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## Molecular dynamics using the tight-binding approximation

K Laasonen and R M Nieminen

Laboratory of Physics, Helsinki University of Technology, SF 02150 Espoo, Finland

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**Abstract.** We present an extension of classical molecular dynamics (MD) to include the forces calculated from electronic degrees of freedom using the tight-binding (TB) approximation. The combined MD–TB problem is solved using the simulated annealing techniques. As an example we study the structures and energetics of small silicon clusters, containing up to 10 Si atoms.

### 1. Introduction

Classical molecular dynamics (MD) has been used for many years for solving various physical problems [1]. MD simulation is most useful for studying materials properties at non-zero temperatures, in cases where quantum mechanical effects in the ionic degrees of freedom are small. The central problem in MD is usually to find a classical inter-atomic potential which produces all or at least most of the observable physical quantities, by mimicking the quantum mechanics of the electrons. In most cases these potentials contain numerous parameters [2–4]. Fitting all these parameters requires a great deal of intuition and work, and after all doubts remain if one uses the potentials in environments very different from where they were developed, e.g. uses bulk potentials for small clusters [5] or surface problems.

There are several accurate quantum mechanically based methods for solving total energies of low-symmetry systems such as the density functional theory (DFT) and its implementation using either periodic supercell or Green function-techniques. DFT methods give reliable results for many systems with the only input being the positions and atomic numbers of the atoms. Usually, however, these computational methods do not allow for the inclusion of real dynamics.

There is one remarkable exception, the method developed by Car and Parrinello (CP) [6]. CP use DFT combined with MD and update electronic and ionic degrees of freedom in unison. The method has been applied for example for solving the structures of small Si [7, 8], S [9], Se [10] clusters and disordered Si [11].

However, the CP method is computationally very demanding and feasible for relatively small systems only, up to a few tens of atoms. It is worthwhile to develop a method which is computationally faster and in some sense closer to normal MD. A natural alternative is to use the tight-binding (TB) (or Hückel) approximation for solving the electronic problem and to combine it with MD. Simulated annealing can then be used to tackle the whole optimisation problem.

In section 2 we introduce the TB formalism suitable for MD. A method for solving the Lagrange multipliers is also introduced. In section 3 the simulated annealing technique is discussed. In section 4 the MD–TB method is applied to Si clusters and the results are presented. While this paper was being written we became aware of similar recent work [12] on the Si<sub>3</sub> trimer. Comparison with the work in [12] and other cluster studies is given. Section 5 contains a summary and discussion.

## 2. Molecular dynamics and the tight-binding approximation

In the TB approximation a minimal basis set is usually applied (only those orbitals which are occupied or partially occupied in the free atom), and the matrix elements of the Hamiltonian are considered as adjustable parameters. These parameters (or matrix elements) are adjusted to fit for example known band structures. The basis functions are often assumed to be orthogonal, but we use here the more general non-orthogonal TB approximation.

Let us first expand the electronic wavefunction of a collection of atoms as a linear combination of some suitably chosen localised basis functions  $\psi_\nu$  (Gaussian functions, atomic orbitals, etc)

$$\Phi^i(\mathbf{r}) = \sum_{\nu n} C_{\nu n}^i \psi_\nu(\mathbf{r} - \mathbf{R}_n) \quad (1)$$

where  $\mathbf{R}_n$  denotes the position of the  $n$ th atom ( $n = 1, \dots, N$ ), and  $i$  labels the electronic eigenstates.

The Hamiltonian and overlap matrices are defined as

$$\begin{aligned} H_{\nu\mu, nm} &= \int \psi_\nu(\mathbf{r} - \mathbf{R}_n) \mathbf{H} \psi_\mu(\mathbf{r} - \mathbf{R}_m) d^3r \\ S_{\nu\mu, nm} &= \int \psi_\nu(\mathbf{r} - \mathbf{R}_n) \psi_\mu(\mathbf{r} - \mathbf{R}_m) d^3r \end{aligned} \quad (2)$$

where  $\mathbf{H}$  is the single-particle Hamiltonian. The matrix elements  $H_{\nu\mu, nm}$  are now taken in the TB approximation as adjustable parameters with a canonical dependence on the distance between atoms and on the symmetry of the basis states [13]. In orthogonal TB it is assumed that the basis functions are orthonormal ( $S_{\nu\mu, nm} = \delta_{\nu\mu} \delta_{nm}$ ) but for example in the case of silicon this does not give a very good band structure for excited states. The non-orthogonal TB method, where the  $S_{\nu\mu, nm}$  is not a unit matrix, does reproduce the full band structure quite well [14].

The Schrödinger equation can be written as

$$\sum_{\nu\mu nm} H_{\nu\mu, nm} C_{\nu n}^i - E^i S_{\nu\mu, nm} C_{\nu n}^i = 0. \quad (3)$$

For notation clarity we change the numeration of  $H_{\nu\mu, nm}$  to  $H_{nm}$ .

The requirement that the wavefunctions  $\Phi^i$  are orthonormal leads to the constraints for the coefficients  $C^i$ :

$$\sum_{nm} C_n^i S_{nm} C_m^j = \delta^{ij}. \quad (4)$$

Now instead of solving equation (3) as an eigenvalue problem we search for a

minimum of the energy expectation value  $\langle \Phi | \mathbf{H} | \Phi \rangle$ . Thus one has to minimise the following functional:

$$E(\{C^i\}, \{\mathbf{R}_n\}) = \sum_{im} C_n^i H_{mm} C_m^i = \sum_i C^i \cdot \mathbf{H} C^i \quad (5)$$

which also depends on the atomic positions  $\mathbf{R}_n$  via  $\mathbf{H}$ .

One can now replace the original quantum mechanical eigenvalue problem (3) by a classical potential problem, where the minimum of the potential  $E(\{C_i\}, \{\mathbf{R}_n\})$  corresponds to the solution of the eigenvalue problem (3). The dynamics that one derives from that classical system is not the true dynamics but, if the mass parameter associated with the electronic part is much smaller than the true mass of the atoms, one can consider the dynamics of the atoms as the real dynamics—that is the Born–Oppenheimer approximation [6]. In this limit, one can perform real MD simulations, and not only find static minima for collections of atoms.

The same algorithm can be used to solve the electronic problem only by making the mass of the atoms large compared with the electronic ‘mass’. If one needs only the few lowest eigenvectors, the algorithm is at least for very large systems faster than normal matrix diagonalisation. The time that the algorithm takes is proportional to  $N^2$ , where  $N$  is the dimension of the Hamiltonian matrix, whereas the cost of diagonalisation routines is proportional to  $N^3$ .

We can write the Lagrangian for the TB system as

$$\mathcal{L} = \frac{1}{2}\mu \sum_i |C_i|^2 + \frac{1}{2}m \sum_n |\mathbf{R}_n|^2 - \sum_i C^i \cdot \mathbf{H} C^i + \sum_{ij} \lambda^{ij} (C^i \cdot \mathbf{S} C^j - \delta^{ij}) + U(\{\mathbf{R}_n\}) \quad (6)$$

where  $\mu$  is the (fictitious) electronic mass parameter,  $m$  is mass of the atoms and  $\lambda^{ij}$  denotes the Lagrange multipliers associated with the orthonormalisation constraints. The ‘external’ potential  $U(\{\mathbf{R}_n\})$  is introduced as a possible short-range correction potential for the TB description [15].

The equations of motion for the coefficients  $C_i$  are easy to derive as

$$\mu \ddot{C}^i = -\mathbf{H} C^i + \sum_j \lambda^{ij} \mathbf{S} C^j. \quad (7)$$

The equations of motion for the atoms are not as straightforward. One can use the Hellmann–Feynman type of force:

$$\delta E / \delta \mathbf{R}_n = \delta \langle \Phi | \mathbf{H} | \Phi \rangle / \delta \mathbf{R}_n = \langle \Phi | \delta \mathbf{H} / \delta \mathbf{R}_n | \Phi \rangle. \quad (8)$$

We neglect the residual  $\mathbf{R}_n$  dependence of  $\lambda^{ij}$  and obtain

$$m \ddot{\mathbf{R}}_n = - \sum_i C^i \cdot \frac{\delta \mathbf{H}}{\delta \mathbf{R}_n} C^i + \sum_{ij} \lambda^{ij} C^i \cdot \frac{\delta \mathbf{S}}{\delta \mathbf{R}_n} C^j + \frac{\delta U(\{\mathbf{R}_n\})}{\delta \mathbf{R}_n}. \quad (9)$$

The integration of the equations of motion can be carried out by using some standard algorithm such as that in [16], if the Lagrange multipliers in equation (7) can be solved. We assume that a small change in the positions of the atoms does not change the overlap matrix  $\mathbf{S}$  (this is trivially true for the orthogonal TB method). Then one can implement the ideas in [17] to solve the Lagrange multipliers for each time step, demanding that the constraints (4) hold for every step. To second order in  $\Delta t$ , one can write

$$C^i(t + \Delta t) = C_0^i + \frac{(\Delta t)^2}{\mu} \sum_{j=1}^i \lambda^{ij} \mathbf{S} C^j(t) = C_0^i + \delta C^i \quad (10)$$

where  $C_0^i$  stands for everything which does not depend on  $\lambda^{ij}$ .

The calculation proceeds by first calculating the lowest eigenvector ( $C^1$ ), then the next lowest and so on. It means that when calculating the  $i$ th eigenvector the lower eigenvectors are known, and from the constraint equation for  $j < i$  one obtains

$$\delta C^i \cdot \mathbf{S} C^j = -C_0^i \cdot \mathbf{S} C^j$$

$$\sum_{k=1}^i \lambda^{ik} C^j \cdot \mathbf{S}^2 C^k = -\frac{\mu}{(\Delta t)^2} C_0^i \cdot \mathbf{S} C^j \quad (j < i). \quad (11)$$

For  $i = j$ ,

$$\frac{2\mu}{(\Delta t)^2} \sum_{k=1}^i \lambda^{ik} C_0^i \cdot \mathbf{S}^2 C^k + \sum_{kl=1}^i \lambda^{ik} \lambda^{il} C_0^l \cdot \mathbf{S}^3 C^k$$

$$= [\mu^2 / (\Delta t)^4] (1 - C_0^i \cdot \mathbf{S} C_0^i) \quad (i = j). \quad (12)$$

From equations (11) and (12),  $\lambda^{ik}$  for  $k = 1, \dots, i$  can be solved. In principle the resulting equation can be solved exactly but this is quite time consuming, and one can make a further approximation. Let us assume that

$$\lambda^{ij} \approx -E^i \delta^{ij} \quad (13)$$

which is accurate at least near the global minimum where  $\ddot{C}^i \approx \mathbf{0}$  and  $\mathbf{H}C^i \approx E^i C^i$ .

With this approximation, equation (12) becomes a simple polynomial

$$(\lambda^{ii})^2 C_0^i \cdot \mathbf{S}^3 C^i + 2[\mu / (\Delta t)^2] \lambda^{ii} C_0^i \cdot \mathbf{S}^2 C^i + [\mu^2 / (\Delta t)^4] (C_0^i \cdot \mathbf{S} C_0^i - 1) = 0 \quad (14)$$

from which  $\lambda^{ii}$  is easy to solve.

When the value of  $\lambda^{ii}$  is known, the remaining  $\lambda^{ij}$ -values can be solved by using equation (11), but better results are obtained if one just ignores the  $\lambda^{ii}$  whence equation (11) becomes

$$\sum_{k=1}^{i-1} \lambda^{ik} \mathbf{D}^{jk} = a^j \quad (j < i) \quad (15)$$

where  $\mathbf{D}^{jk} = C^j \cdot \mathbf{S}^2 C^k$  and  $a^j = -\mu C_0^i \cdot \mathbf{S} C^j / (\Delta t)^2$ . Now  $\mathbf{D}^{jk}$  is a square matrix and has a well defined inverse. Also  $\mathbf{D}$  is easy to invert, because it is nearly a unit matrix:  $\mathbf{D} = \mathbf{1} + \varepsilon$  gives  $\mathbf{D}^{-1} \approx \mathbf{1} - \varepsilon$ , where  $\varepsilon$  contains small non-diagonal elements. Thus

$$\lambda^{ij} = \sum_{k=1}^{i-1} (\mathbf{D}^{-1})^{jk} a^k \quad (j < i). \quad (16)$$

From equations (14) and (16), one can efficiently compute the Lagrange multipliers. For example for an orthogonal TB scheme the time that it takes to solve the Lagrange multipliers is proportional to  $M^2 N$ , where  $M$  is the number of eigenvalues required and  $N$  is the length of the vector  $C^i$ .

The above procedure is easy to reduce for an orthogonal TB form by putting simply  $S_{ij} = \delta_{ij}$ .

### 3. Simulated annealing

Simulated annealing is a very general minimisation procedure for finding a global optimum. It has been introduced in [18] and subsequently applied in various problems

to physics [6, 19] as well as for several optimisation problems in computer science [20, 21]. Originally, simulated annealing was used in the context of Monte Carlo methods but the method that we use is more suitable for dynamical systems. The method was first introduced in [6].

In simulated annealing, one aims to minimise some energy functional (or in general a cost function)  $E(C_i)$  which depends on variables  $C_i$  ( $i = 1, \dots, N$ ). Usually there are some constraints  $\sigma_i$  ( $i = 1, \dots, M$ , where  $M < N$ ) for the variables  $C_i$ . A physical analogy is that  $E$  is a classical potential in space  $\Omega$  and the variables  $C_i$  fix one point in that space. One can use the normal Lagrangian formalism to calculate the equation of motion for a fictitious particle represented by coordinates  $C = \{C_i\}$  and an arbitrary mass.

The Lagrangian of the combined system is

$$\mathcal{L} = \frac{1}{2} \sum_{i=1}^N m_i \dot{C}_i^2 + E(C_i) + \sum_{i=1}^M \lambda_i \sigma_i \quad (17)$$

where  $\lambda_i$  is a Lagrange multiplier associated with the constraint  $\sigma_i$  and the  $m_i$  are the mass parameters for the particles.

By using a normal variational procedure, one can derive equations of motion for the variables  $C_i$  as

$$m_i \ddot{C}_i = \delta \mathcal{L} / \delta C_i. \quad (18)$$

To find the minimum of  $E(C_i)$ , one starts from some arbitrary point  $C_0$  and initial velocity components  $\dot{C}_i$  so that the kinetic energy corresponds to a given temperature  $T$ . By integrating the equations of motion, one allows the system to evolve and slowly reduces the temperature (the kinetic energy of the system). If the cooling is slow enough, the system should finally reach the global minimum. How many time steps this will take depends crucially on the system itself but also on the cooling schedule. One simple way to cool the system is the so-called exponential cooling where the cooling speed depends linearly on  $T$ :

$$dT/dt = -vT. \quad (19)$$

Above,  $t$  is the iteration ‘time’ and  $v$  is a constant. In this schedule the number of time steps which are needed to reach the minimum depends on the value of  $v$ . The exponential cooling is somewhat problematic because it has the tendency to cool too fast at the end of the calculation.

There are several more sophisticated cooling schedules [20, 22], which allow one to solve the problem in much fewer time steps than needed for the exponential cooling schedule [23]. Keeping our programs simple, we have used the exponential cooling method, but other strategies can be implemented in a straightforward way.

#### 4. Application to silicon clusters

The TB formalism presented here is based on the work in [15, 24], where the TB method was used to find an initial atomic configuration for the density-functional calculation. Also in [12] a method similar to ours was used for studying the Si<sub>3</sub> trimer and silicon surfaces.

In a TB formulation for silicon we take four basis functions for each atom site—these basis functions are labelled  $(s, p_x, p_y, p_z)$ . We choose the orthogonal TB parametrisation first introduced in [25]:

$$\begin{aligned} E_s &= -5.25 \text{ eV} & E_p &= 1.20 \text{ eV} \\ V_{ss\sigma} &= -1.938 \text{ eV} & V_{sp\sigma} &= 1.745 \text{ eV} & V_{pp\sigma} &= 3.050 \text{ eV} & V_{pp\pi} &= -1.075 \text{ eV}. \end{aligned}$$

The  $V$  are the Slater–Koster [26] parametrised nearest-neighbour hopping integrals, corresponding to a bulk distance of  $2.35 \text{ \AA}$ . These hopping integrals have the distance dependence  $1/|\mathbf{R}_i - \mathbf{R}_j|^2$  [27]. The diagonal terms  $E$  are assumed to be independent of the distance between atoms.

In the dynamical simulation the coordination of atoms changes continuously, and thus one also needs the angular dependence of each matrix element. They can be found from [26] as

$$\begin{aligned} H_{ss} &= V_{ss\sigma} \\ H_{sx} &= -H_{xs} = \cos \theta_x V_{sp\sigma} \\ H_{xx} &= \cos^2 \theta_x V_{pp\sigma} + \sin^2 \theta_x V_{pp\pi} \\ H_{xy} &= H_{yx} = \cos \theta_x \cos \theta_y (V_{pp\sigma} - V_{pp\pi}) \end{aligned} \quad (20)$$

where  $\theta_x$  is the angle between the vector  $\mathbf{R}_i - \mathbf{R}_j$  and the  $x$  axis.

When building the TB matrix, we have used a smooth spatial cut-off because of the dynamical nature of our simulation program. We choose the following cut-off function:

$$f_{\text{cut}}(r) = \{\exp[(r - r_{\text{cut}})/\Delta] + 1\}^{-1} \quad (21)$$

where  $r_{\text{cut}}$  is the cut-off distance, which should lie between the nearest-neighbour ( $2.35 \text{ \AA}$ ) and the next-nearest-neighbour distances of bulk silicon ( $3.83 \text{ \AA}$ ). The value of  $\Delta$  should not be too small, as otherwise the cut-off can cause spurious forces. We have used the value  $r_{\text{cut}} = 3.3 \text{ \AA}$  and for  $\Delta$  we have taken the value of  $0.2 \text{ \AA}$ . The results are not sensitive to changes in these values. Using this smooth cut-off differs from the work in [15, 24] and this brings about some differences in the results (see below).

The ‘band structure’ energy can be written as

$$E_{\text{TB}} = 2 \sum_{i=1}^{2N} \mathbf{C}^i \cdot \mathbf{H} \mathbf{C}^i - N E_{\text{Si}}^{\text{free}} \quad (22)$$

where  $N$  is the number of atoms in the cluster and  $E_{\text{Si}}^{\text{free}}$  is the energy of a free Si atom.

The distance dependence used above for the  $V$ -values does not give correct repulsion at short distances, and a short-range correction is needed. The correction potential is written as a sum of pair potentials:

$$U(\mathbf{R}_n) = \sum_{n < m} E_{\text{corr}}(|\mathbf{R}_n - \mathbf{R}_m|) \quad (23)$$

where  $E_{\text{corr}}$  can be calculated as the difference between the *ab initio* pair potential for  $\text{Si}_2$  [15] and the corresponding TB potential:

$$E_{\text{corr}}(r) = E_{\text{Si}_2}(r) - E_{\text{TB}}(r). \quad (24)$$

Another correction term, which depends only on the number of occupied bonds in the cluster, is also used in [15]:

$$E_{\text{bond}} = -N[\varphi_1(n_b/N)^2 + \varphi_2(n_b/N) + \varphi_3]. \quad (25)$$

The coefficients  $\varphi$  were chosen to reproduce the cohesive energies of both diamond and BCC structures of silicon:

$$\varphi_1 = 0.225 \text{ eV} \quad \varphi_2 = 1.945 \text{ eV} \quad \varphi_3 = -1.03 \text{ eV}.$$

To apply the bond-counting term, one has to define when two atoms are bonded. When the distance between atoms is less than some cut-off distance  $r_{\text{cut}}$ , we consider them to form a bond. Owing to the dynamical nature of our method, we again must introduce a smooth cut-off function for bond counting as

$$n_b = \sum_{i < j} f_{\text{cut}}(|\mathbf{R}_i - \mathbf{R}_j|). \quad (26)$$

The same cut-off parameters as before ( $\Delta$  and  $r_{\text{cut}}$ ) are used.

A ‘Hubbard’ term which prevents large charge transfers between atoms was also introduced in [15, 24]:

$$E_{\text{Hubbard}} = U \sum_i (q_i - q_0)^2 \quad (27)$$

where

$$q_i = 2 \sum_{j=1}^{2N} \sum_{k=4(i-1)+1}^{4i} (C_k^j)^2 \quad q_0 = 4.0 \quad (28)$$

and the value of  $U$  is about 1 eV. The results in [15, 24] were found to be not very sensitive to the value of  $U$ , and accordingly we usually choose it to be zero, although other values can easily be tested (see below).

In the simulated annealing, we set the mass parameters to  $\mu = 1.0$  and  $m = 200\text{--}1000$  and the time step is chosen as  $\Delta t \approx 10^{-15}$  s. We have used the exponential cooling schedule and used values of  $\nu = 0.05\text{--}0.3$  for the cooling parameter. As for initial values for the atomic positions  $\mathbf{R}_n$ , we choose different plausible starting configurations. We have used several different initial configurations for each cluster, and in particular for the larger clusters ( $N = 8\text{--}10$ ) we have chosen initial geometries near those proposed in [28, 29] and used relatively high cooling speeds. Thus, in the case of the larger clusters, we have not done full global minimum searches but find at least local minima near the initial configurations.

The initial velocities for atoms  $\dot{\mathbf{R}}_n$  and initial values for  $C_i$  and  $\dot{C}_i$  have been chosen randomly. Subsequently the velocities have been scaled so that the kinetic energy corresponds to a given initial temperature.

Small (between two and 10 atoms) Si clusters have been investigated as a representative application of the general scheme. The MD-TB method is particularly suitable for finding minimum configurations for small clusters. It is clearly more physically based than methods relying on classical potentials derived from bulk properties, which do not give good results in the case of silicon [5]. In most of the published *ab initio* calculations, one has resorted to local minimisation—typically only the bond lengths have been optimised for some selected geometries. These methods often overlook low-symmetry minima.

Our results are in general similar to those given by *ab initio* quantum chemistry (Hartree-Fock-based) calculations [28, 29], but in the case of  $\text{Si}_5$  we find a different minimum. The results are summarised in tables 1 and 2 and figures 1–3.



**Table 1.** Binding energies of Si clusters.  $N$  is the number of atoms, and the second column gives the results for the energy minima. The third column is the energy of the same structure but including the Hubbard correction  $U = 1$  eV (see text). The fourth column contains the scaled energies obtained in [29]. The last column lists the binding energy per atom.

$N$	$E$ (eV)	$E$ with $U$ (eV)	$E$ [29] (eV)	$E/N$ (eV)
2	3.07	3.07	3.12	1.54
3	7.33	6.96	7.61	2.44
4	12.63	12.45	12.68	3.16
5	15.58	15.38		3.12
5	15.28	14.58	16.48	
6	20.82	20.49	21.62	3.47
7	26.56	26.52	26.59	3.79
8	29.67	29.29	29.17	3.71
9	33.14	32.94	32.27	3.68
10	39.06	38.84	38.16	3.91

Our results differ in some cases from those obtained in [15], because of using the smooth cut-off function and a different cut-off distance. Typically our results are closer to the *ab initio* calculations [8, 28, 29] than to those in [15].

As mentioned earlier, we have not used the ‘Hubbard’ correction in the dynamical simulations but have tested the energetics of the found geometries by using different values of  $U$  (equation (28)). The energy differences are in general quite small (see table 1), and the ‘Hubbard’ correction does not change the ordering of the minima at least for  $U < 2.0$  eV.

The obtained binding energy of  $\text{Si}_2$  is  $E_2 = -3.06$  eV and the equilibrium distance between the atoms is  $d = 2.27$  Å. The experimental value for the binding energy of the  $\text{Si}_2$  dimer is 3.24 eV [28].

For  $\text{Si}_3$  the binding energy is  $E_3 = -7.33$  eV and the cluster is an isosceles triangle with a side length of 2.26 Å and an opening angle  $\theta$  of 85.3°. These results are very close to those obtained in [12, 15] and the energy is in good agreement with the experimental values of  $-7.4 \pm 0.5$  and  $-7.7 \pm 0.2$  eV [28].

For  $\text{Si}_4$  the minimum structure is a flat rhombus with a side length of 2.39 Å and diagonal lengths of 2.54 and 4.05 Å. The binding energy of this structure is  $E_4 = -12.63$  eV. The symmetric tetrahedron structure has a higher energy of  $E = -10.62$  eV.

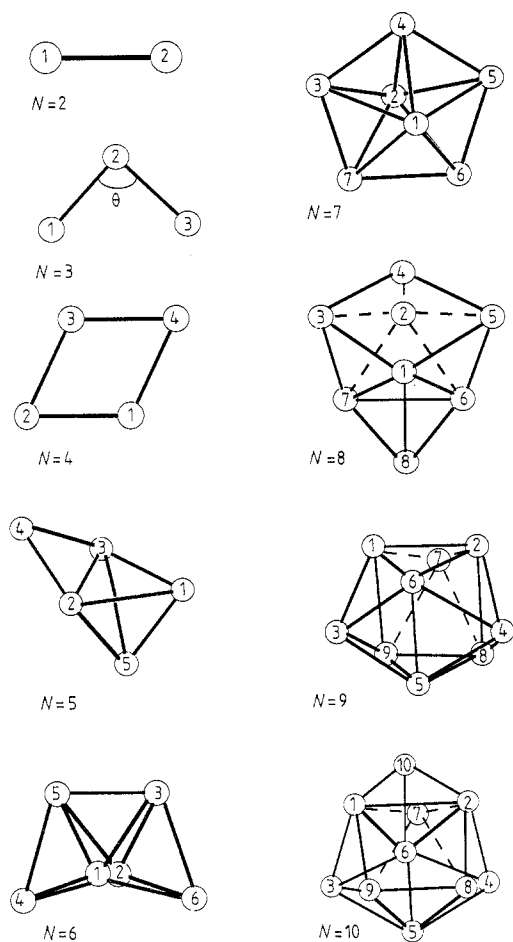
In the case of  $\text{Si}_5$ , we find a minimum corresponding to a low-symmetry structure. The energy of this structure is  $E_5 = -15.58$  eV. We also find a local energy minimum for the trigonal bipyramid structure [15], which has an energy  $E$  of  $-15.28$  eV. The side length of the base triangle is 3.56 Å and the distance from vertex to base is 2.48 Å. The minimum structure is quite asymmetric and therefore presumably not recognised in other work. We have also calculated the energy of this minimum structure and the trigonal bipyramid structure using another TB parametrisation [30]. In this case the energy difference between these two structures is almost zero.

For  $\text{Si}_6$  the tetracapped trigonal prism [28] gives the minimum energy of  $E_6 = -20.82$  eV, which is close to the energy of a distorted octahedron structure [15] of  $E = -20.44$  eV. In the minimum configuration of  $\text{Si}_6$  the bond lengths are between 2.4 and 2.8 Å (see table 2). For the distorted octahedron the side length of the base square is to

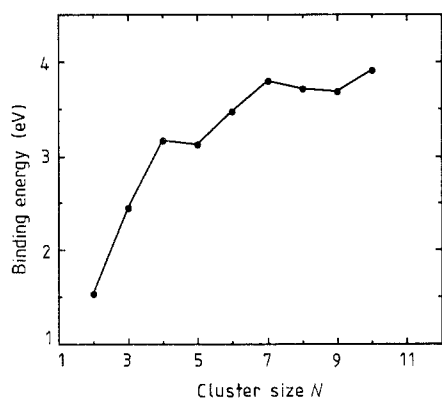
**Table 2.** Bond lengths for Si clusters.  $N$  is the number of atoms, and the second column defines the bond (see figure 1). The third column gives the bond lengths from our calculations. The fourth column contains the corresponding bond lengths from *ab initio* calculations [28, 29].

$N$	Bond	$d_{\text{cur}}$ (Å)	$d_{\text{ab initio}}$ (Å)
2	1-2	2.27	2.23
3	1-2	2.26 $\theta = 85.3^\circ$	2.17 $\theta = 77.2^\circ$
4	1-2	2.39	2.30
	1-3	2.54	2.40
5	2-4	2.41	
	2-5	2.44	
	1-2	3.07	
	2-3	2.59	
	1-5	2.35	
5 <sup>a</sup>	1-2	3.56	3.26
	1-4	2.48	2.34
	4-5	2.78	2.78
6	1-2	2.77	2.86
	1-3	2.52	2.49
	1-5	2.62	2.69
	3-5	2.63	2.93
	5-6	2.36	2.38
7	3-4	2.55	2.48
	1-3	2.60	2.47
	1-2	2.88	2.58
8	1-3	2.81	2.53
	1-5	2.74	2.56
	1-2	3.18	3.26
	2-3	2.72	2.57
	1-6	2.53	2.77
	2-5	2.74	2.79
	2-6	2.64	2.49
	3-4	2.77	2.48
	4-5	2.50	2.32
	5-6	2.48	2.48
	1-8	2.40	2.37
	3-8	2.55	2.42
9	1-6	2.57	2.57
	1-2	2.53	2.50
	1-9	3.06	2.53
10	1-2	3.11	2.75
	1-9	2.67	2.56
	5-9	2.78	2.54
	1-10	2.52	2.35
	1-3	2.57	2.45
	3-9	2.54	2.54

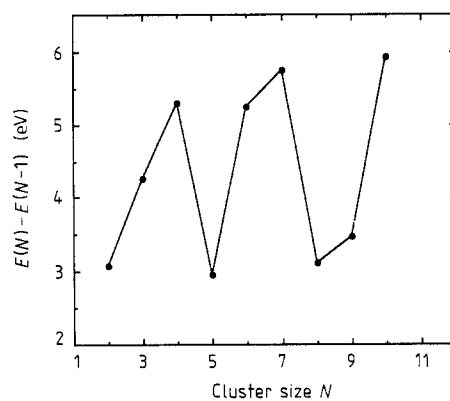
<sup>a</sup> In the case of Si<sub>5</sub> we have compared the bond lengths of the trigonal bipyramid structure.



**Figure 1.** Structures of small silicon clusters ( $N = 2-10$ ). In some clusters, not all the bonds are drawn; also the broken lines are used for clarity.



**Figure 2.** Binding energy per atom for silicon clusters.



**Figure 3.** Fragmentation energy  $E_N - E_{N-1}$  for silicon clusters.

2.65 Å and the distance from cap to basis is 2.54 Å. The octahedron structure is also the minimum for the classical Lennard-Jones cluster, where the atoms interact via a simple pair potential [31].

For  $\text{Si}_7$  the pentagonal bipyramid structure is most stable. The side length of the basis pentagon is 2.55 Å and the cap-to-basis distance is 2.60 Å. The energy of this structure is  $E_7 = -26.56$  eV. These results are very close to the values obtained in [29]. The tricapped tetrahedron structure [29] has the energy  $E = -25.50$  eV. The pentagonal structure is also the minimum for the classical Lennard-Jones cluster [31].

For  $\text{Si}_8$  we find the minimum structure to be like the  $\text{Si}_7$  structure with one added atom [3]. The energy of this structure is  $E_8 = -29.67$  eV, and the bond lengths are close to the values found in [29]. We also find a local minimum at the energy  $E = -28.05$  eV, corresponding to the distorted bicapped octahedron structure which is found to be the minimum in [29].

For  $\text{Si}_9$  the tricapped trigonal prism structure [29] is most stable. The energy of this structure is  $E_9 = -33.14$  eV. The distorted tricapped octahedron structure has the energy  $E = -31.34$  eV. The energies of these two structures, were found to be almost equal in [29].

For  $\text{Si}_{10}$  the tetracapped trigonal prism structure [29] gives the minimum energy of  $E_{10} = -39.06$  eV. The tetracapped octahedron structure has an energy  $E$  of  $-36.07$  eV. The bond lengths involving the capping atoms are 2.43 Å while in the octahedron they are 3.1 Å.

For the larger clusters ( $N = 8-10$ ) our TB parametrisation seems to favour close-packed structures. In [29], octahedron structures were found to be more stable than or equally stable as the close-packed structures. In our calculations the octahedron structures have higher energies.

It is quite surprising that the present results are so close to more elaborate (*ab initio*-type) calculations, considering how simple a model we have used. There are few experimental results for small silicon clusters, so we basically have to compare our results with *ab initio* type of calculations [8, 15, 28, 29]. The energies correspond quite well to the scaled energies by Raghavachari and Rohlfing [29] (see table 1). The bond lengths are usually slightly longer (typically 0.1 Å; see table 2) than in *ab initio* calculations. The differences from the results in [15] are most probably due to the smooth cut-off function introduced here.

The fragmentation spectrum has been experimentally observed [32, 33] for small  $\text{Si}^+$  clusters ( $N = 2-12$ ). These experiments show that clusters with six, seven and ten atoms should be the most stable. Our calculations give a fragmentation spectrum (figure 3) which agrees with these results.

## 5. Discussion

The method presented here is a general, flexible way to extend classical MD to include many-atom non-classical interactions. It has the advantages of normal MD, as one can study systems at non-zero temperatures, and one can also use the knowledge of existing MD simulation codes. The method takes the quantum mechanical effects into account at a more fundamental level than MD does, and therefore we believe that it describes 'quantum mechanical' systems better and with fewer parameters than classical MD does.

On comparison of the method with *ab initio* methods, it is much faster and therefore useful also for larger systems. The example of silicon clusters shows that a proper TB

parametrisation gives, for small clusters, results comparable with those of *ab initio* calculations. For larger systems, including defects and surfaces, the parametrisation should be even easier.

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