Self-consistent tight-binding molecular-dynamics method for cluster studies

Antonis N. Andriotis
Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, Heraklio, Crete 71110, Greece

Madhu Menon
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045
(Received 29 May 1998; revised manuscript received 24 September 1998)

The Hubbard-type tight-binding (TB) Hamiltonian is generalized to incorporate effects of charge transfer efficiently into the TB (Slater-Koster-type) parameters. The generalization is such that charge transfer as well as Madelung-type interactions are included in a self-consistent manner. In particular, the intrasite Coulomb interactions of our Hubbard Hamiltonian are calculated from the chemical hardness matrices, and are used to modify the diagonal elements of the TB Hamiltonian. The proposed computational scheme is applied in the studies of Si and Ni clusters. [S0163-1829(99)02123-2]

I. INTRODUCTION

Our previous studies have demonstrated that computational methods based on tight-binding (TB) molecular-dynamics (MD) methodology are very efficient in studies of nonmagnetic and magnetic clusters, as well as in the study of semiconductor surfaces and their interactions with adatoms. Furthermore, our studies have also shown that the TB-MD method, based on Harrison’s universal scheme and employing an orthogonal set of parameters (of the Slater and Koster type), and including only nearest-neighbor interactions, is equally well applicable to both covalent and metallic systems. Improvements to this computational scheme are sought, mainly in two areas. In particular, one can either try to extend the interaction range of the Hamiltonian to include second- and third-nearest neighbors, and/or use system-specific TB parameters. The latter are usually obtained from fittings to band-structure calculations based on ab initio methods.

In both cases, however, the major problem of scaling the TB parameters with the interatomic distance remains crucial. Its resolution requires fittings to a number of band-structure calculations performed for various lattice constants and lattice structures. Since the transferability of the TB parameters with the scaling thus obtained is not always satisfactory, their usage must be dealt with cautiously, especially in small cluster calculations, in which the local environment and the atomic coordination numbers are considerably different from those of the bulk structures to which the TB parameters were fitted.

In covalent systems, the use of universal TB parameters, along with simple scaling schemes and explicit inclusion of the nonorthogonality of the orbitals, has led to a successful resolution of the transferability problem. In metallic systems, however, and especially in the case of magnetic materials, the situation is more complex. The TB method can result in an overestimation of charge transfers between atoms of the cluster, which in turn affects the cluster geometry (and, therefore, its electronic and magnetic properties) substantially. Considering the fact that magnetic properties of small magnetic clusters are the outcome of a delicate interplay between magnetic and geometric ordering, it is clear that an accurate estimation of the charge transfer among cluster atoms is very critical. Even in the case of nonmagnetic clusters, the inclusion of a Hubbard-U term in the TB cluster Hamiltonian was found to be necessary in order to prevent superficial overestimation of charge transfers.

On the other hand, the inclusion of a Hubbard-U term in the TB Hamiltonian of a system (cluster) is more substantial in that it is related to the degree of approximation by which correlation effects, being so important in the study of magnetism, are taken into account in the description of the system. Thus Hubbard-U terms are expected to play a dominant role in providing an understanding of the magnetic properties of the clusters of transition-metal atoms. Similarly, the incorporation of electron-correlation effects through a Hubbard-U term is found in model descriptions for the formation of local moments in amorphous Si.

In more technical terms, the issue of charge transfer is related to the accuracy of the description of the changes induced in the TB formulation of a system by including electron correlations. In practice, this problem is mainly handled by examining changes in intrasite (diagonal) TB parameters due to electron correlations. Changes in the intrasite TB parameters are the results of charge transfer and exchange interactions. The common practice is to describe these interactions for each atom by the effective intrasite Coulomb, $U_{\text{eff}}^{(i)}$ and effective intrasite exchange $J_{\text{eff}}^{(i)}$, interaction matrices, respectively. Denoting by $E_{m}^{(i)}$ the diagonal TB matrix elements associated with the $i$th atom of a cluster, where $m = s, p, d, \ldots$ specifies the orbital type, the change $\Delta E_{m}^{(i)}$ in $E_{m}^{(i)}$, caused by the charge transfer, the exchange interaction, and the changes in the local environment of each atom, is customarily written as

\[
\Delta E_{m}^{(i)} = \sum_{n} \left[ U_{\text{eff}}^{(i)} \right]_{mn} \Delta n_{n}^{(i)} - \sum_{n} \left[ J_{\text{eff}}^{(i)} \right]_{mn} \mu_{n}^{(i)}
\]

\[
+ \Delta E_{\text{Mad}}^{(i)} + \Delta E_{\text{m,config}}^{(i)}, \quad m, n = s, p, d, \quad (1)
\]
where \( \sigma \) denotes the spin (+1 for spin-up and −1 for spin-down), \( n_{m\sigma}^{(i)} \) is the occupation number of the \( |m\sigma\rangle \) orbital at the lattice site \( \mathbf{R}_i \) and

\[
\mu_m^{(i)} = n_{m\sigma}^{(i)} - n_{-m\sigma}^{(i)},
\]

(2)

\[
\Delta n_m^{(i)} = \sum_\sigma n_{m\sigma}^{(i)} - n_{0m}^{(i)},
\]

(3)

where \( n_{0m}^{(i)} \) are the corresponding orbital occupancies for the bulk material. The term \( \Delta E_{m,\text{config}}^{(i)} \) on the right-hand side of Eqn. (1) denotes the Madelung-type interactions among atoms of the cluster arising from charge transfer. Finally, \( \Delta E_{m,\text{exch}}^{(i)} \) denotes the correction to \( E_{m}^{(i)} \) due to changes in the local environment of the \( i \)th atom.\(^{17-21} \) For later purposes, we introduce the symbol \( \Delta E_{m,\text{exch}}^{(i)} \) to denote the second term on the right-hand side of Eq. (1).

As is apparent from Eqs. (1)–(3), the implementation of Eq. (1) into a computational scheme needs to be done in a self-consistent manner, because the various \( \Delta n_m^{(i)} \), resulting from the solution of the Schrödinger’s equation for the cluster, become the input data for the description of the cluster Hamiltonian. In addition to the self-consistency, judicious choice must be made in determining the values of \( U_{\text{eff}}^{(i)} \) and \( J_{\text{eff}}^{(i)} \), as well as in obtaining reliable expressions for \( \Delta E_{m,\text{exch}}^{(i)} \) and \( \Delta E_{m,\text{config}}^{(i)} \).

Our previous investigations\(^4-6 \) of magnetic clusters were based on the approximation that

\[
\Delta E_{m\sigma}^{(i)} = -\sigma s_0, \quad \forall i,m,
\]

(4)

where \( s_0 \) is a fitted parameter corresponding to the product \( J_{\text{eff}}^{(i)} \mu^{(i)} \). The approximation dictated by Eq. (4), which ignores charge transfer altogether, was found to work reasonably well for clusters consisting of single species used in our earlier works.\(^1-6 \) However, due to the fact that properties of magnetic clusters depend on a delicate interplay among many factors (one of which is the charge transfer), an investigation into effects of charge transfer on cluster properties appears warranted.

To our knowledge, a complete implementation of Eqs. (1)–(3) into a self-consistent MD computer code has not yet been reported. This is because of the numerical difficulties encountered in such an endeavor, and the excess computer resources that are required for such an investigation. Instead, a self-consistent implementation of Eqs. (1)–(3) into a cluster Hamiltonian of a given geometric configuration was reported by Vega et al.\(^8 \) and also by Bouarab et al.\(^19 \) Missing in these approaches, however, is the important issue of how charge transfer affects the cluster geometry because self-consistency is imposed independently of any MD process.

In the present work, we report on a fully self-consistent incorporation of charge transfer into a TB-MD computer code. In particular, we implement Eqs. (1)–(3), which have been used in our studies of magnetic clusters,\(^4-6 \) into our TB-MD code. In the following, we will refer to this as the self-consistent tight-binding molecular-dynamics (SC-TBMD) method, while the acronym TBMD will be used for our approach involving the approximation dictated by Eq. 4. Additionally, within the SC-TBMD method used in the present work, we also try to avoid any approximations in choosing the values of \( [U_{\text{eff}}^{(i)}]_{mn} \). In particular, \( [U_{\text{eff}}^{(i)}]_{nn} \) are obtained in an ab initio way by calculating the chemical hardness matrices according to the calculational schemes of Liu\(^22 \) and Bandyopadhyay and Sarma.\(^23 \)

The paper is organized as follows: In Sec. II, we describe in detail the method used in the calculation of the intrasite Coulomb interaction matrix \( U_{\text{eff}}^{(i)} \) as well as the implementation of Eq. (1) into our SC-TBMD method. In Sec. III, we present applications of the SC-TBMD in studies of small Si and Ni clusters.

II. METHOD

The present SC-TBMD method is a generalization of our TBMD method used in the studies of magnetic clusters. According to the proposed generalization, Eq. (4) of the TBMD method is replaced by Eq. (1) of the SC-TBMD method. The calculational details of the SC-TBMD method follow those of the TBMD scheme described in detail in our previous reports,\(^3-6 \) and will not be repeated here. Instead, we focus only on the pertinent aspects of our theory. These refer to the computation of the intrasite Coulomb interaction matrix \( U_{\text{eff}}^{(i)} \) and the implementation of the self-consistency with respect to the charge transfer. Furthermore, we discuss the incorporation of the other correction terms, i.e., the intrasite exchange interaction \( J_{\text{eff}}^{(i)} \), the Madelung term \( \Delta E_{m,\text{exch}}^{(i)} \), and finally, the term \( \Delta E_{m,\text{config}}^{(i)} \) which depends on the local configuration of the \( i \)th atom.

A. Intrasite Coulomb interaction matrix

Following Liu,\(^22 \) the contribution of the intrasite Coulomb interaction to the diagonal TB matrix elements is expressed in terms of the first- and second-order chemical hardness matrices \( \eta^{(1)} \) and \( \eta^{(2)} \), respectively, according to the following expression (assuming, for practical reasons, that the electronic configurations of the cluster atoms contain only two types of valence orbitals):

\[
\begin{pmatrix}
\Delta E_{m\sigma}^{(i)} \\
\Delta E_{m,\text{exch}}^{(i)}
\end{pmatrix} = \begin{pmatrix}
\eta_{nm}^{(1)} & \eta_{nm}^{(1)} \\
\eta_{nm}^{(2)} & \eta_{nn}^{(2)}
\end{pmatrix} \begin{pmatrix}
\Delta n_{m\sigma}^{(i)} \\
\Delta n_{m\sigma}^{(i)}
\end{pmatrix} + \begin{pmatrix}
\eta_{nm}^{(1)} & \eta_{nm}^{(2)} & \eta_{mm}^{(2)} & \eta_{nm}^{(2)} \\
\eta_{nm}^{(2)} & \eta_{nn}^{(2)} & \eta_{mm}^{(2)} & \eta_{nn}^{(2)}
\end{pmatrix} \begin{pmatrix}
\{\Delta n_{m\sigma}^{(i)}\}^2 \\
\{\Delta n_{m\sigma}^{(i)}\}^2 \\
\{\Delta n_{m\sigma}^{(i)}\}^2 \\
\{\Delta n_{m\sigma}^{(i)}\}^2
\end{pmatrix},
\]

(5)
where the matrix elements of the chemical hardness matrices are defined as follows (suppressing the index $i$ in $\eta^{(1)}$ and $\eta^{(2)}$):

$$\eta_{mn}^{(1)} = \frac{\partial E_m^{(i)}}{\partial n_n^{(i)}}, \quad (6)$$

$$\eta_{mni}^{(2)} = \frac{\partial^2 E_m^{(i)}}{\partial n_m^{(i)} \partial n_n^{(i)}}. \quad (7)$$

Equations (5)–(7) are obtained by a Taylor-series expansion of the orbital energies with respect to the orbital occupation numbers. Usually, the free electron or the bulk electron occupancies are used as the zeroth-order values. We calculate the partial derivatives in Eqs. (6) and (7) for these occupancies.

The diagonal matrix elements $\eta_{mn}^{(1)}$ of the chemical hardness matrix of the first order are the unscreened intrasite Coulomb interactions. These can, to a very good approximation, be obtained from total-energy calculations of free atoms. For example, for a free atom with a valence-electron configuration consisting of $n_s$ electrons (of both spins) in the $s$ orbital and $n_d$ electrons (of both spins) in the $d$ orbital, we have $^{23}$

$$\eta_{dd}^{(1)} = U_{unscreened}^{(dd)}(n_d,n_s) = \left( \frac{\partial E_d^{(i)}}{\partial n_d^{(i)}} \right)_{n_i = \text{const}}$$

$$= E^{(i)}(n_d + 1,n_s) + E^{(i)}(n_d - 1,n_s) - 2E^{(i)}(n_d,n_s), \quad (8)$$

where $E^{(i)}(n_d,n_s)$ is the total energy of the free $i$th atom, the latter in a valence electron configuration $(n_d,n_s)$.

The unscreened $U_{mn}$ values are different from the screened ones, which, for the previous example, take the expression $^{23}$

$$U_{unscreened}^{(dd)}(n_d,n_s) = E^{(i)}(n_d + 1,n_s - 1) + E^{(i)}(n_d - 1,n_s + 1)$$

$$- 2E^{(i)}(n_d,n_s). \quad (9)$$

Approximate expressions for the $\Delta E_{m,n}^{(i)}$’s can be found in the work of Tersoff and Falikov$^{24}$ and that of Bisi and Calandra.$^{25}$ In these reports, the chemical hardness matrix $\eta^{(2)}$ is assumed identical to zero, while the matrix $\eta^{(1)}$ is calculated either from free-atom calculations or from spectral data according to the valence orbital ionization potential scheme. The agreement found in the results of these two approaches is remarkable.

In the present work, we obtain the matrix elements of $\eta^{(1)}$ and $\eta^{(2)}$ from free-atom calculations performed within the local-density approximation. Our results have been obtained numerically according to Eqs. (6) and (7) using standard numerical approximations for the first and second derivatives. The level of accuracy achieved is reflected at the small differences between the calculated nondiagonal matrix elements of $\eta^{(1)}$ for both Si and Ni [see Eqs. (25) and (27) below]. As will be shown in Sec. III, our results are in excellent agreement with previously reported ones for Ni and Si. It should be noted, however, that due to the fact that our atomic calculations cannot provide us with accurate results for the negative ions, we have extrapolated the results obtained for positive ions, using these extrapolated values for the negative ions. It should also be emphasized that our results, like those of Refs. 24 and 25 correspond to unscreened intrasite Coulomb interactions. The agreement found in earlier works for the $\eta_{mn}^{(1)}$ values obtained from theory and experiment led us to use the unscreened values in our calculations.

### B. Other correction terms

In addition to the intrasite Coulomb interactions, the other terms of Eq. (1) include the intrasite exchange interaction $\Delta E_{m,\text{exch}}^{(i)}$, the Madelung potential term $\Delta E_{\text{Madel}}^{(i)}$, and the correction $\Delta E_{m,\text{config}}^{(i)}$ which arises from changes in the local environment of each cluster atom.

In the present work, the intrasite exchange interaction is approximated by the expression

$$\Delta E_{m,\text{exch}}^{(i)} = -\sigma J_{m}\mu_{m}^{(i)}, \quad (10)$$

where $\mu_{m}^{(i)}$ is calculated according to Eq. (2), and $J_{m}$ are fitted parameters chosen in such a way so as to reproduce energy levels of the lower spin states of small clusters.$^{4-6}$

The empiricity involved in using Eq. (10) could have been avoided if the spin dependence had been retained in the definition of the chemical hardness matrices $\eta^{(1)}$ and $\eta^{(2)}$. Ignoring, for example, the second-order matrix $\eta^{(2)}$, a spin-dependent chemical hardness matrix $\tilde{\eta}^{(1)}$ with matrix elements,

$$\tilde{\eta}_{mn}^{(1)\sigma,\sigma'} = \frac{\partial E_m^{(i)}}{\partial n_{m\sigma}}, \quad (11)$$

allows one to write the first two terms on the right-hand side of Eq. (1) as $\sum_{\sigma\sigma'} \tilde{\eta}_{mn}^{(1)\sigma,\sigma'} \Delta n_{m\sigma'}$. In terms of the matrix elements of $\tilde{\eta}^{(1)}$, the matrix elements of $U_{\text{eff}}^{(i)}$ and $J_{\text{eff}}^{(i)}$ take the forms

$$[U_{\text{eff}}^{(i)}]_{mn} = \frac{1}{2} \left[ \tilde{\eta}_{mn}^{(1)\sigma,\sigma} + \tilde{\eta}_{mn}^{(1)\sigma',\sigma'} \right], \quad (12)$$

$$[J_{\text{eff}}^{(i)}]_{mn} = \frac{1}{2} \left[ \tilde{\eta}_{mn}^{(1)\sigma,\sigma'} - \tilde{\eta}_{mn}^{(1)\sigma',\sigma} \right]. \quad (13)$$

However, second-order corrections would have been more difficult to be incorporated via a spin-dependent chemical hardness matrix of second order. On the other hand, by employing the empirical term described by Eq. (10), we have the opportunity to correct (through the appropriate fitting) some of the errors involved in using the chemical hardness matrices $\eta^{(1)}$ and $\eta^{(2)}$. Furthermore, by parametrizing our Hamiltonian using Eq. (10), we can extend our studies to a wider class of problems.

The correction term $\Delta E_{m,\text{config}}^{(i)}$ is taken to be zero in our calculations, although one can easily incorporate the correction scheme for this term proposed by Vega et al.$^{18}$ Such an incorporation has been used in our recent study of $Si_{\text{m}}Ni_{\text{n}}$ binary clusters.$^{26}$ Our reason for not including corrections due to the changes in the local environment of each atom in the present work is that we want to see the net effect of the
charge transfer on the cluster stability for the clusters that have been studied in the absence of charge transfer in our previous works.\textsuperscript{1–6} Finally, the Madelung correction term $\Delta E_{\text{Mad}}^{(i)}$ is calculated according to the expression proposed in Ref. 17:

$$\Delta E_{\text{mad}}^{(i)} = \sum_{\ell \neq i} V_{i\ell} = \sum_{\ell} y_{i\ell} \Delta n^{(i)},$$

(14)

where

$$\Delta n^{(i)} = \sum_{m\sigma} n_{m\sigma}^{(i)} - \sum_{m} n_{0m},$$

(15)

and

$$y_{i\ell} = \frac{\left[U_{\text{eff}}^{(i)}\right]_0}{1 + \left[U_{\text{eff}}^{(i)}\right]_0 | \mathbf{R}_i - \mathbf{R}_\ell |}.$$  

(16)

In Eq. (16), $\left[U_{\text{eff}}^{(i)}\right]_0$ is taken to be the average number of the diagonal matrix elements of the matrix $\eta^{(i)}$ as defined by Eq. (6). It should be noted that Eq. (16) provides a consistent way to describe the two limiting cases, namely, that for which $| \mathbf{R}_i - \mathbf{R}_\ell | \to 0$ and that for which $| \mathbf{R}_i - \mathbf{R}_\ell | \to \infty$.

**C. Calculation of interatomic forces**

Having described the corrections to the diagonal TB matrix elements, we now turn our attention to the remaining major problem involving implementation of the formalism into a MD code by obtaining interatomic forces. Unlike in the case of the TBMD code, the spatial dependence of the correction terms, $\Delta E_{\text{m} \sigma}^{(i)}$, introduces an extra term in the Hellmann-Feynman forces which is difficult to implement in the SC-TBMD code. In particular, the spatial partial derivatives of the $\Delta E_{\text{m} \sigma}^{(i)}$ terms cannot be easily calculated, and the high accuracies required for a reliable determination of the interatomic forces cannot be easily achieved. More precisely, the calculation of the partial derivative $\partial E_{\text{m} \sigma}^{(i)} / \partial r_{i\alpha}$, $\alpha = x, y, z$, requires the evaluation of the corresponding partial derivative of each one of the components of $\Delta E_{\text{m} \sigma}^{(i)}$ [given by Eq. (1)], because each component is coordinate dependent. Such calculations, however, constitute a difficult numerical task not only because of the effort to achieve satisfactory accuracies but also because they become computationally prohibitive for large clusters. A computationally more feasible way to overcome this difficulty is to calculate, in a direct numerical way, the spatial derivatives of the energy eigenvalues. Such a procedure requires one-fifth the computer time as compared to the time needed for the evaluation of the partial derivatives of $\Delta E_{\text{m} \sigma}^{(i)}$. Our approach is briefly explained in the following.

The force $\mathbf{f}_i$ acting on the $i$th atom due to the interatomic interactions is obtained by taking the gradient of the total energy with respect to the spatial coordinates of each atom:\textsuperscript{3,5}

$$\mathbf{f}_i = -\nabla_i (U_{\text{el}} + U_{\text{rep}}).$$

(17)

The electronic part $U_{\text{el}}$ is obtained by performing a sum over the eigenvalues $\epsilon_{i\sigma}(\mathbf{r}_N)$ of the occupied one-electron states of the TB Hamiltonian, i.e.,

$$U_{\text{el}} = \sum_{i\sigma} \epsilon_{i\sigma}(\mathbf{r}_N) \theta_{i\sigma},$$

(18)

where $\theta_{i\sigma}$ is the occupation number of the $|i\sigma\rangle$ state,\textsuperscript{3,6} and $\{\mathbf{r}_N\}$ is used to denote the set of position vectors of a cluster of $N$ atoms, i.e.,

$$\{\mathbf{r}_N\} = \{ \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \}.$$  

(19)

The second term in Eq. (17), $U_{\text{rep}}$, is a pair repulsive potential term that includes contributions from the ion-ion interactions and a correction to the double-counting terms included in $U_{\text{el}}$, coming either from Coulomb and exchange interactions or the (Hubbard) correlation terms. This term is given by a sum of repulsive pair potentials, $\phi_{ij}$,

$$U_{\text{rep}} = \sum_i \sum_{j>\ell} \phi_{ij}(r_{ij}).$$

(20)

$\phi_{ij}$ is taken to scale exponentially with the interatomic distance $r_{ij}$:

$$\phi_{ij}(r_{ij}) = \phi_0 \exp(-4 \alpha (r_{ij} - d)),$$

(21)

where $d$ is the equilibrium bond length in the corresponding bulk material, and $\phi_0$ and $\alpha$ are fitted parameters. The parameter $\alpha$ is also used to scale the off-diagonal Hamiltonian TB matrix elements with the interatomic distance.\textsuperscript{3,6} The constants $\phi_0$ and $\alpha$ are chosen so as to reproduce the correct experimental bond length and the vibrational frequency of the dimer at its correct magnetic state.\textsuperscript{6}

The simple analytic form of $U_{\text{rep}}$ [Eqs. (20) and (21)] makes the evaluation of the corresponding force term rather straightforward. As mentioned earlier, in the TBMD approach, the contribution to the force $\mathbf{f}_i$ from $U_{\text{el}}$ was obtained by using the Hellmann-Feynman theorem. In the SC-TBMD approach, however, due to the nonvariational nature of our energy expression, the Hellmann-Feynman theorem cannot be applied, and hence it is more efficient to obtain the electronic contribution $\mathbf{f}_{\text{el}}^{(i)}$ to the force $\mathbf{f}_i$ by direct numerical differentiation of Eq. (18), i.e.,

$$f_{\alpha}^{(i)} = \frac{\partial U_{\text{el}}}{\partial r_{i\alpha}} = -\sum_{j\sigma} \theta_{j\sigma} \frac{\partial \epsilon_{j\alpha}(\mathbf{r}_N)}{\partial r_{i\alpha}}$$  

$$= -\sum_{j\sigma} \theta_{j\sigma} \left[ \epsilon_{j\alpha}(\mathbf{r}_N; \Delta r_{i\alpha}) - \epsilon_{j\alpha}(\mathbf{r}_N) \right] / \Delta r_{i\alpha}, \hspace{0.1cm} \alpha = x, y, z,$$

(22)

where $r_{i\alpha}, \alpha = x, y, z$, are the components of the position vector $\mathbf{r}_i$, $\Delta r_{i\alpha}$ is a small change in the $r_{i\alpha}$ component, and...
The numerical derivatives are calculated for every cluster atom and at every MD step. Even though the evaluation of all the $f_{i\alpha}^{(\ell)}$ in Eq. (22) can become prohibitively expensive for large clusters, considerable speedup can be achieved by combining SC-TBMD scheme with the simpler (and faster) TBMD scheme in such a way as to perform the numerical work associated with Eqs. (17)–(22) only at every suitably chosen $N$ steps with $N \gg 100$. Additional approximations that can be also employed can lead to very efficient computational schemes. This depends on the required accuracy and the size of the calculation.

It may be argued that the strictly nonvariational character of the total-energy expression that we are using in the self-consistent case could seriously affect our results. This is not the case in the present approach for two reasons. First, when the explicit spatial dependence of the atomic charges is not taken into account exactly, our formulas reduce to those of a variational approach in the same approximation (see below). Second, the deviations of our formulas from a strictly variational approach are expected to be eliminated to a great extent as a consequence of the inherent character of our theory. In fact, our fitted parameters, especially for $E_{\text{rep}}$, can cancel any possible errors arising from double-counting terms using an approximate variational expression for the total-energy, etc. We note that a strictly variational total-energy expression was recently proposed by Elstner et al.\(^{27}\)

Having defined the interatomic forces within the SC-TBMD approach, we proceed with the optimization of the cluster geometry following computational procedures identical to our original TBMD studies.\(^{3,6}\)

## III. APPLICATIONS

The efficacy of the proposed SC-TBMD method is demonstrated in two applications representing covalent and metallic (magnetic) clusters. In particular, we apply our method in the studies of small Si and Ni clusters. For both, our previous studies\(^{1–6,10–12}\) and a large number of other reported works (see, for example, Refs. 28–33 for Si, and Refs. 34–42 for Ni) provide us with sufficient data to allow us to make the necessary comparisons and for testing the efficacy of the proposed SC-TBMD method.

### A. Si clusters

In the case of Si we take $J_{ij}^{(\ell)} = J_{ij} = 0$, $\forall m,i$. The chemical hardness matrices $\eta^{(1)}$ and $\eta^{(2)}$ have been calculated with reference to the $3s^23p^2$ valence electron configuration of the free Si atom, and therefore, we have taken

$$ n^{(i)}_{0m} = 2.0, \quad m = s,p. \quad (24) $$

Our results, in very good agreement with those of Liu,\(^{22}\) are as follows:

$$ \eta^{(1)} = \begin{pmatrix} 8.95 & 7.90 \\ 8.23 & 7.29 \end{pmatrix} \text{ eV/electron}, \quad (25) $$

It is worth noting that $\eta^{(1)}$ is much greater than the $U$ values that have been employed in other works.\(^{13–15}\)

As in our previous TBMD simulations, we started our applications of the SC-TBMD method with the dimer cluster. The result of this calculation is used in determining the parameters $\phi_0$ and $\alpha$. It should be recalled that these parameters are uniquely determined by fitting our results so as to reproduce the experimental bond length of the dimer ($r_c = 2.246$ Å, Ref. 28) and its (experimental) vibrational frequency ($\nu = 511$ cm$^{-1}$).\(^{28}\) Once the fitting of these parameters is accomplished, we keep them fixed in subsequent applications of our method to larger clusters. The values of $\phi_0$ and $\alpha$ in the SC-TBMD calculational scheme are found to be exactly the same as in the TBMD method, i.e., $\phi_0 = 2.693$ eV and $\alpha = 0.574$ Å$^{-1}$.

Our results for the Si$_n$, $n \leq 5$ clusters are presented in Table I along with reported \textit{ab initio} results\(^{28,29}\) for comparison. In particular, we present results for the bond lengths $R_{ij}$, the vibrational frequencies $\nu$, the atomic charges $Q^{(i)}$, the index $i$ indicating the $i$th atom and the binding energies (BE’s). The contribution $Q_s^{(i)}$ of the $s$ orbital of the $i$th atom to its total charge $Q^{(i)}$ is indicated in parentheses. The BE’s have not been scaled with any $U_{\text{bond}}$ term.\(^{4}\)

As seen in Table I, the results obtained with the SC-TBMD method are in excellent agreement with those obtained with the original TBMD method for the clusters Si$_2$ and Si$_3$. Small differences between the two methods begin to appear in the cases of Si$_4$ and Si$_5$, indicating that, within the SC-TBMD approach, there is a tendency for minimizing the charge transfer among the cluster atoms when compared with the TBMD results. Although these changes in the charge transfer are quite small, they tend to induce noticeable changes in the bond lengths and the vibrational frequencies. Also, a slight increase in the BE’s is obtained in going from the TBMD description to the SC-TBMD description.

Similar trends were also found in a calculation for the cluster Si$_4S$ on which we tested the applicability of the SC-TBMD in larger clusters. In this test, we compared the outputs of the first iteration of both the TBMD and SC-TBMD computer codes. In particular, we found a reduction of the interatomic charge transfer when self-consistency in charge transfer is applied. This reduction fluctuates between 0.30% and 2.20%.

Both the SC-TBMD and TBMD methods lead to results that are in very good agreement with \textit{ab initio} results. This observation, while demonstrating the reliability of these methods, gives further support to the argument that the orthogonal set of the universal TB parameters of Harrison\(^{8}\) offer adequate transferability in going from bulk Si to small Si clusters.

From a computational point of view, it should be noted that the SC-TBMD method is considerably slower when compared to the simple TBMD method, becoming computationally prohibitive for large clusters. It is, however, very useful, as it helps to answer transferability and reliability questions pertaining to the applicability of various semi-empirical TB models. Of particular interest appears to be the
TABLE I. Results for Si clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Property</th>
<th>SC-TBMD</th>
<th>Method TBMD</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₂</td>
<td>( R_{ij} (\text{Å}) )</td>
<td>2.242</td>
<td>2.242</td>
<td>2.246(^a), 2.265(^b)</td>
</tr>
<tr>
<td></td>
<td>( \nu (\text{cm}^{-1}) )</td>
<td>511</td>
<td>511</td>
<td>511(^a), 507(^b)</td>
</tr>
<tr>
<td></td>
<td>( Q^{(i)}(Q^{(i)}), i=1,2 )</td>
<td>4.000(1.937)</td>
<td>4.000(1.937)</td>
<td></td>
</tr>
<tr>
<td>Si₃</td>
<td>( R_{ij} (\text{Å}) )</td>
<td>2.38x2, 2.39</td>
<td>2.38x3</td>
<td>2.179x2, 2.719(^c)</td>
</tr>
<tr>
<td></td>
<td>( \nu (\text{cm}^{-1}) )</td>
<td>383,385,531</td>
<td>385x2, 532</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(i)}(Q^{(i)}), i=1,2 )</td>
<td>4.000(1.908)</td>
<td>4.000(1.908)</td>
<td></td>
</tr>
<tr>
<td>Si₄ (rhombus)</td>
<td>( R_{ij} (\text{Å}) )</td>
<td>2.35, 2.36x3</td>
<td>2.35x4, 2.47</td>
<td>2.303, 2.401(^c)</td>
</tr>
<tr>
<td></td>
<td>( \nu (\text{cm}^{-1}) )</td>
<td>2.44, 4.03</td>
<td>3.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(i)}(Q^{(i)}), i=1,2 )</td>
<td>3.876 (1.909)</td>
<td>3.838(1.908)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(i)}(Q^{(i)}), i=3,4 )</td>
<td>4.123 (1.786)</td>
<td>4.162(1.792)</td>
<td></td>
</tr>
<tr>
<td>Si₅ (trigonal bipyramid)</td>
<td>( R_{ij} (\text{Å}) )</td>
<td>2.28x2.2, 4.02, 2.41</td>
<td>2.32x2, 2.49x4</td>
<td>2.338, 2.403, 2.476(^c)</td>
</tr>
<tr>
<td></td>
<td>( \nu (\text{cm}^{-1}) )</td>
<td>188,271,284</td>
<td>212, 265, 274</td>
<td>201, 280, 440(^c)</td>
</tr>
<tr>
<td></td>
<td>( Q^{(1)}(Q^{(1)}) )</td>
<td>3.935 (1.575)</td>
<td>3.844 (1.551)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(2)}(Q^{(2)}) )</td>
<td>3.909 (1.804)</td>
<td>3.871 (1.817)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(3)}(Q^{(3)}) )</td>
<td>3.908 (1.814)</td>
<td>3.871 (1.817)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(4)}(Q^{(4)}) )</td>
<td>4.121 (1.877)</td>
<td>4.207 (1.884)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Q^{(5)}(Q^{(5)}) )</td>
<td>4.126 (1.876)</td>
<td>4.207 (1.884)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Experimental results as quoted in Refs. 28 and 29.

\(^b\)Theoretical results (Ref. 28 and 29) obtained within a scaled MP4 level of calculation.

\(^c\)Theoretical results (Ref. 28 and 29) obtained within the HF/6-31G* level of calculation.

use of the SC-TBMD method in studies of small binary clusters in which charge transfer plays a dominant role.\(^{26}\)

### B. Ni clusters

In the case of Ni clusters, neglecting valence \( p \) orbital interactions, the chemical hardness matrices \( \eta^{(1)} \) and \( \eta^{(2)} \) were found to be as follows (with respect to the 3\( d^8 4s^1 \) ground-state valence-electron configuration of the free Ni atom):

\[
\eta^{(1)} = \begin{pmatrix}
6.52 & 7.99 \\
8.08 & 13.01
\end{pmatrix} \text{eV/electron},
\]

\[
\eta^{(2)} = \begin{pmatrix}
-0.53 & -1.33 & -2.09 \\
-0.92 & -2.36 & -2.98
\end{pmatrix} \text{eV/(electron)}^2.
\]

In Eqs. (27) and (28) the \( s \) valence-electron index precedes that of the \( d \) electrons.

For comparison purposes, we mention the results for \( \eta^{(1)} \) found for Cu by Tersoff and Falicov (TF) (who assumed these to be approximately the same as those for Ni):\(^{24}\)

\[
\eta^{(1)}_{TF} = \begin{pmatrix}
6.50 & 7.77 \\
7.77 & 13.45
\end{pmatrix} \text{eV/electron}.
\]

For Ni, Bisi and Calandra (VC),\(^{25}\) utilizing spectral data, found \([\eta^{(1)}_{VC}]_{11} = 7.95\) and \([\eta^{(2)}_{VC}]_{22} = 12.57\) eV/electron. The very good agreement observed among all these results allows us to point out the following useful remarks: (i) It is observed that the anticipated relationships\(^{18}\) \( U_{ss} : U_{sd} : U_{dd} = 0.32 : 0.42 : 1.00 \) for Fe clusters cannot be used in the case of Ni clusters. In fact, our results give us \( U_{ss} : U_{sd} : U_{dd} = 0.50 : 0.62 : 1.00 \). (ii) The calculated value for \( U_{dd} = [\eta^{(1)}]_{22} = 13.01 \) eV/electron, referring to the unscreened intrasite Coulomb interaction, is larger than the values used in other reports [namely, the value of 4.50 eV/electron (Refs. 17 and 38) and the value of 3.30 eV/electron (Ref. 34) and much larger than the screened value of 2.73 eV/electron found by Ban- dyopadhyay and Sarma.\(^{23}\) It should be noted that our results reproduce the screened value of Ref. 23 if instead of using Eq. (8) we use Eq. (9). Due to the fact that along with Harrison’s\(^{8}\) universal set of TB parameters we take \( E_{ti}^{(s)} = E_{ti}^{(1)} \), for consistency reasons, in our calculations we take \( \eta_{ss}^{(1)} = \eta_{ss}^{(1)} ; \eta_{ss}^{(2)} = \eta_{ss}^{(2)} ; \eta_{dd}^{(2)} = \eta_{dd}^{(2)} ; \eta_{ss}^{(2)} = \eta_{ss}^{(2)} \).

Following our standard calculational approach, we initially calculated the values \( \phi_0 \) and \( \alpha \) by fitting to the experimental results for the bond length (\( r_c = 2.20 \) Å) and the vibrational frequency (\( \nu = 330 \) cm\(^{-1}\)) of the dimer (see Ref. 6 and references therein). Setting \( J_{eff} = J_{eff}^{(1)} = J_{eff}^{(2)} = 0.5 \) eV, as in the case of the ordinary TBMD, we find \( \phi_0 = 0.264 \) eV and \( \alpha = 1.040 \) Å\(^{-1}\) (as in the case of the ordinary TBMD).
It should be noted, however, that contrary to the case of Si, the SC-TBMD method exhibits profound calculational difficulties when applied to Ni clusters. In particular, it has been found that the MD relaxation process depends strongly on the choice of the values \( n_{0d}^{(i)} \) and \( n_{od}^{(i)} \). Thus if \( n_{0d}^{(i)} \) and \( n_{od}^{(i)} \) are given the values of 1.0 and 9.0, respectively (following the \( 3d^4s^1 \) valence-electron configuration of the free Ni atom), the MD process is found not to be convergent, due mainly to the large energy shifts resulting from the large values of the matrix elements of the hardness matrices and the relatively large changes of the orbital occupation numbers. The latter are due to a redistribution of the valence electrons between the \( s \) and \( d \) atomic orbitals. In order to overcome this difficulty, we take

\[
 n_{0s}^{(i)} = 1.45, \quad n_{od}^{(i)} = 8.55, \tag{30}
\]

which correspond to the values that were obtained by running the ordinary TBMD code with the same values of the other fitted parameters. With such a choice the MD relaxation process converges self-consistently with respect to the other fitted parameters. With such a choice the MD relaxation process converges self-consistently with respect to the other fitted parameters. With such a choice the MD relaxation process converges self-consistently with respect to the other fitted parameters.

The whole picture deteriorates if the SC-TBMD method is applied to larger Ni clusters. For example, for Ni\(_3\) and Ni\(_4\) clusters, the MD process within the SC-TBMD scheme was found not to be convergent even if we use values for \( n_{0s}^{(i)} \) and \( n_{od}^{(i)} \) as obtained from the outputs of the corresponding ordinary TBMD calculations. We have tried a large number of combinations of \( n_{0s}^{(i)} \) and \( n_{od}^{(i)} \) under the condition

\[
 n_{0s}^{(i)} + n_{od}^{(i)} = 10.0 \tag{31}
\]

in order to check if there exists a range of values of \( n_{0s}^{(i)} \) and \( n_{od}^{(i)} \) for which the SC-TBMD process is convergent, always keeping the same value for the other fitted parameters: \( J_{0s}^{(i)} = J_{od}^{(i)} = 0.5 \) eV. These tests proved negative, as no MD convergence with simultaneous self-consistency in charge transfer could be obtained.

It is well known that interatomic charge transfer causes tremendous numerical problems with self-consistent field convergence in fully self-consistent density-functional calculations in metallic systems (see, for example, Refs. 43 and 44). This, however, does not seem to be the only reason in our calculations on Ni clusters. One additional reason for not achieving self-consistency in charge transfer and cluster geometry simultaneously in the present calculations for Ni clusters may be attributed to the fact that use of the given set of the universal TB parameters causes a significant intraatomic redistribution of the electrons among the orbitals of a cluster atom, although the interatomic charge transfer may be not considerable. As a result, large energy shifts \( \Delta E_{dr}^{(i)} \) and \( \Delta E_{dd}^{(i)} \) are obtained according to Eq. (5), which are beyond the perturbative limit of this equation. This may indicate a poor transferability of the particular set of the TB parameters for Ni. Perhaps one way to avoid this problem is to use system-specific TB parameters. Nevertheless, the present results point to the computational limits of the proposed method, and reveal the various transferability problems in a TB description.

On the other hand, when the cluster geometry is kept fixed (at the geometry found by the ordinary TBMD calculation), self-consistency in charge transfer is easily obtained. However, the disappointing result is that at such a restricted self-consistency, the atomic forces are far from equilibrium. This indicates a delicate dependence of the geometric order on charge transfer, and justifies our argument\(^b\) that cluster results, although self-consistent in charge transfer, obtained without imposing self-consistency in the cluster geometry (as is usually the case\(^1\)\(^b\)\(^8\)\(^4\)\(^4\)\(^5\)) should be dealt with carefully; they might not correspond to the correct ground state of the cluster.

The difficulty in achieving self-consistency in charge transfer and cluster geometry simultaneously reflects on the lack of any relevant reports (to the best of our knowledge). It is worth emphasizing that even if the cluster geometry is kept fixed, calculations requiring self-consistency in the charge transfer demand excessive computer resources. For this reason, existing reports on such constrained simulations are restricted to clusters of medium size (\( n \leq 60 \)) (see, for example, the most recent work of Ref. 45 and references therein). Our computer code, on the other hand, has the options to incorporate charge self-consistency and geometry optimization either simultaneously or independently. However, for reasons discussed above, we have restricted our present calculations to geometry-constrained ones. Thus, keeping the cluster geometry fixed, we have performed a series of calculations in order to test the efficiency of the proposed SC-TBMD method in calculations of large Ni\(_n\) clusters as well. In particular, we tested our computer code on the icosahedral Ni\(_{55}\) using two computational approaches. In the first, we imposed self-consistency in the charge transfer, at every stage of the calculational process that involves a change in the cluster geometry. This means that self-consistency was imposed at every cluster configuration that follows each atom displacement \( \Delta r_{ia} \) applied in order to evaluate the derivatives \( \partial \epsilon_{ia} / \partial r_{ia} \) according to Eq. (22). Contrary to the case of Si\(_{55}\), discussed above, where this approach proved successful, in Ni\(_{55}\) such a procedure becomes computationally prohibitive. This is due to the convergence problems that we have already discussed. For this reason, we introduced a second, much faster, approach in which we make the following approximation: We do not impose self-consistency in charge transfer when we evaluate the derivatives \( \partial \epsilon_{ia} / \partial r_{ia} \). Instead we impose self-consistency only in the final charge distribution. We were able to check our second approach by comparing its results with that of the first method at the same (satisfactory) level of self-consistency. In both cases the results of the final charges on each atom did not differ by more than 1%. Subsequently, we applied our second approach to Ni\(_{55}\), for which we could let self-consistency reach any desired level of accuracy. Comparing our SC-TBMD results with those obtained in our previous works using the standard TBMD technique (at the same level of approximation), we found that self-consistency prevents excessive charge transfer among the cluster atoms. The reduction that we find by applying self-consistency may reach the level of 6%. At the same time we find that the average magnetic moment per atom is reduced by almost 15% when self-consistency is imposed. However, as we have stated above, these results cannot be
We have presented a TBMD computational scheme which incorporates electron correlations of the Hubbard type and interatomic (as well as intra-atomic) charge transfer in a self-consistent way. In our SC-TBMD method, the intraatomic Coulomb interactions are calculated from the chemical hardness matrices, and are used to modify the diagonal elements of the TB Hamiltonian. For the off-diagonal matrix elements we use the universal TB parameters of Harrison. The proposed method has been applied with success in the case of small Si clusters and the Ni dimer. For larger Ni clusters, however, it was found not to be convergent self-consistently in both the charge transfer and cluster geometry. The results presented make amply clear the delicate interplay between charge transfer and cluster geometry, while allowing us to test the transferability limits of a given set of a TB Hamiltonian description.

ACKNOWLEDGMENTS

The present work was supported by NATO Grant No. CRG 970018, by NSF Grant No. OSR 94-52895, and by the University of Kentucky Center for Computational Sciences.

---

9 Electronic address: andriot@iesl.forth.gr
10 Electronic address: super250@pop.uky.edu