

Simple quantum-mechanical model of covalent bonding using a tight-binding basis

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(Received 10 August 1992)

We present a method which uses a tight-binding basis set to describe the energetics of covalent bonds. While having the same ability to model covalent bonding, the current method is significantly faster than the direct diagonalization of the tight-binding Hamiltonian, and has the merit of being linear in the size of the system, resulting in the ability to do molecular dynamics for thousands of atoms. At present, the method works only for systems with fixed bonding topologies.

The tight-binding (TB) method has been frequently used to do molecular dynamics (MD) in recent years.¹ However, the direct diagonalization of the TB Hamiltonian matrix scales as the cube of the system size. The recursion method of solving the TB Hamiltonian² is linear in the size of the system, but a large prefactor is needed, making TB impractical to be used dynamically for thousands of atoms. While superior to three-body potentials,³ TB is a model which approximately incorporates quantum-mechanical features of the system and uses its Hamiltonian matrix parameters to fit the experimental or *ab initio* computational results.⁴ In this paper we will introduce another model which can be thought of as an approximation to the TB solution, but has the same ability as the TB solution to fit *ab initio* data. The great speed of this model makes it possible to do MD for thousands of atoms and for thousands of time steps.

In this paper, we will follow the tight-binding bond model of Sutton *et al.*⁵ But instead of solving the band energy exactly by direct diagonalization of the TB Hamiltonian or the recursion method, we will use maximally localized wave functions (LWF).⁶ The LWF's are generalizations of the Wannier functions of periodic systems. Like the Wannier functions, the LWF can be achieved by a unitary transformation of the eigenfunctions and can be used to describe the system and get the band energy. Using the variational principle, we will minimize the band energy and solve the LWF (i.e., the coefficients of LWF based on the TB basis). The LWF's are orthonormal. As an approximation, one can truncate each LWF within a specific local region. For large enough regions, this should be a good approximation because the LWF's decay exponentially at large distances for systems having a gap.⁷ As a simple model, we use only linear combinations of the TB bases of the two atoms of a covalent bond to form a LWF and use this LWF to describe that bond. If the orthogonality condition between different LWF's were enforced exactly, there would be two problems. First, because the basis set for each LWF is very small, the orthogonality condition between neighboring wave functions will drive the total energy high above its correct value. Second, it is difficult and slow to imple-

ment the exact orthogonality condition computationally. Consequently, we will relax the orthogonality condition. Instead of enforcing the exact orthogonality condition, we will use a penalty function to mimic its effects. Then the total energy to be minimized by variation is

$$E = \sum_{i=1}^n \langle \psi_i | H | \psi_i \rangle + \lambda \sum_{i=1}^n \sum_{j=\text{neighbor of } i} |\langle \psi_j | \psi_i \rangle|^2. \quad (1)$$

Here, the ψ_i is the LWF for bond i , n is the total number of bonds in the system, and each LWF is normalized to one. H is the tight-binding Hamiltonian matrix. The orthogonality of the tight-binding basis is assumed as in conventional TB theory.³ The last term in Eq. (1) is the penalty function for the lack of exact orthogonalization between ψ_i 's. If λ equals infinity, the orthogonalization will be exact, and the magnitude of the last term is zero. However, it is difficult to variationally minimize E for very large λ . The current method is based on the discovery that in order to match the correct energy and to get a good electron density, a small λ is needed. The smaller the localized basis set used in the description of the LWF, the smaller λ needs to be. For our LWF, the proper λ is larger than, but of the same order as, the Hamiltonian matrix elements. Because λ is so small, the conjugate gradient scheme⁸ can be used efficiently to minimize the energy in Eq. (1), and the λ term in that equation does not slow down the convergence of the conjugate gradient scheme. Thus the introduction of the penalty term and the small size of λ have solved the two problems mentioned above. Equation (1) is the main equation in the current method; its properties will be discussed below.

In this paper, we chose silicon in the diamond structure as our example. There are four sp^3 basis functions on each atom in the conventional tight-binding treatment. We will use the same basis set for our LWF. Using that basis set, each LWF has only eight coefficients. For the conjugate gradient algorithm, we need the func-

tional derivative of E :

$$\frac{\delta}{\delta\psi_i} E = H\psi_i + \lambda \sum_{j=\text{neighbor of } i} \langle \psi_j | \psi_i \rangle \psi_j. \quad (2)$$

Starting from this steepest-descent direction, one can get the conjugate gradient search direction by the conventional conjugate gradient step, and then carry out the line minimization along that search direction simultaneously for all wave functions. For the purposes of comparison to the direct diagonalization tight binding (DDTB), we follow the work of Wang, Chan, and Ho⁹ (WCH). We compare the results of the current method to the DDTB results. The tight-binding matrix elements shown in Table I are chosen from Chadi's work,¹⁰ as used by WCH. The $1/r^2$ radial-dependent form of the Hamiltonian matrix elements are used as in Ref. 9. Using the same Hamiltonian matrix parameters as in DDTB, to get the right total band energy by the current model, it is necessary that the value of λ be 7.94 eV. Using this λ , the electron density on each basis is found to have a root-mean-square error of 4% comparing to the DDTB density. Although qualitatively similar, the energy changes (which correspond to frequencies and forces) for some atomic displacements can have errors as large as 50%. However, this does not mean we cannot use this method. As discussed above, we are seeking a model which, like the tight-binding model, correctly incorporates the most important quantum-mechanical features, and hence can fit the *ab initio* data with good precision. Because in the exact tight binding the Hamiltonian matrix parameters are varied to fit either the electronic band structure¹¹ or the energetics of the systems,¹² it is legitimate here for us to do the same thing. This readjustment of the Hamiltonian matrix is used to compensate the effects of the locality of the wave functions and the relaxation of the orthogonality condition. It is much like what was done for the DDTB Hamiltonian matrix when the tight-binding basis set overlaps are ignored.¹³ The real test is to see how well this model can be used to fit the *ab initio* or experimental data and how does that compare to the ability of the DDTB model. Although the final goal is to fit the *ab initio* or experimental data to get the best parameters, in this paper, we also want to know how well this model can replace the DDTB model. For this purpose, we have fitted the Hamiltonian matrix parameters and the λ to the DDTB data. The resulting parameters are shown in Table I. To get these parameters, we have minimized the errors in several phonon modes and elastic constants with respect to the DDTB results. As can be seen from Table I, the new parameters are significantly different from the old ones, but are still qualitatively similar. The current model with the new parameters typically has the band energy versus atomic displacement curves within 8% of the DDTB results. In Fig. 1, we show one such energy curve. One can see, despite a consistent difference, these two curves look very similar, including the unusual feature at large displacement. In order to get the total energy, energy terms other than the band energy must be included. Following Refs. 5 and 9, we use a pair potential to approximate these energy terms. To do that, we have the *ab initio* total energy (per atom) taken from Yin

TABLE I. Overlap matrix elements of tight-binding Hamiltonian. The parameters are in eV. The λ in Eq. (1) corresponding to the values in the second row is 19.503 eV.

	$V_{ss\sigma}$	$V_{sp\sigma}$	$V_{pp\sigma}$	$V_{pp\pi}$	$E_p - E_s$
DDTB	-1.94	1.75	3.05	-1.08	6.40
This work	-2.569	2.336	1.884	-2.525	6.118

and Cohen¹⁴ and WCH (Ref. 9) for silicon in the diamond structure and fitted in the following form:

$$E_{\text{tot}}(r) = E_0 [1 + (r - r_0)/A] \exp[-(r - r_0)/A] \quad (3)$$

with $E_0 = -4.8060$ eV, $r_0 = 2.3627$ Å, and $A = 0.5076$ Å. Here r is the interatomic distance. The band energy per atom for the current and DDTB results for the same structure are fitted to a fourth-order polynomial, which is

$$E_{\text{band}}(r) = \sum_{i=0}^4 A_i (r - r_0)^i. \quad (4)$$

Here for DDTB we have $A_0 = -10.4504$ eV, $A_1 = 6.9148$ eV/Å, $A_2 = -4.9244$ eV/Å², $A_3 = 2.7729$ eV/Å³, $A_4 = -1.4406$ eV/Å⁴, and for the current model, we have $A_0 = -9.912484$ eV, $A_1 = 7.2977$ eV/Å, $A_2 = -4.6644$ eV/Å², $A_3 = 2.6710$ eV/Å³, $A_4 = -1.5721$ eV/Å⁴. These two curves look rather similar. Then the pair potential can be defined as

$$\Phi(r) = \frac{1}{2} [E_{\text{tot}}(r) - E_{\text{band}}(r)]. \quad (5)$$

After this step, we can compute phonon frequencies and elastic constants. We repeated the quantities computed in WCH,⁹ and the results are shown in Table II. The DDTB results have a very small difference from the values in Ref. 9, due to different parametrizations for E_{band} . Between the current method and DDTB, there is a 4% difference for phonon frequencies and 2–4%

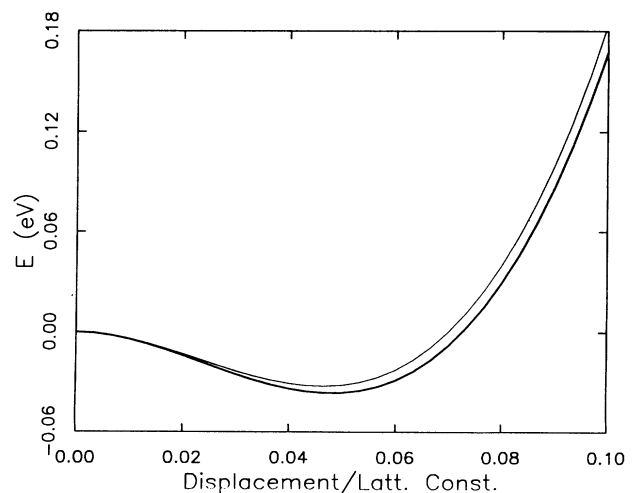


FIG. 1. Energy curves for a displacement of one atom. One atom is moved from its equilibrium position in one direction and the band energy is plotted vs the displacement of that atom. The thick line is DDTB and the thin line is the current model.

TABLE II. $T=0$ K equilibrium properties of diamond Si. Unit of lattice constant is angstrom. Unit of elastic constants is 10^{11} erg/cm³. Unit of phonon frequencies is THz. For the definition of the mode-Gruneisen constants γ , see Ref. 14. The *ab initio* LDA results, experimental results, and the Stillinger-Weber (SW) results are all quoted from Ref. 16.

	DDTB	This work	SW	LDA	Expt.
Latt. const	5.456	5.456	5.456	5.456	5.44
B	9.13	9.13	10.14	9.20	9.78
$C_{11} - C_{12}$	7.34	7.25	7.50	9.80	10.12
C_{44}^0	10.15	10.30		11.10	
C_{44}	6.26	6.54	5.64	8.5	7.96
$\nu_{LTO(\Gamma)}$	16.88	16.22	17.83	15.16	15.53
$\nu_{TA(X)}$	5.03	4.76	5.96	4.45	4.49
$\nu_{TO(X)}$	14.62	14.30		13.48	13.90
$\nu_{LOA(X)}$	12.34	11.82		12.16	12.32
$\gamma_{LTO(\Gamma)}$	1.01	1.12	0.80	0.92	0.98
$\gamma_{TA(X)}$	-1.04	-1.55	-0.04	-1.50	-1.40
$\gamma_{TO(X)}$	1.42	1.52	0.89	1.34	1.50
$\gamma_{LOA(X)}$	1.05	1.12	0.83	0.92	0.90

difference for the elastic constants (note that, most of the quantities listed in Table II are not directly fitted in our readjustment of Hamiltonian parameters). This agreement is rather good compared to the errors in DDTB. A large discrepancy between the current model and DDTB model is in the γ_{TA} . Its unusual negative value stems from a cancellation between band energy effects and electron static effects.¹⁴ As a result, the exact value is sensitive to the model used. That is why DDTB gets a 50% error for this value. Fortunately, the current model gets a much better result when compared to the *ab initio* value. Also shown in Table II are the results of the Stillinger-Weber¹⁵ (SW) three-body classical force model. As can be seen in Table II, the DDTB and the current model have in general better results than the classical model, especially for some quantities like γ_{TA} . The atomic forces due to the band-structure energy are computed using the Hellman-Feynman theorem, which is applicable to both the DDTB and the current model. And the pair potential force can be readily computed from the pair potential given in Eq. (4). In Fig. 2, we randomly moved all the atoms from their equilibrium positions in a diamond-structure 64-atom cell, and the forces on every atom are computed and comparison is made between our method and DDTB. Band-energy forces and the total forces have root-mean-square differences of about 6% and 4% between the DDTB and the current model. The average displacements in Fig. 2 are rather large, and the DDTB used here is no longer good. The DDTB has a 19% difference for its forces compared to the *ab initio* local-density approximation (LDA) results, while for our model, the difference is 18%. MD simulations have been carried out for a 64-atom cell for both the DDTB and the current model. The atomic pair correlation functions are plotted in Fig. 3. The peak positions are the same for these two methods. The first peak heights have a difference of 1%. The second and third peak heights have differences of about 6%. This difference is of about the same order as the difference between DDTB and *ab*

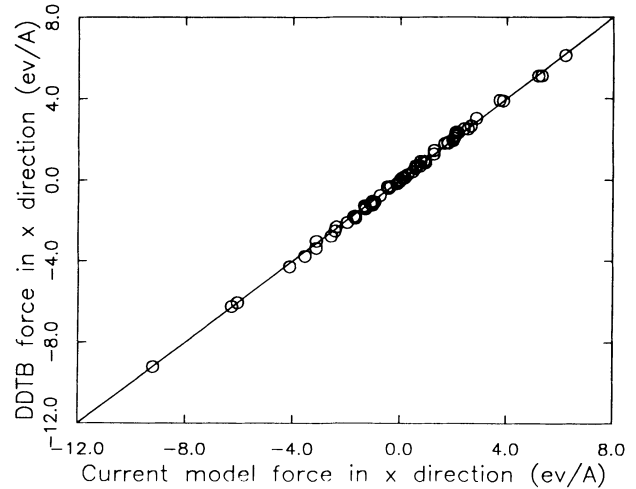


FIG. 2. Atomic forces for the random displacement described in text. Each circle represents one atom. The straight line stands for (DDTB force)=(current model force). The band energy forces graph which is not plotted here looks similar and has a similar average magnitude as this total forces graph.

initio LDA computations.¹⁶ In summary, we have learned that for a wide variety of properties, the current model results are comparable to the DDTB results. We conclude that the current model has the same ability to accurately model the silicon diamond structure as the direct diagonalization tight binding. We hope that the same is true for other covalent systems.

The advantage of the current model over the DDTB is its great speed. In the following, we will give the computing time for these two methods on IBM RS/6000 work station model 560. The direct diagonalization of 64 atoms takes 4.03 sec, while the current model takes 1.04 sec to carry out 80 conjugate steps, which converge the wave functions to residuals of 10^{-9} . [The residual is defined as $|(\delta/\delta\psi_i)E - \epsilon_i\psi_i|$; here ϵ_i is the Lagrange

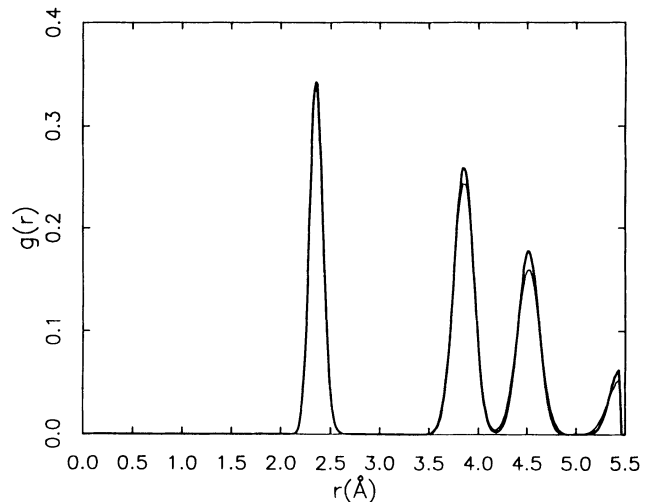


FIG. 3. Pair-correlation functions of diamond Si. The thick line is DDTB molecular-dynamics result and the thin line is current model result. The temperatures for both curves are 472 K.

multiplier for the normalization of ψ_i .] To compute 10 000 steps in MD as shown in Fig. 3, it takes 11 h using direct diagonalization. For the time step we used, which is 1×10^{-15} sec, by setting up a residual requirement of 10^{-4} (which results in a 10^{-4} relative error of forces), on average it only takes 16 conjugate steps to reach that accuracy for each MD step. As a result, it only takes 35 min to compute the 10 000 steps for the current model. This time saving is even more significant for larger systems. For a 4000-atom system, it takes 10 days for the direct diagonalization to compute one step, thus doing MD for such systems is out of the question. By using the current model, it can do the MD of a 4000-atom system for 10 000 time steps within 45 h. Surprisingly, the number of conjugate gradient steps needed to converge the system to a same error residual under the same conditions (temperature and the MD time step) is the same for these two different systems (one 64 atoms, one 4000 atoms), they are both 16 in our cases. This is because, for our case, the large system is homogeneous in space. So, the span of the electronic energy spectrum of the large system is almost the same as the small system. As a result, the conjugate gradient method converges the large system as fast as the small one, because the rate of convergence only depends on the eigenvalue spectrum span of the system.¹⁷ In conclusion, the speed of this model makes it possible and practical to do MD for several thousand atoms and several thousand steps.

In its current form, the model can only describe well-defined covalent bonds for fixed topology (i.e., no bond breaking and forming). There are a number of applications within that category, especially for polymer and large biological molecules. It can also be used to compute the ground-state energies of different topological structures and compare the energies between them. It is evident, from the data in this paper and in Ref. 3, that, like the DDTB, the current model is better than any

three-body force model, at least for the system we studied. Hence, the current model can be used to replace the three-body force model. The simplicity of this model also provides a way to think about the covalent bond behavior. At first glance, it is very much like the bond-orbital model used by Harrison.^{18,4,13} But one important difference is that we use a penalty function to describe the effects of the orthogonality condition between neighboring bonds. The orthogonalization penalty function term at one atom forces the covalent bonds of that atom in their proper direction, and thus preserves the energy versus bond-angle relation. On the other hand, like the bond-orbital model, the strength of a bond mainly depends on the atomic distance of this bond through the change of the Hamiltonian overlap matrix. One extension of the current model is to use a larger LWF, for example, not only include the bases on the two atoms of one bond, but also include the bases on nearest-neighbor atoms of those two atoms. The hope is that one can get solutions closer to the exact tight-binding results. This requires caution since we have determined that there are numerous local minima as larger LWF's are used. These local minima slow down the conjugate gradient step tremendously and make it impractical. Efforts to make the current model workable for breaking and forming bonds are under way.

The authors would like to thank Dr. Andrew Horsfield for many stimulating discussions. We would also like to thank Dr. Robert Phillips for a careful reading of the manuscript. This work was funded by Corning Inc. The computing facilities of this work were provided by the Cornell-IBM Joint Study on Computing for Scientific Research. We gratefully acknowledge resources provided by LASSP and the Cornell Theory Center in carrying out this research.

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