Curvature dependence of the metal catalyst atom interaction with carbon nanotubes walls

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Abstract

Interactions of the transition metal atoms with carbon nanotube walls are investigated using a tight-binding molecular dynamics method that allows for spin unrestricted geometry optimization. Comparison with the results for bonding on graphite indicates major differences in bonding sites, magnetic moments and the direction of charge transfer. The significant values of magnetic moments obtained for the metal atoms on nanotube walls is consistent with the recent experimental findings. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Single-wall carbon nanotubes (SWNT) are now routinely being produced in experiments. A key to the abundant production of these nanotubes is the widespread use of transition metal (TM) catalysts such as Ni, Co or Fe, whether in an arc-discharge [1,2] or in a pulsed laser vaporization apparatus [3,4]. Recently, it has been suggested that the TM catalysts may ultimately end up residing in close contact with the nanotube walls, affecting many of the transport properties of these nanotubes [5].

The interactions of TM atoms with graphite or graphene sheet has been the subject of extensive investigations, both experimentally [6–12], and theoretically [13–15]. These studies show that a carbon layer interacts strongly with TM atoms and that, depending on the specific transition metal, this interaction exhibits a strong variation of the hybridization strength between carbon p and the TM d orbitals. Consequently, the value of the magnetic moment of a TM atom on the surface of the graphite was found to depend strongly on the adsorption site. More recently, a tight-binding Hamiltonian incorporating magnetic effects was introduced by us and used in performing spin and geometry unrestricted molecular dynamics (MD) study of the interactions of Ni atoms with graphite [16] and C60 [17].

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The interaction of TM atoms with carbon nanotubes offers another related and challenging problem. This is because one now also has to deal with the effects of curvature and zone folding as additional complications among various factors affecting the delicate interplay between the geometric and magnetic ordering of the TM atoms on nanotubes. Curvature of the surface can be expected to alter the bonding features on carbon nanotubes when compared with graphite as a result of the curvature-induced rehybridization of carbon bonding orbitals [18,19]. A simple interpolation of the results for TM interaction with graphite to predict similar properties for TM with nanotube can lead to qualitatively different results. At present, to the best of our knowledge, a fully quantum-mechanical MD treatment of the interaction of TM atoms with carbon nanotubes has not yet been reported.

In this work, we present results from applications of our recently developed tight-binding molecular dynamics (TBMD) method which has been generalized to treat complex hetero-nuclear magnetic systems [16,20,21]. The scheme is orders of magnitude faster than ab initio methods while allowing one to perform spin and geometry unrestricted energy minimization realistically for the determination of lowest energy structures. The method uses a minimal parameter basis set to obtain a transferable tight-binding parametrization applicable to binary Ni-C clusters. In Section 2, we briefly review the TBMD formalism.

2. Tight-binding molecular dynamics method

In tight-binding theory, $U$ is written in its general form as a sum of several terms [22],

$$ U = U_{el} + U_{rep} + U_0, $$

(1)

where $U_{el}$ is the sum of the one-electron energies $E_n$ for the occupied states:

$$ U_{el} = \sum_n E_n, $$

(2)

and $U_{rep}$ is given by a repulsive pair potential

$$ U_{rep} = \sum_i \sum_{j>i} \chi(r_{ij}). $$

(3)

$U_0$ is constant that merely shifts the zero of energy.

The force $F_s$ associated with an atomic coordinate $x$, for performing MD simulations, is given by

$$ F_s = -\frac{\partial U}{\partial x}. $$

(4)

In particular, the electronic part of the force is obtained using the Hellmann–Feynman theorem:

$$ \frac{\partial E_n}{\partial x} = \psi_n^* \frac{\partial H}{\partial x} \psi_n $$

(5)

where $H$ is the parametrized Hamiltonian matrix of the system and we have made use of Eqs. (2) and (4).

The eigenvalues, $E_n$, and eigenvectors, $\psi_n$, are obtained by diagonalizing $H$. The diagonal elements of the Hamiltonian are taken from Ref. [22]. The off-diagonal matrix elements of the Hamiltonian are obtained using the universal scheme by [22]:

$$ V_{\lambda\lambda'} = \frac{\hbar r_{\lambda\lambda'}}{md^{1+z}}, $$

(6)

where $r_{\lambda\lambda'}$ is a characteristic length for each transition metal. The parameter $\tau = 0$ for s-s, s-p and p-p interactions, $\tau = 3/2$ for s-d and p-d, $\tau = 3$ for d-d interactions [22].

In the case of the magnetic TM clusters, the necessary spin dependence of the diagonal matrix elements is introduced using the Hubbard approximation according to which [20] the intra-atomic Coulomb and exchange interactions result in the following correction effective intra-atomic exchange interaction, $J_{\text{eff}}^{(i)}$, in terms of which the corrections $\Delta E_{m}^{(i)}(\alpha)$, $m = \text{s,p,d}$, to the diagonal elements, $E_{m}^{(i)}$, $m = \text{s,p,d}$, take the form

$$ \Delta E_{m}^{(i)} = \sum_{\alpha} \Delta n_{\alpha}^{(i)} - \sum_{\alpha} \alpha \mu_{m}^{(i)} J_{\text{eff}}^{(i)} + \Delta E_{\text{Mad}}^{(i)}, $$

$$ m = s,d $$

(7)

where $\alpha$ denotes the spin (+1 for spin-up and −1 for spin-down), $n_{m\alpha}^{(i)}$ denotes the occupation number of the $m\alpha > 0$ orbital at the lattice site $R_i$ and

$$ \mu_{m}^{(i)} = n_{m+\alpha}^{(i)} - n_{m-\alpha}^{(i)} $$

(8)

$$ \Delta n_{m\alpha}^{(i)} = n_{m\alpha}^{(i)} - n_{0m\alpha}^{(i)}, $$

(9)
where \( n_{0m}^{(i)} \) are the corresponding orbital occupancies for the bulk material. The terms \( \Delta E_{\text{Mae}}^{(i)} \) and \( \Delta E_{\text{config}}^{(i)} \) contained in the right-hand side of Eq. (7) denote Madelung-type interactions (resulting from the charge transfer among the atoms of the cluster) and the coordination dependence of the matrix elements, respectively.

To make our calculations tractable, we make the assumption that

\[
\Delta E_{\text{Mae}}^{(i)} = -\sigma s_{0m}^{(i)},
\]

where \( s_{0m}^{(i)} \) are adjustable parameters, to be adjusted so as to reproduce the correct spacing of the higher spin-states of small clusters (for cluster size \( n \leq 5 \)), whose values are available from results of accurate \( \text{ab initio} \) calculations. From Eq. (9), it is apparent that the parameters \( s_{0m}^{(i)} \) correspond to an effective exchange interaction \( J_{\text{eff}}^{(i)} \) terms according to the relation

\[
s_{0m}^{(i)} = \mu_n^{(i)} J_{\text{eff}}^{(i)}. \tag{10}
\]

In order to further simplify our model, we assume the effective exchange interaction to depend only on \( \langle \mu_n \rangle \) (and not on the individual \( \mu_n^{(i)} \) value) and be independent of the types of the orbitals and lattice sites, i.e. we take,

\[
s_{0m}^{(i)} = s_q, \quad \forall \ m, i. \tag{11}
\]

As a test of the validity of the present formalism we have applied it to study \( \text{Ni}_n \), \( \text{Fe}_n \), and \( \text{Co}_n \) clusters [20]. In particular, experimental results are available for \( \text{Ni}_n \) clusters [23]. Our theoretical results are in excellent agreement with the experimental results reported in Ref. [23].

The extension of the TBMD scheme to treat interactions in hetero-atomic systems involves fitting of the adjustable parameters to the values obtained either from experiments (when available) or from \( \text{ab initio} \) calculations [16,21]. For the purposes of the present work the data base for fitting the parameters is obtained from experimental and \( \text{ab initio} \) results for small \( \text{Ni}_n \), \( \text{C}_n \), and \( \text{Ni}_n\text{C}_n \), \( n + m \leq 4 \) clusters, the latter obtained using the density functional method and the single, double and triple coupled-clusters method [16]. This parametrization, incorporated into the TBMD scheme, has been used with success to study \( \text{Ni}_m\text{C}_n \) clusters of arbitrary sizes as well as the interaction of Ni with graphite [16].

### 3. Results

In this Letter, we focus our efforts on the interaction of Ni atoms with SWNTs and compare it with our findings for the interaction of Ni atoms with graphite. This comparison will enable us to gain an understanding of the curvature dependence of the interactions by observing contrasting results. For the needs of the present work, we repeat the calculations for the Ni–graphite systems by employing a much larger graphitic cluster than that used in our previous work [16]. In particular, we simulate the graphite surface by choosing a cluster consisting of 116 atoms forming a portion of the bulk graphite plane. This size cluster was found to be large enough to obtain converged results while allowing us to compare the relative stability of the various bonding sites of Ni on graphite [2]. The carbon nanotube is simulated by two ‘arm-chair’ \((n,n)\)-tubes with \( n = 5 \) and \( n = 10 \). Here we use the standard notation in which each tube is uniquely determined by the chiral vector \((n,m)\), where \( n \) and \( m \) are integers [18]. The ends of both tubes have been capped off to avoid effects of dangling bonds. The resulting ‘capsules’ consist of 150 and 321 atoms, respectively, for the \((5,5)\) and \((10,10)\)-tubes. The electronic structure of the nanotubes can be either metallic or semiconducting, depending on the chirality. The ‘arm-chair’ \((n,n)\)-tubes chosen here are metallic in nature. In our calculations, both the graphitic cluster and the nanotube were fully relaxed without any symmetry constraints before introducing Ni atoms. We then carry out TBMD optimizations to determine the energetically most favorable sites at which Ni atoms can bind.

The summary our results are given next. Table 1 provides a quick overview of all the numerical results.

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The slightly different numerical results obtained here for graphite when compared to those reported in Ref. [16] are due to the smaller size of the substrate used there.
Table 1
Summary of results for Ni and Ni$_2$ on graphite and nanotube wall. Positive values of charge transfer indicate loss of charge on Ni, while negative values indicate gain in charge on Ni. The values of the magnetic moment $\mu$ are in Bohr magnetons ($\mu_B$). The numbers in parentheses denote the number of times the given quantity is repeated. The square brackets indicate the range of bond lengths.

<table>
<thead>
<tr>
<th>Site</th>
<th>Charge transfer (e)</th>
<th>$\mu$ ($\mu_B$)</th>
<th>Ni–Ni bond (Å)</th>
<th>Ni–C bonds (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–graphite</td>
<td>atop</td>
<td>0.98</td>
<td>0.3</td>
<td>1.80, 1.94(3)</td>
</tr>
<tr>
<td></td>
<td>hole</td>
<td>0.44</td>
<td>0.29</td>
<td>[2.07–2.20]</td>
</tr>
<tr>
<td>Ni-tube(5,5)</td>
<td>atop</td>
<td>–0.05</td>
<td>0.15</td>
<td>1.79, 1.95(2)</td>
</tr>
<tr>
<td></td>
<td>bridge</td>
<td>–0.18</td>
<td>0.10</td>
<td>1.76(2)</td>
</tr>
<tr>
<td>Ni-tube(10,10)</td>
<td>atop</td>
<td>0.234</td>
<td>0.13</td>
<td>1.78, 1.98, 2.04</td>
</tr>
<tr>
<td></td>
<td>bridge</td>
<td>0.253</td>
<td>0.10</td>
<td>1.77(2)</td>
</tr>
<tr>
<td>Ni$_2$–graphite</td>
<td>atop–atop (a)</td>
<td>0.93</td>
<td>0.26(2)</td>
<td>[1.80–1.95]</td>
</tr>
<tr>
<td></td>
<td>atop–atop (b)</td>
<td>0.59</td>
<td>0.22(2)</td>
<td>[1.80–2.24]</td>
</tr>
<tr>
<td></td>
<td>hole–hole</td>
<td>0.29, 0.21</td>
<td>0.21, 0.23</td>
<td>[2.0–2.3]</td>
</tr>
<tr>
<td>Ni$_2$–tube</td>
<td>atop–atop</td>
<td>–0.18, –0.23</td>
<td>0.12(2)</td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>bridge–bridge</td>
<td>0.32, 0.35</td>
<td>0.61, 0.65</td>
<td>2.34</td>
</tr>
</tbody>
</table>

3.1. Single Ni atom

Three distinct sites were considered for a single Ni atom on graphite and the nanotube wall. These consisted of a Ni atom (i) directly above a C atom (atop site), (ii) above the center of an hexagon (hole site) and, (iii) over a C–C bond (bridge site).

3.1.1. Ni on graphite

At the atop site, the Ni atom moves to a distance of 1.80 Å from the C-atom lying just beneath it and also bonds to the three next nearest C-atoms. A striking feature of the atop bonding site is that the C-atom beneath the Ni atom undergoes a significant relaxation which pushes this C-atom below the graphite plane while the three next nearest C-atoms move outwards. As a result, three equidistant Ni–C bonds of 1.94 Å are formed between the Ni atom and the next nearest C-atoms. At this position, the Ni atom looses 0.98/e of charge to the carbon atoms and also exhibits a magnetic moment of 0.3 $\mu_B$.

At the hole site, Ni forms six unequal bonds with the six nearest carbon atoms on relaxation (see Table 1). The strong Ni–C interactions result in considerable distortions in the planar structure beneath the Ni atom. The Ni atom exhibits a magnetic moment of 0.29$\mu_B$ and looses charge to the carbon atoms ($\approx 0.44/e$).

There was no bonding of Ni on the C–C bridge site. The Ni atom moved to the atop position instead.

The bonding at the hole site was found to be more stable than at the atop site by 15.4 eV using the tight-binding total energy calculations. This rather large energy difference is an artifact of the fact that the diagonal matrix elements of the Ni atom depend on its coordination number (see footnote 2) and the slightly different relaxation the graphene sheet undergoes in the case of Ni adsorbed at atop and hole sites. The dependence of the diagonal matrix elements on the coordination number was necessary for obtaining the correct charge transfer while fitting our TBMD results to ab initio values.

3.1.2. Ni on nanotube wall

In the case of interaction of Ni with the nanotube wall, only the atop and bridge sites were found to be stable on MD relaxation. The hole site is found to be unstable for Ni on the nanotube wall. Instead, a Ni atom, initially placed at a hole site, moves and relaxes on an atop site. This is in striking contrast to the case of the interaction of Ni with graphite where the hole site was found to be the most stable.

At the atop site (Fig. 1a) the Ni atom forms three Ni–C bonds and gains electronic charge ($\approx 0.05/e$) from the carbon atoms while displaying a magnetic moment of 0.15$\mu_B$.

The Ni atom relaxed at the bridge site (Fig. 1b) forms bonds of length 1.76 Å each with the carbon atoms. There is a gain of electronic charge of
Fig. 1. The two stable binding sites for a single Ni on carbon nanotube wall: (a) atop site and (b) bridge site.

magnitude 0.18|e|. The magnetic moment on the Ni atom is 0.10μB. The atop site is energetically more favorable than the bridge site by 9.1 eV.

The bonding features were found not to change substantially. The atop site remained more stable, but 9.46 eV lower in energy when compared with the bridge site. Also, as shown in Table 1, the Ni–C bond lengths and the Ni magnetic moment on a (10,10)-tube are almost the same as those found in the case of the (5,5)-tube. Only the charge transfer was found to differ substantially. On the (10,10)-tube, the Ni atom looses some charge, in agreement with the expected trend as we compare the charge transfer found on graphite and the (5,5)-tube.

3.2. Ni₂ dimer

In order to study the binding of Ni₂ on graphite and nanotube surfaces we release a Ni₂ dimer within bonding distances on these surfaces at various initial positions. The results can be summarized as follows.

3.2.1. Ni₂ on graphite

Three distinct stable bonding geometries were obtained for the Ni₂ chemisorption on graphite. In the first case, there was a separation between the two Ni atoms on relaxation, mediated by the graphite surface. In the final stable configuration the Ni atoms are found to bind at adjacent hole sites with the Ni–Ni distance of 2.74 Å. The Ni atoms loose charge to carbon atoms (0.2|e| and 0.29|e|, respectively) while exhibiting magnetic moments of magnitudes 0.21μB and 0.23μB, respectively.

In the second case, the Ni atoms separate and bond at atop sites on opposite corners of the same hexagon (Atop–atop (a) in Table 1). The Ni–Ni distance for this configuration is 2.91 Å. Each of the Ni atoms looses charge of magnitude 0.93|e| to the carbon atoms while exhibiting magnetic moments of magnitudes 0.26μB each. The geometry obtained in the first case is more stable than the latter. Another geometry, in which the two Ni atoms separate and bond at atop sites over the next-nearest carbon atoms was also found to be a local minima (Atop–atop (b) in Table 1), but less stable than the first two cases. The Ni–Ni bond length here was obtained to be 2.77 Å.

3.2.2. Ni₂ on nanotube wall

The two stable bonding geometries obtained here are considerably different from Ni₂ on graphite. In
the first case the Ni₂ dimer placed within bonding distance of the nanotube moved apart from each other with each atom binding at atop sites on adjacent hexagons as shown in Fig. 2a. The Ni–Ni distance for this configuration is 2.78 Å. The Ni atoms gain electronic charge from the carbon atoms (0.18|e| and 0.23|e|, respectively). Each of the Ni atoms forms three Ni–C bonds and exhibit a magnetic moment of 0.12μ_B.

In the second case the Ni atoms bond at the diametrically opposite bridge sites as shown in Fig. 2b. The equilibrium Ni–Ni bond length is found to be 2.34 Å, close to the value obtained for an isolated Ni₂ dimer. The Ni atoms forms Ni–C bonds of lengths 1.77 Å each and loose electronic charge to the carbon atoms (0.35|e| and 0.32|e|, respectively). The magnetic moment, however, is obtained to be rather large for the Ni atoms; having values 0.61 and

![Fig. 3. The HOMOs for Ni on graphite at the: (a) atop and (b) hole sites.](image-url)
0.65 $\mu_B$, respectively. The bonding configuration in the first case is found to be preferable over the second.

4. Discussion

Our TBMD study of Ni and Ni$_2$ interactions with graphite and nanotube walls reveals many interesting features. While the most stable bonding of Ni is obtained at the hole site for graphite, the same site is found to be unstable for Ni bonding on nanotube walls. Similarly, while the bridge site is one of the stable geometries for Ni bonding on the nanotube walls, it is found to be unstable for graphite. The atop site for Ni is stable for both graphite and nanotube walls, although the number of carbon atoms to which Ni bonds is found to be different. Also, the Ni bonding is accompanied by larger distortions on the graphite surface than on the nanotube walls.

The relative stability of the Ni atoms on different adsorption sites on graphite and on the nanotube.
walls is the outcome of a delicate interplay among various factors which affect the hybridization strength between the C–p and the Ni–d orbitals. The point group symmetry of the adsorption site, the length of the Ni–C bonds, the surface relaxation and the charge transfer are the most crucial factors in this respect. Although a quantification of the contribution of each of these factors in the bonding process (between Ni and graphite or nanotube) is very difficult, a very good insight can be obtained by studying the bonding characteristics of the corresponding highest occupied molecular orbitals (HOMO) of each system. The molecular orbital graphs were obtained by ab initio calculations using the GAUSSIAN program [24]. In Fig. 3a,b we present the HOMOs for Ni at the atop and the hole sites, respectively. From these it can be seen that the Ni–C bonds appear quite different at these two sites. In particular, at the atop site the bond appears to have ionic character while exhibiting weak covalent character at the hole site. It

Fig. 4. The HOMO for Ni on (5,5)-nanotube at the atop site.
is also worth noting that while the bonding orbital at the atop site is found to be $d_{\pi z}$, at the hole site it is $d_{\sigma z}$.

Furthermore, curvature of the surface causes a rehybridization of the bonding orbitals and, as seen in Fig. 4, when the Ni atom is at the atop site on nanotube, the Ni–C bond takes an additional partial covalent character. In view of these bonding pictures we can argue that the smaller charge transfer seen for Ni bonding on nanotubes indicates the hole covalent bonding to be stronger than the ionic-atop bonding for Ni relaxation on graphite.

The amount and direction of the charge transfer accompanying the bonding of Ni provides another interesting case study. While the direction of charge transfer is from Ni to carbon on graphite, and which can be relatively large (up to $1e$), the direction for this transfer is from carbon to Ni in the cases for the (5,5)-nanotube and of a smaller magnitude. The same trends are also exhibited in the case of the interaction of a Ni$_2$ dimer with graphite and tube, respectively.

As the radius of the tube is increased, the charge transfer on the nanotube starts reversing its direction tending to approach the value found for graphite. Also, the Ni bonding always results in finite magnetic moments for both graphite and the nanotubes.

The Ni atoms of the Ni$_2$ dimer when placed on a graphitic surface or nanotube wall tend to separate in a reaction mediated by the underlying carbon atoms. The situation is much more pronounced for Ni$_2$ bonding on graphite. As a result of this carbon-induced weakening of the Ni–Ni bond, and in combination with the different bonding sites possible for Ni on tube (as compared to those on graphite), the Ni$_2$ dimer can be found on the tube in relatively more configurations than on graphite. Thus, Ni$_2$ on the tube walls can be found in configurations exhibiting a larger range of Ni–Ni bond lengths (2.34–2.78 Å) and Ni charge/magnetic states. Due to the expectation that the bonding sites of Ni will vary with the curvature of the tube (because of the differing amounts of curvature-induced rehybridization process), the number of Ni$_2$ configurations on a tube can be expected to vary with the curvature.

In conclusion, we can summarize our results as follows: (i) While the Ni–Ni bond is greatly weakened on chemisorption on graphite, curvature of the surface is found to suppress this weakening consider-
ably; (ii) curvature promotes the bonding on bridge sites while suppressing bonding on hole sites; and (iii) curvature also reduces the amount of charge transfer and may affect its direction.

All these results strongly point to the dependence of the interaction on the curvature of the surface to which the TM atoms bond and give a clear indication that a naive interpolation of results from the graphitic to the nanotube regime can lead to qualitatively incorrect results. Our results also show the necessity of performing spin and geometry unrestricted optimization simultaneously for the realistic determination of the chemisorbed geometry. It should be noted that even though our TBMD calculations give larger energy differences between various chemisorption sites when compared with ab initio values for the same sites, the relative ordering of the energies remain the same.

The significant values of magnetic moments on the Ni atoms on nanotube walls and the charge transfer between Ni and carbon may be consistent with the recent work of Grigorian et al., [5] who propose that the thermopower and electrical resistivity of bundles of single wall carbon nanotubes are strongly effected by the spin moment of the catalyst atoms in contact with the tube wall.

Finally, our results also lead to the prediction of the existence of a critical value for the curvature of the tube at which all three bonding sites may become accessible for Ni. This will provide a way to control the bonding characteristics of the substrate by varying its curvature, allowing for the growth of TM films with adjustable inter-atomic distances in an efficient manner.

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The energy differences between the binding sites were found to be insensitive to large changes in the diagonal matrix elements as well as in the case where the diagonal matrix elements are kept constant, i.e., independent of the local coordination number.
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