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A transferable nonorthogonal tight-binding scheme for germanium

Madhu Menon†

Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, and Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045, USA

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Abstract. A minimal-parameter tight-binding theory incorporating explicit use of nonorthogonality of the basis is used to generate a transferable scheme for germanium. Good results are obtained for high-pressure bulk phases and vibrational frequencies. Diamond structure is found to be the ground state even when compared with the clathrate structure. The results for clusters show good agreement with *ab initio* predictions.

1. Introduction

Among the group IV elements, carbon and silicon have been the focus of extensive research due to their technological importance. In contrast, germanium has not been studied in such detail. Recently, a total-energy scheme based on the orthogonal tight-binding method has been reported [1]. The tight-binding parameters were obtained by fitting to the band structure of *ab initio* calculations. Additional fitting information was obtained from the high-pressure *ab initio* phase diagram of Yin and Cohen [2]. Furthermore, a complex distance dependence of the parameters was invoked for obtaining the elastic constants in the diamond phase of bulk Ge. More recently, a density-functional-based nonorthogonal tight-binding approach has been used for studying Ge [3], although no vibrational analysis was reported for any phases of Ge. There have been a number of experimental [4, 5] and theoretical [6–12] studies of small germanium clusters.

In this work we introduce a transferable nonorthogonal tight-binding scheme for Ge that works all the way from dimer to bulk phases of Ge. 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. In keeping with the spirit of our early approach for Si [13–17], we employ the universal scheme of Harrison [18] which allows us to keep the number of adjustable parameters to a minimum. The physical quantities used to determine the adjustable parameters include bulk lattice constant and the vibrational frequencies. Explicit incorporation of the nonorthogonality of the orbitals [19] allows better description of the local coordination information when compared to the conventional orthogonal tight-binding schemes. The local coordination information has been found to be crucial in obtaining accurate energetic ordering of different isomers of Si clusters [13–15, 17].

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† E-mail: super250@pop.uky.edu.

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The atomic forces can also be easily evaluated in tight-binding theory if the distance dependence of the parameters is known. This enables molecular dynamics simulations for determining minimum energy structures to be performed. Furthermore, one can also construct the dynamical matrix for the determination of vibrational frequencies by invoking higher derivatives of the Hamiltonian matrix elements [16].

In this paper we present the construction of a transferable nonorthogonal tight-binding Hamiltonian for Ge systems, and obtain results for structural and vibrational properties for bulk and cluster phases. In the following section we briefly review the formalism. The results are presented in section 3.

2. Technique

The details of the construction of the nonorthogonal tight-binding Hamiltonian and the evaluation of the total energy and forces can be found in references [13–17]. Here we give a brief summary.

In the tight-binding theory, the total energy of the system is given by the sum

$$U = U_{\mathrm{el}} + U_{\mathrm{rep}} + U_0 \tag{1}$$

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

$$U_{\mathrm{el}} = \sum_{k}^{\mathrm{occ}} \varepsilon_k \tag{2}$$

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

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

Here r_{ij} is the separation of atoms i and j. $\phi(r)$ is short ranged and taken to scale exponentially with distance [17]. U_0 is a constant that simply shifts the zero of energy.

In the nonorthogonal tight-binding scheme the characteristic equation is written, in matrix form, as

$$(\mathsf{H} - E_n \mathsf{S})\boldsymbol{C}^n = 0 \tag{4}$$

where $\boldsymbol{C}^n$ is a column vector of LCAO coefficients. H is the Hamiltonian matrix and S the overlap matrix of the LCAO basis set [13, 19].

The Hellmann–Feynman theorem for obtaining the electronic part of the force is given by [13]

$$\frac{\partial E_n}{\partial x} = \frac{\boldsymbol{C}^{n\dagger}(\partial \mathsf{H}/\partial x - E_n\, \partial \mathsf{S}/\partial x)\boldsymbol{C}^n}{\boldsymbol{C}^{n\dagger}\mathsf{S}\boldsymbol{C}^n}. \tag{5}$$

The $\boldsymbol{C}^n$ are normalized so that

$$\boldsymbol{C}^\dagger \mathsf{S} \boldsymbol{C} = \mathbf{1}. \tag{6}$$

In the Slater–Koster scheme the Hamiltonian matrix elements are obtained from the parameters $V_{\lambda\lambda'\mu}$ in terms of the bond direction cosines l, m, n [13, 18, 20], and the $V_{\lambda\lambda'\mu}(r)$ are taken to decrease exponentially with r:

$$V_{\lambda\lambda'\mu}(r) = V_{\lambda\lambda'\mu}(d_0)\mathrm{e}^{-\alpha(r-d_0)} \tag{7}$$

where d_0 is the sum of the covalent radii of the pair of interacting atoms and α is an adjustable parameter. The four $V_{\lambda\lambda'\mu}(d_0)$ are derived from the dimensionless *universal* parameters through a prescription given by Harrison [18]:

$$V_{\lambda\lambda'\mu}(d_0) = \eta_{\lambda\lambda'\mu}\frac{\hbar^2}{md_0^2}. \tag{8}$$

The *universal* parameters were taken from reference [21] and have the values $\eta_{ss\sigma} = -1.73$, $\eta_{sp\sigma} = 1.84$, $\eta_{pp\sigma} = 2.42$, $\eta_{pp\pi} = -0.78$. The corresponding Hamiltonian parameters are $V_{ss\sigma} = -2.214$, $V_{sp\sigma} = 2.355$, $V_{pp\sigma} = 3.097$ and $V_{pp\pi} = -0.998$.

The scaling of the repulsive term is also taken to be exponential:

$$\phi(r) = \phi_0 e^{-\beta(r-d_0)} \tag{9}$$

where $\beta = 4\alpha$ [17].

Table 1. Parameters used in the present scheme for germanium.

A priori parameters[a]			Adjustable parameters			
ϵ_s (eV)	ϵ_p (eV)	d_0 (Å)	α (Å^{-1})	K_0	ϕ_0 (eV)	σ (Å^{-2})
−14.38	−6.36	2.44	1.604	1.5	0.22	1.8

[a] Reference [18].

In the nonorthogonal scheme, the overlap matrix is calculated in the spirit of extended Hückel theory [22] by assuming a proportionality between **H** and **S** [19]:

$$S_{ij} = \frac{2}{K}\frac{H_{ij}}{H_{ii}+H_{jj}}. \tag{10}$$

The diagonal elements of H_{ij}, as in the orthogonal theory, are taken to be the valence s and p energies. The off-diagonal inter-atomic matrix elements are given in terms of the Hamiltonian matrix elements in orthogonal theory, V_{ij}, by

$$H_{ij} = V_{ij}\left[1 + \frac{1}{K} - S_2^2\right] \tag{11}$$

where

$$S_2 = \frac{S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma}}{4} \tag{12}$$

is the nonorthogonality between sp^3 hybrids [19]. The quantities $S_{\lambda\lambda'\mu}$ are determined from

$$S_{\lambda\lambda'\mu} = \frac{2V_{\lambda\lambda'\mu}}{K(\varepsilon_\lambda + \varepsilon_{\lambda'})}. \tag{13}$$

We take a simple exponential distance dependence in the expression for the nonorthogonality coefficient, K:

$$K(r) = K_0 e^{\sigma(r-d_0)^2}. \tag{14}$$

In table 1 we list all of the *a priori* (ϵ_s, ϵ_p and d_0) and adjustable (α, K_0, ϕ_0 and σ) parameters used for Ge.

3. Results

3.1. Solid

In this section we present our results obtained using the nonorthogonal scheme. All of the results are obtained without introducing any artificial cut-off in the interactions. In practice this is achieved by increasing the shell size until the results remain unchanged. This implies inclusion of up to the third-neighbour shell (corresponding to a cut-off of 5.5 Å).

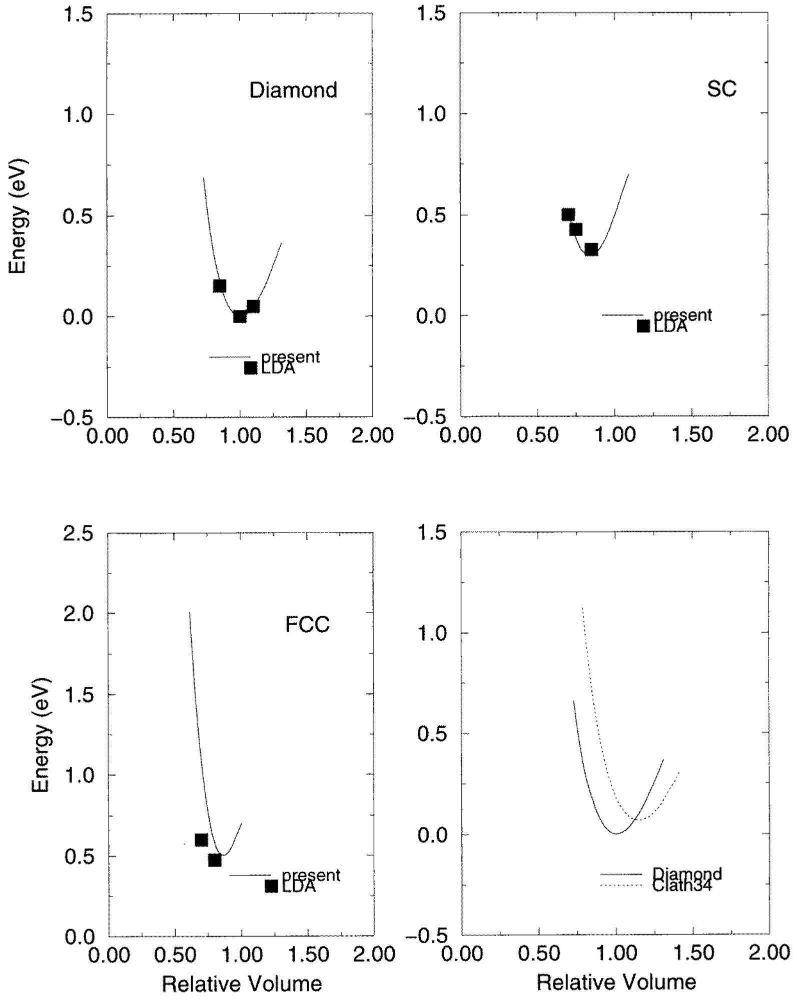

Figure 1. The cohesive energies of various structures of germanium using the present scheme.

Figure 1 shows the zero-temperature phase diagram for germanium obtained by our method. The high-pressure-phase (fcc, sc) results are in good agreement with those obtained from LDA-based calculations. The energy differences between various phases are also in good agreement with the results of Sitch *et al*, obtained using a density-functional-based nonorthogonal tight-binding approach [3]. In computing the electronic energies, special-point integrations were performed and tested for convergence. As can be seen in the figure,

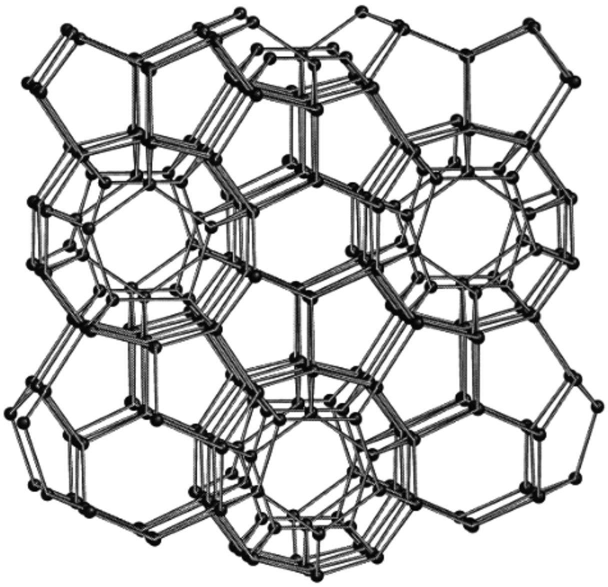

Figure 2. The clathrate structure containing 34 atoms in a face-centred cubic (fcc) unit cell ($Fd3m$ symmetry).

Table 2. Comparisons showing transferability for germanium. The numbers in parentheses are *ab initio* and experimental values.

	Bond length (Å)	Vibrational frequency (cm^{-1})
Ge (dimer)	2.35 (2.36–2.42)[a]	258 (275)[b]
Ge (diamond)	2.44 (2.44)[c]	Γ_{TO}: 344 (301)[d] L_{LO}: 259 (250)[d] L_{LA}: 204 (217)[d] X_{LO}: 303 (275)[d] X_{TO}: 246 (248)[d]

[a] References [6–11].

[b] Reference [12].

[c] Reference [18].

[d] Experimental values given in references [28, 29].

the diamond structure is the lowest in energy—even when compared with the clathrate structure [23, 24] with the same coordination—with a difference in energy of 0.07 eV/atom. The clathrate structure considered contains 34 atoms in a face-centred-cubic (fcc) unit cell [23, 24]. The structure was fully relaxed by incorporating a constant-pressure ensemble [25–27] into the molecular dynamics scheme to allow for simultaneous relaxation of the lattice and basis degrees of freedom. The relaxed structure is shown in figure 2. The lattice constant for the 34-atom unit-cell Ge clathrate was obtained to be 14.93 Å. We note that Sitch *et al* [3] did not report comparisons of the stability of the clathrate structure to those of other phases of Ge.

The force constants for the evaluation of vibrational modes are obtained by employing analytic second derivatives of the electronic structure Hamiltonian matrix elements [16].

This method, while providing better accuracy than conventional schemes, greatly expedites the determination of vibrational modes for large-size clusters. The vibrational frequencies at some symmetry points for the bulk diamond phase are given in table 2. Both the acoustic and optical branch phonons are in excellent agreement with experiment, with maximum mode deviations of only up to about 14% from experiment [28, 29]. As shown in the next section on clusters, the same scheme gives a reasonable vibrational frequency for the symmetric stretch mode of the dimer. The authors of reference [3] did not provide any results for vibrational frequencies for the bulk diamond phase of Ge.

3.2. Clusters

We next briefly describe our results for small germanium clusters using the present scheme. All of the geometries were optimized by molecular dynamics relaxation using precisely the same tight-binding parameters. No cut-off is used in the present calculations.

For Ge_2, we obtain a dimer bond length of 2.35 Å and a vibrational frequency of 258 cm^{-1}. The *ab initio* values for the bond lengths are in the range 2.36–2.42 Å [8–12]. The *ab initio* coupled-cluster calculations give a dimer frequency of 275 cm^{-1} [12]. In table 2 we compare our results with experiment for bond lengths and vibrational frequencies at the dimer and bulk ends to illustrate the transferability of the present scheme.

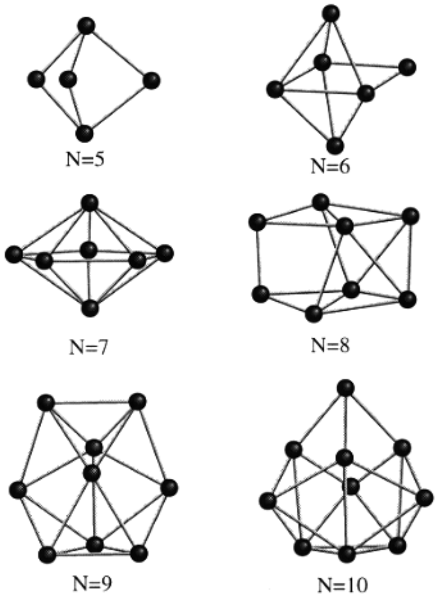

Figure 3. Geometries of the lowest-energy structures of small germanium clusters for sizes from $N = 5$ to $N = 10$ obtained using the present molecular dynamics scheme.

The minimum-energy structure for Ge_3 is found to be an open triangle with C_{2v} symmetry. Two sides of the triangle have bond lengths of 2.348 Å each and the third side has a bond length of 2.892 Å. For $N = 4$ we find the stable structure to be a rhombus (D_{2h} symmetry) with side length of 2.473 Å. The shorter diagonal has a length of 2.731 Å. For Ge_5, the lowest-energy configuration is found to be a strongly compressed trigonal bipyramid (D_{3h} symmetry) with apex atoms holding the triangle together, as shown

Table 3. Cohesive energies (in eV/atom) for Ge_N clusters. The value of the constant shift U_0 in equation (1) is taken to be 1.0 eV to bring the absolute values into agreement with experiment.

		Binding energy (eV/atom)	
N	Symmetry	Present work	Experimental values[a]
2		1.31	1.41 ± 0.10
3	C_{2v}	2.11	2.15 ± 0.07
4	D_{2h}	2.66	2.58 ± 0.09
5	D_{3h}	2.85	2.78 ± 0.09
6	C_{2v}	3.05	
7	D_{5h}	3.19	
8	C_2	3.17	
9	C_{3v}	3.25	
10	C_{3v}	3.32	

[a] Reference [30].

in figure 3. Our results for the ground-state structures for Ge clusters for N up to 5 are in complete agreement with the *ab initio* results [6–11].

The *ab initio* predictions for the ground-state geometries of larger-size clusters have not been reported. Our results for these sizes of clusters should, therefore, be considered as predictions. In the case of Ge_6, we find the edge-capped trigonal bipyramid (figure 3) to be isoenergetic with a distorted face-capped trigonal bipyramid. For Ge_7, we find the pentagonal bipyramid (figure 3) to be the most stable. In the case of Ge_8, the lowest-energy structure is a distorted bicapped octahedron with C_2 symmetry (figure 3). This is in agreement with the results of Sitch *et al* [3]. Another distorted octahedron with C_{2h} symmetry was found to be 0.03 eV/atom higher in energy. For Ge_9, we find a distorted tricapped trigonal prism proposed by Ordejon *et al* [14] (C_{2v} symmetry) to be the most stable. For Ge_{10} the lowest-energy structure is found to be a tetracapped trigonal prism with C_{3v} symmetry (figure 3). The bicapped tetragonal anti-prism structure proposed by Sitch *et al* [3] as the ground state for Ge_{10} was found to be 0.04 eV/atom higher in energy than the tetracapped trigonal prism.

In table 3 we give binding energies of low-energy stable clusters. In comparing our *absolute* cohesive energies with *ab initio* results, a constant shift of $U_0 = 1.0$ eV (see equation (1)) applied to our computed values brought all of the values into excellent agreement with experiment [30].

Transferability from solid to cluster is crucial to the study of crystal growth. Clusters with $N \geqslant 7$ are particularly challenging on account of the high-coordination and low-symmetry geometries. Our earlier studies of Si clusters have shown that incorporation of nonorthogonality of the orbitals is essential to obtaining correct energetic ordering of isomers [15, 17]. Also, as seen in table 2, there is better transferability between cluster and bulk solid for bond lengths and vibrational frequencies.

4. Discussion and summary

We have presented a transferable nonorthogonal tight-binding scheme for germanium which incorporates the overlap interactions explicitly and obtained agreement on a wide range of properties for different phases. The simplicity of the original formalism is retained, and good agreement has been obtained in the area of high-pressure metallic phases and the vibrational frequencies.

Acknowledgments

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