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Tight-binding molecular-dynamics study of transition-metal clusters

Madhu Menon
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0055

John Connolly
Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0055

Nectarios Lathiotakis and Antonis Andriotis
Institute of Electronic Structure and Laser, Foundation for Research and Technology–Hellas,
P.O. Box 1527, Heraklion, 71110 Crete, Greece
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An efficient semiempirical molecular-dynamics technique to treat interactions in transition metals is introduced. The method is based on the tight-binding scheme incorporating d electrons. Optimized geometries are obtained using this scheme for Ni_n clusters for n up to 10. The expected general trends for the various cluster properties are well described by our results. Important qualitative differences from semiconductor clusters are observed. The technique appears to be promising in modeling interactions in alloys containing semiconductor and metal atoms.

I. INTRODUCTION

A first step toward developing an interaction model for commercially important semiconductor and metallic alloys is the necessity of devising a universal model capable of treating interactions in both covalent and metallic systems. Such a scheme must be computationally fast, efficient, sufficiently flexible, and capable of accurately reproducing known properties when applied to the respective component systems.

Until recently the most widely used approaches for accurate first-principles calculations of the electronic structure of d-band metals made use of the local-density approximation (LDA) and were based on computational schemes like the linearized-augmented-plane-wave, the linearized-muffin-tin-orbital (Refs. 1–3) and the Korringa-Kohn-Rostoker methods.[4,5] More recently, the LDA scheme has been used in the study of the nickel dimer and for Ni_4 and Ni_5 clusters.[6] The *ab initio* calculations on the other hand have made use of either the effective core potentials (ECP), the Hartree-Fock (HF) method, and a Gaussian-type-function (GTF) basis[7] or an all-electron GTF basis at both HF and configuration-interaction (CI) levels.[6,8] It is worth noting that the *ab initio* calculations at the CI level are strictly restricted to the free Ni atom and the Ni dimer Ni_2.[6,8] Ni clusters with more than two atoms have so far been studied either within the LDA (sometimes improved by including nonlocal corrections[6]) or within the method of the self-consistent field at the nonlocal Hartree-Fock level of approximation.[7–9] The complexity of the *ab initio* calculation for transition metal atoms and clusters is reflected in the numerical difficulties involved in obtaining the correct ground state of the free Ni atom. The *ab initio* results obtained for Ni_n clusters, while satisfactorily describing trends in the variation of various cluster properties with the cluster size (i.e., number of atoms), fail to agree among themselves and with experiment.[6–10] As a consequence of these difficulties the *ab initio* calculations, even when considering optimization, limit themselves to symmetry restricted geometries.

At present, a molecular dynamics simulation of transition metal clusters based purely on *ab initio* methods seems to be difficult, if not impossible, to carry out on account of the prohibitive requirements in both computer time and computer capacity. Clearly, there is a need for a semiempirical interface which will bridge the gap between accurate *ab initio* calculations for small systems and the phenomenological theories for larger materials. The semiempirical, tight-binding methods are orders of magnitude faster than *ab initio* schemes and, therefore, permit a much larger sampling of the configuration space to determine minimum energy structures. The computational efficiency of the tight-binding method derives from the fact that the Hamiltonian can be parametrized. Furthermore, the electronic structure information can be easily extracted from the tight-binding Hamiltonian, which in addition also contains the effects of angular forces in a natural way. The real space nature of the tight-binding method also readily lends itself to Green's function treatments[11,12] for an efficient reduction of the problem when dealing with large transition metal systems.

The recent advances in the matrix isolation and beam techniques have made it possible to obtain transition metal clusters of arbitrary size and to provide information about their reactivity through chemisorption experiments.[13–19] Nickel clusters seem to be the primary target of previous investigations because of their important catalytic and magnetic properties.

In this paper we present our results for small nickel clusters for which some *ab initio* results are available for comparison. First, we briefly present the tight-binding molecular dynamics method for transition metals. The details of this scheme will be given in a longer paper. The tight-binding molecular dynamics for covalent systems is

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detailed in Refs. 11, 12, and 20.

In the tight-binding scheme the total energy is written as a sum,[12,20,21]

$$U = U_{\text{el}} + U_{\text{rep}} + U_{\text{bond}}, \tag{1}$$

where U_{el} is the sum of the one-electron energies E_k,

$$U_{\text{el}} = \sum_{i}^{\text{occ}} \varepsilon_i, \tag{2}$$

and U_{rep} is given by a repulsive pair potential $\chi(r)$,

$$U_{\text{rep}} = \sum_{i} \sum_{j(>i)} \chi(r_{ij}). \tag{3}$$

Here r_{ij} is the separation of atoms i and j. U_{rep} contains corrections to the double counting of the electron-electron Coulomb repulsions present in U_{el} and the ion-ion repulsion term. The bond counting term U_{bond} was introduced by Tomaňek and Schluter,[21] and shown to be necessary to reproduce cohesive energies of dimers through bulk structures. They fitted it with a quadratic polynomial in n_b/n, where n_b is the total number of occupied bonds in the cluster,

$$U_{\text{bond}} = n[a(n_b/n)^2 + b(n_b/n) + c]. \tag{4}$$

The coefficients a, b, and c are determined by fitting the difference between $U_{\text{el}} + U_{\text{rep}}$ and cohesive energies from accurate *ab initio* calculations for a given set of optimized clusters.[20,21] The number of bonds term n_b is determined by having a smooth cutoff (R_c) between nearest and next-nearest neighbors.[20,28] The expression for the total force for performing molecular dynamics is obtained using the Hellmann-Feynman theorem.[11,12,20]

The electronic structure Hamiltonian can be constructed from the parameters $V_{\lambda\lambda'\mu}$ using the Slater-Koster scheme.[22] The Slater-Koster expressions for constructing the off-diagonal Hamiltonian matrix elements V_{ij} (V_{xy}, etc.) in terms of the direction cosines (l, m, n) of the bond vector $\vec{d}$ are found in Ref. 22 and in Table 20-1 of Ref. 23. The d-electron parameters for all transition metal systems are readily available for use in tight-binding methods.[24] We, however, make use of Harrison's universal scheme[11,23] for the determination of the electronic tight-binding parameters to preserve the *a priori* nature of the calculations. This enables us to keep the number of adjustable parameters to a minimum. Also, these universal parameters have been found to be transferable.[23] In this scheme the Hamiltonian parameters are determined from the dimensionless universal parameters $\eta_{\lambda\lambda'\mu}$ in terms of the bond length in the solid ξ_0 by the prescription,

$$V_{\lambda\lambda'\mu}(\xi_0) = \frac{\eta_{\lambda\lambda'\mu}\hbar^2 r_d^n}{m\xi_0^{n+2}}, \tag{5}$$

where $n = 0$ for s-s, s-p, and p-p interactions, $n = \frac{3}{2}$ for s-d and p-d interactions, and $n = 3$ for d-d interactions. Here, r_d is a length that is characteristic of each transition metal and is listed in the Solid State Table of Ref. 23. The value for Ni is given to be 0.71 Å. This leaves us with only one adjustable parameter, the coefficient of the repulsion term χ_0, which is adjusted to give the experimental bond length for the dimer, taken to be 2.20 Å.[7,25] This gives us a value for χ_0 of 0.367 eV. The dimensionless universal parameters $\eta_{\lambda\lambda'\mu}$ used in the construction of all the off-diagonal matrix elements of the Hamiltonian were taken from the Solid State Table of Harrison.[23] The diagonal matrix elements ε_s, ε_p, and ε_d of the Hamiltonian are simply the atomic term values, also taken from Ref. 23. We set $\varepsilon_s = \varepsilon_d$ and ε_p large enough to prevent p-orbital mixing. This choice of our tight-binding parameters reproduces the band structure of the fcc bulk Ni crystal given by Harrison.[23] Finally, in our calculations we have taken the $3d^8 4s^2$ (^3F) configuration as the ground state for the Ni atoms and all clusters in the paramagnetic state.

The $V_{\lambda\lambda'\mu}(\xi)$ as well as the coefficient of repulsion $\chi(r)$ are taken to decrease exponentially with distance.[12,20] The exponential scaling employed for the electronic parameters, besides its calculational simplicity, has been justified by recent results obtained from *ab initio* calculations.[26]

Based on our experience with semiconductor clusters, we take $R_c = 3.5$ Å. This together with the choice of $a = 0.052$ eV, $b = 0.213$ eV, and $c = -0.509$ eV gives a satisfactory trend in the variation of various cluster properties (e.g., cohesive energies, bond lengths, etc., see Table I) with the cluster size for an entire set of 22 clusters we considered. There is also good agreement with corresponding *ab initio* values where detailed optimization results were reported.

II. RESULTS

Our tight-binding molecular dynamics scheme, with the incorporation of d electrons, has been used to obtain minimum energy structures for a set of 22 Ni_n clusters for $n \leq 10$. Since the present scheme imposes no *a priori* symmetry restrictions, we can perform full optimization of geometries. The equilibrium bond lengths and cohesive energies are calculated for these geometries. The values of the cohesive energies for the relaxed geometries of various isomers of Ni atoms for each n are compared to determine the most stable cluster geometry. In Table I we give our calculated energies (per atom) and average bond lengths for our lowest energy structure for each n.

Unfortunately, the majority of the existing *ab initio* data for Ni clusters with $n > 3$, even when optimization is carried out, refer only to symmetry restricted

TABLE I. Cohesive energies per atom and average bond lengths for Ni clusters.

n	Cluster Symmetry	Binding energy (eV/atom)	$\langle r_e \rangle$ (Å)
2		0.93 (0.93[a])	2.20
3	D_{3h}	1.66	2.30
4	D_{4h}	1.87	2.26
5	T_d	2.16	2.42
6	D_{4h}	2.36	2.47
7	D_{5h}	2.42	2.51
8	C_{2h}	2.45	2.50
9	C_s	2.53	2.46
10	T_d	2.72	2.50

[a] Reference 7.

geometries.[9] For example, for $n = 3$ Basch *et al.*[7] reported a detailed optimization study only for one type of cluster symmetry, namely $D_{\infty h}$. The symmetry-lowering Jahn-Teller distortions occurring as a consequence of degenerate electronic states have been found to lower the energy for these clusters by removing some of these degeneracies.[27] In the absence of a sufficiently large and reliable *ab initio* data base for fully optimized cluster geometries for Ni, a direct comparison between our results and that obtained by other methods is not possible. Thus our results for fully optimized cluster geometries of Ni atoms with $n \leq 3 \leq 10$ may be considered as predictions, although some common features between our results and the existing data may be found, as will be shown later below.

For the Ni_3 cluster we find that the cluster with D_{3h} symmetry (triangular) with bond length $r_e = 2.30$ Å has the lowest energy. Basch *et al.*,[7] however, found the linear geometry ($D_{\infty h}$ symmetry), with bond length equal to 2.38 Å, to be energetically slightly more favorable. In our case the linear geometry was found to be 1.7 eV less favorable than the D_{3h} one.

For the Ni_4 cluster our calculations predict the cluster with a perfect square (D_{4h}) geometry to be the most stable with side length equal to 2.26 Å, although only slightly higher in energy (0.09 eV) than a planar rhombus (D_{2h} symmetry). This finding is in agreement with the *ab initio* result of Basch *et al.*,[7] which found the ground state for the Ni_4 cluster to have D_{4h} symmetry. A Ni_4 cluster with T_d symmetry with a bond length of 2.49 Å for each side was considered by Mlynarsky and Salahub.[6] We find the T_d structure to be unstable in our simulations, however, distorting to a planar D_{4h} geometry.

For the Ni_5 cluster we chose the following geometries as our initial starting configurations for the molecular-dynamics simulations: A strongly compressed trigonal bipyramid with apex atoms holding the triangle together (A_5), the lowest energy structure of Laasonen and Nieminen for Si_5 (B_5),[28] a trigonal bipyramid (C_5), and the C_{2v} planar geometry of Nygren *et al.* (D_5).[9] Each of the first three initial geometries relaxed to the same stable final geometry, i.e., a distorted tetragonal pyramid (see Figs. 1 and 2) with bond lengths ranging from 2.28 to 3.35 Å. The fourth geometry (D_5) was found to be stable but energetically less favorable (by 1.02 eV) than the distorted T_d structure. Again, the lack of full optimization for the geometries of various isomers of the Ni_5 cluster by Nygren *et al.*[9] does not allow a direct comparison with our results. The instability of the strongly compressed trigonal bipyramid for the nickel cluster is illustrated in Fig. 1 where in the final stage of the simulation a distorted tetragonal pyramid was obtained.

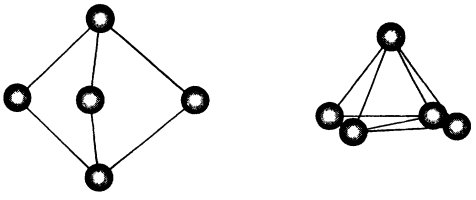

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FIG. 1. Figure showing the instability of the strongly compressed trigonal bipyramid for a cluster of Ni_5. We start with the ideal compressed trigonal bipyramid (initial) and find this structure to be unstable, distorting into a less compact distorted tetragonal pyramid, our ground state structure for $n = 5$.

The initial starting configurations for Ni_6 included the following geometries: An edge-capped trigonal bipyramid (A_6), a face-capped trigonal bipyramid (B_6), a tetragonal bipyramid (C_6), and the C_{5v} of Nygren *et al.*[9] (D_6). The tetragonal bipyramid (D_{4h} symmetry) is found to be the ground state (Fig. 2) with bond lengths ranging from 2.26 to 2.47 Å. The relaxed geometry shows the base to be a rhombus rather than being a square. This is in qualitative agreement with the results of Yu and Almlof[27] who considered Jahn-Teller distortions in octahedral Ni_6. The edge-capped trigonal bipyramid was found to be unstable, relaxing to a tetragonal bipyramid in our simulations. This is in qualitative agreement with the results of Yu and Almlof.[27] The relaxed geometry for the face-capped trigonal bipyramid (B_6) was 0.46 eV higher in energy over our ground state structure. The initial geometry D_6, on the other hand, relaxed to an edge-capped tetragonal pyramid. This relaxed structure is 0.83 eV higher in energy over our ground state geometry.

In the case of Ni_7, we considered a tri-capped tetrahedron (A_7) and a pentagonal bipyramid (B_7) as our initial starting geometries of which the pentagonal bipyramid (B_7) (with distortion, see Fig. 2), with D_{5h} symmetry, was found to be the most stable. Our finding is in good agreement with the results of Nygren *et al.* who found the ground state to have D_{5h} geometry with distortions.[9] The tri-capped tetrahedron was 1.26 eV higher in energy. The bond lengths for our ground state relaxed structure range from 2.34 to 2.86 Å.

For Ni_8, the distorted bi-capped octahedron (A_8) (C_{2h} symmetry, see Fig. 2) was found to be lower in energy over the tetra-capped tetrahedron (B_8) by 0.10 eV. In the relaxed configuration the base of the octahedron is a rhombus with equal bond lengths rather than being a

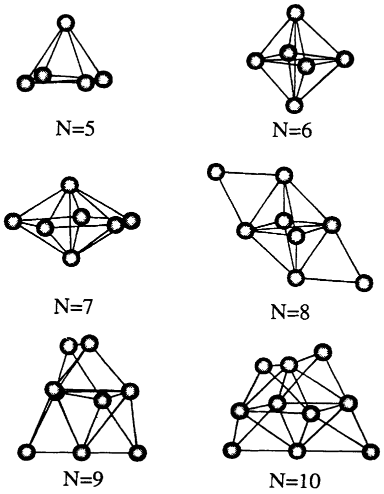

FIG. 2. Geometries of the lowest energy structures of small nickel clusters from $N = 5$ to $N = 10$ obtained using the present molecular dynamics scheme.

square. The bond lengths for this structure lie between 2.29–3.00 Å.

For Ni_9, we obtained the lowest energy for a distorted tri-capped octahedron (B_9), with C_s symmetry (Fig. 2). This structure shows maximum distortions in the relaxed state of all the geometries considered. The base of the octahedron has lower symmetry than a rhombus and is not even planar. The shortest and the longest bond lengths for this capped octahedron are 2.30 Å and 3.18 Å, respectively. Another minimum was obtained for a tri-capped trigonal prism (A_9), although slightly higher in energy (by 0.15 eV).

For Ni_{10} we considered the following energy structures, a tetra-capped octahedron (A_{10}), and a tetra-capped trigonal prism (C_{10}). Of these geometries, the tetra-capped octahedron (A_{10}) was found to be the most stable, with some distortions (Fig. 2). The base of this octahedron is found to be a planar rhombus. The bond lengths for this structure range between 2.32–2.77 Å. The tetra-capped trigonal prism (C_{10}) is found to be 1.19 eV higher in energy over the tetra-capped octahedron for Ni_{10}.

III. CONCLUSION

We have introduced an efficient molecular dynamics scheme to treat transition metal clusters. The method has been used to obtain low energy structures for Ni clusters for $N \leq 10$. The expected general trends for the various cluster properties are well described by our findings. In particular, as shown in Table I, we observe an increase in the binding energy and $r_e^{(n)}$ with the cluster size. The method is orders of magnitude faster than *ab initio* or LDA schemes and provides a much needed semi-empirical interface to bridge the gap between accurate *ab initio* calculations for small systems and the phenomenological theories for larger materials. The computational efficiency of the present scheme readily allows us to do an unconstrained search for local minima for reasonably large clusters.

The angular forces present in the tight-binding Hamiltonian readily give the symmetry-lowering Jahn-Teller distortions. These distortions allow for the lowering of energy by the removal of some of the degeneracies present in more symmetric geometries. Even though we have used the universal parameter scheme of Harrison to keep the number of adjustable parameters to a minimum, the method is sufficiently flexible so as to allow the use of other parametrization schemes. The real space nature of the tight-binding method will readily lend itself to the use of Green's function techniques to reduce the size of the matrices used in the treatment of infinite systems with local disorders. This is particularly useful when dealing with interactions of various defect complexes in transition-metal systems and alloys.

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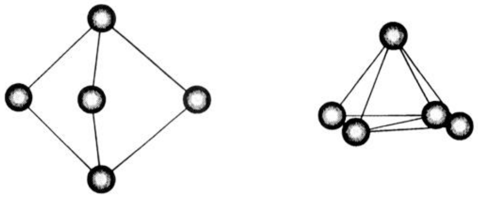

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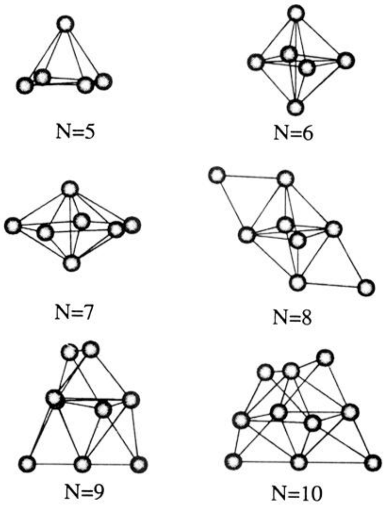

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