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.

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:

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

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:

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

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:

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

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

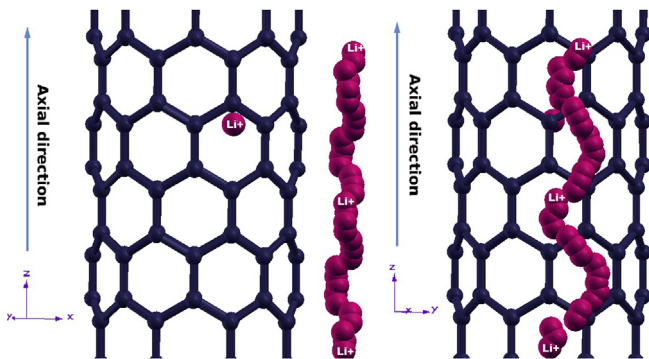$$\Delta E_{pair} = E_{(CNT+Li_{ins}+Li_{out})} - 2E_{Li} - E_{CNT} \tag{4}$$

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.)
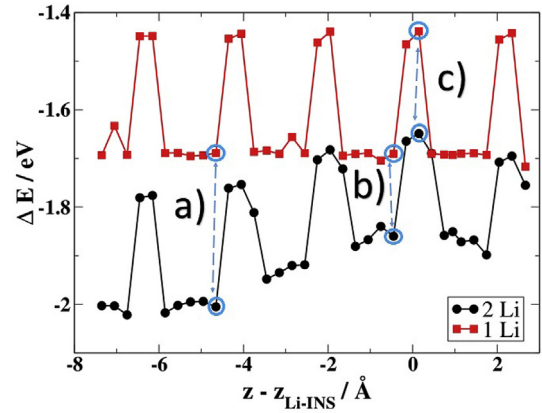

Fig. 2. Adsorption energy ($\Delta E_1, \Delta E_2$) versus axial component of Li-Li distance (z-$z_{Li\text{-}INS}$). The black and red curves were obtained using equations (1) and (2), respectively. Thus the lower black curve is the adsorption energy of the outside ion in the presence of the ion inside, 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:

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

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.