiated by a quantitative estimate.

Pristine (8,0)CNT is a semiconductor. When a Li-atom adsorbs on its inside surface, it transfers an electron to the CNT. This lifts the Fermi-level into the conduction band, and the nanotube becomes conductive in the vicinity of the Li-ion [5,11,12]. The image charge, which compensates the charge of the ion, is formed by electrons close to the Fermi level [5,10]. This major change in the occupation of the conduction band requires a certain energy. When a second Li-atom is placed outside, the tube is already conductive, and the energy required to accept the second electron and to form the image charge is less, since there already is a substantial density of electrons at the Fermi level.
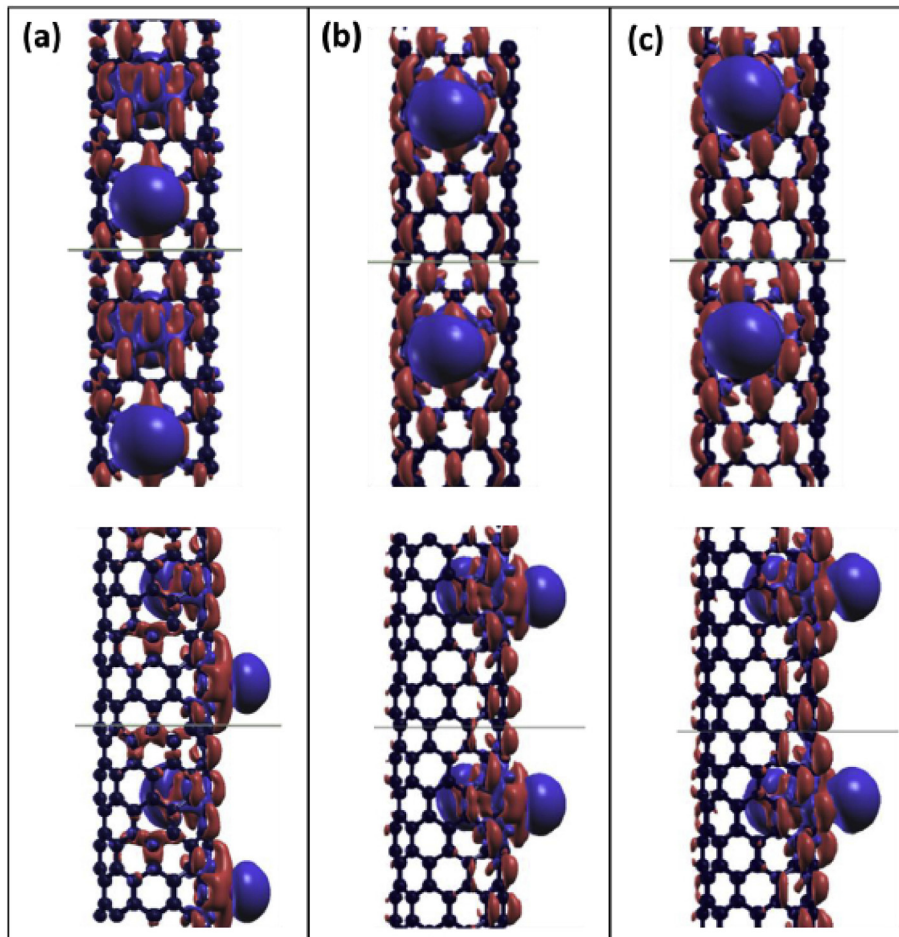
Fig. 3. Density difference $\Delta\rho$, calculated according to equation (5). The systems are labelled as (a), (b), and (c) as in Fig. 2. The isosurfaces correspond to an isovalue of $\pm$ 0.00025 e/ Å^3. (A colour version of this figure can be viewed online.)

A quantitative argument can be based on the work of Liu et al. [12]. These authors observed that during the adsorption of Li the band structure of various carbon structures, CNTs being amongst them, does not change much, but the Fermi level is lifted into the conduction band. This is also the case for our (8,0)CNTs, as can also be seen from Fig. 4. The energy ε_1 to which the Fermi level is lifted can be estimated from:
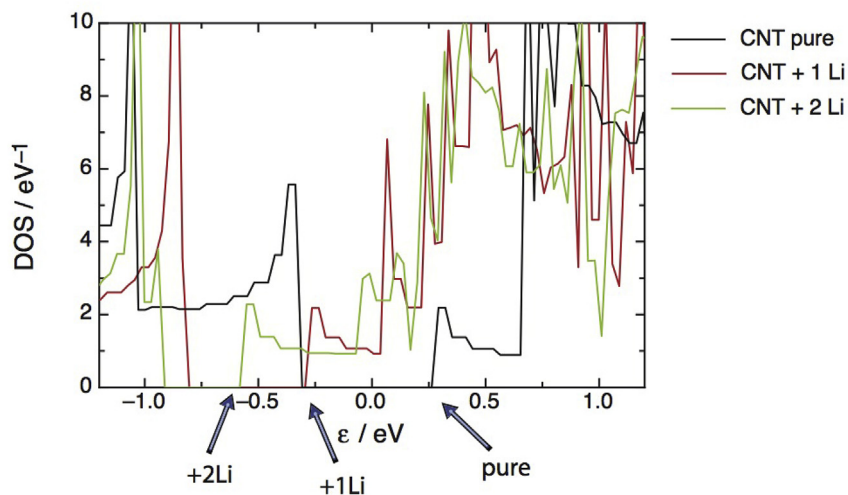

Fig. 4. DOS for a pristine (8,0)CNT, and for the same tube with 1 Li outside, and for 1 Li inside and 1 Li outside. The arrows indicate the onset of the conduction band for the cases indicated. The Fermi level has been set to zero. (A colour version of this figure can be viewed online.)

$$\int_{\varepsilon_L}^{\varepsilon_1} D(\varepsilon)d\varepsilon = 1 \tag{6}$$

where ε_L is the lowest empty level before adding the Li-ion, $D(\varepsilon)$ is the electronic density of states (DOS) of the nanotube, which is supposed to remain unchanged. Liu et al. then define the filling energy for adding a Li-ion as:

$$W_{\text{fil}}^1 = \int_{\varepsilon_L}^{\varepsilon_1} \varepsilon D(\varepsilon)d\varepsilon \tag{7}$$

They calculated this filling energy for a large variety of carbon structures and observed an excellent correlation with the energy of adsorption. Indeed, in a one-electron model this correlation would be exact. The filling energy for adding a second electron is:

$$W_{\text{fil}}^2 = \int_{\varepsilon_1}^{\varepsilon_2} \varepsilon D(\varepsilon)d\varepsilon \tag{8}$$

where the highest filled level ε_2 is obtained from:

$$\int_{\varepsilon_1}^{\varepsilon_2} D(\varepsilon)d\varepsilon = 1 \tag{9}$$

The band structure of pristine (8,0)CNT is well known [5]. It is a semiconductor with the Fermi level in the center of the gap. The density of electronic levels in the conduction band increases with energy. Therefore, the electronic density of states will also increase on an average with energy; hence $W_{\text{fil}}^2 < W_{\text{fil}}^1$. To see this explicitly, we replace $D(\varepsilon)$ in eqs. (6) and (7) by its average value $\overline{D}$. We obtain: $\varepsilon_1 = 1/\overline{D}$ and $W_{\text{fil}} = 1/2\overline{D} = \varepsilon_1/2$, where we have set $\varepsilon_L = 0$. Thus the cost in energy is the lower, the higher the average DOS in the region of integration; this corresponds with chemical intuition.

The DOS of CNTs shows an acute spike wherever the energy passes the minimum of a level in the band structure plot. Therefore, it is difficult to calculate the integrals for the determination of the filling energies W_{fil}^1 and W_{fil}^2. However, to prove that $W_{\text{fil}}^2 < W_{\text{fil}}^1$ it is sufficient to show that $\varepsilon_2 - \varepsilon_1 < \varepsilon_1 - \varepsilon_L$.

This can be ascertained from Fig. 4, which shows the DOS for the pristine (8,0)CNT and for the CNTs with just one Li outside and with one Li inside and one Li outside. Note that the Fermi level has been set to zero, which shifts the energy scale in an obvious way. One notices the acute spikes which appear whenever a new level sets in. For our purpose, the most important features are the lower edges of the conduction band, which are marked by arrows. The shift between the pure tube and the tube with 1 Li is $\varepsilon_1 - \varepsilon_L = 0.57$ eV, and the shift from 1 Li to 2 Li corresponds to $\varepsilon_2 - \varepsilon_1 = 0.31$ eV. The difference between these two values is of the same order of magnitude as the gain in the adsorption energy of the Li outside due to the presence of the Li inside. So this explains the observed effect.

This argument holds, because there is no chemical binding between the lithium ions and the CNT. Any chemical interaction would perturb the DOS of the CNT beyond shifting the Fermi level. Thus the lithium atoms dope the CNT, and are then attracted to the tube by the Coulomb interaction. Pauli repulsion prevents them from entering the wall of the tube.

Next we want to discuss why, within the tube considered, the attraction is weaker when the ions are closer. The electric field generated by the Li ion inside vanishes outside the tube, so this effect cannot be caused by the Coulomb repulsion between the two ions. We surmise that this is caused by the overlap between the image charges generated by the two ions. When the two ions are close, the image charges overlap (see Fig. 3); this accumulation of charge causes a strong local perturbation, which is less favorable than a wider distribution of the induced charge.

An intriguing problem which we leave for further research, is: how does this effect depend on the length of the tube, or better — since we use cyclic boundary conditions — how does it depend on the coverage? Obviously, the effect must vanish when the ions are sufficiently far apart. But it would be interesting to know how far the effect of the doping actually extends, and over which regions the CNT becomes conductive.

The question arises, if this lattice induced attraction is limited to semiconducting carbon nanotubes. If our arguments are correct it requires a low density of states at the Fermi level, so that the addition of one electron leads to a marked upward shift. Further, on an average the density of states must increase with energy above the Fermi level, so that the addition of a second ion costs less energy. Finally, the direct Coulomb interaction between the ions must be strongly screened so that it is negligible. Therefore it is favorable if the ions are separated by a carbon layer. These conditions rule out metal tubes or layers, because their density of states at the Fermi level is too high, but also wide-band semiconductors, where the shifting of the Fermi level into the conduction band costs too much energy — in other words, the Li-ion would not ionize. However, other carbon structures such as graphene and graphite meet these conditions. Our arguments are not limited to lithium; other alkali ions such as Na^+, which do not adsorb chemically, should show the same effects. Indeed, a recent study of sodium adsorption on graphene [13] also shows that the Fermi level is raised during adsorption. For halides the situation is not so clear, since they seem to induce larger changes in the band structure of CNTs [5], so that the arguments presented in eqs. (6)–(9), based on the work of Liu et al. [12] do not hold, since they presume that the band structure is only little affected by the addition of an extra electron. So we suggest that this effect is limited to carbon structures like CNTs, graphene and graphite, and may thus explain the attractive interaction observed in Li-ion batteries.

Acknowledgements

Appendix. Technical details of the calculations

Periodic density functional theory (DFT) calculations based on plane waves have been performed as implemented in the VASP code [14]. The electron-ion interactions were accounted through ultrasoft pseudopotentials [15], while the valence electrons were treated within the generalized gradient approximation (GGA) in the version of Perdew, Burke and Ernzerhof (PBE) [16]. The electron wave functions were expanded in a plane-wave basis set up to a kinetic energy cutoff of 400 eV (450 eV for the density).

The infinite (8,0) CNTs were described using periodic boundary conditions and a unit cell of (21 × 21 x 12.82) Å^3. We placed one lithium atom inside of the nanotube and the second one outside of it. The optimal adsorption geometries were found following the procedure described in the manuscript. The convergence was achieved when the forces were lower than 0.02 eV/Å. We used

neutral slabs to study these systems. Nevertheless, we always observed a redistribution of the charge that places a positive charge on the lithium atoms. The ionic character of the lithium was confirmed using: Bader charge analysis [17], projection of the DOS, and electronic density difference calculations (see our previous works [7]). The Bader charges of these ions were $+1$ within DFT error ($+0.89$ - $+0.99$).

The optimization of the geometries and the calculation of the energies were performed using only the Gamma point. For a more accurate plot of the total density of states, we used the tetrahedron method [18] and ($1 \times 1 \times 16$) k-points grid. Figs. 1 and 3 were made using XCrySDen software [19].

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