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Bond-order potentials: Theory and implementation

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The background theory and the details required for implementation of bond-order potentials are presented in a systematic fashion. The theory is an O(N) implementation of tight binding that is naturally parallelizable. Further, it is straightforward to show how the lowest-order approximation to the two-site expansion can reproduce the Tersoff potential. The accuracy of the forces is demonstrated by means of constant-energy molecular dynamics, for which the energy is found to be very well conserved. Thus, the method is both an efficient computational method and a useful analytic tool for the atomistic simulation of materials.

I. INTRODUCTION

In this paper, we present an approach to atomistic modeling based on the bond-order potential (BOP). It is designed to be a self-contained account of both the underlying theories[1–11] and the technical details required to implement them as computer programs. The formalism contains mathematical methods with which readers may not be familiar, so attention is given to explaining these methods in some detail.

The motivation for developing the BOP scheme for atomistic modeling derives from the rapid growth of interest in computer simulations at the level of the atom. Whereas it is certainly true that other length scales are extremely important (both mesoscopic and macroscopic), and need to be treated in their own ways, phenomena observed at these length scales can be strongly influenced by processes at the atomic level. Atomistic computer simulations have an important role to play in bridging the gap between the atomic and longer length scale phenomena.

There are three constraints that apply to successful computer models: they must be able to be implemented efficiently on a computer; they must be able to produce results that accurately reproduce observed experimental results; and they should be able to be applied to a wide range of materials under diverse conditions within a single framework.

Satisfying all three criteria is an extremely demanding task, and as yet to our knowledge no model exists that can claim to achieve this. However, it is straightforward to translate these criteria into some basic decisions, which can then be developed further. The third criterion (the single framework) requires that we work with a quantum mechanical model for electron motion, since the difference in properties between materials derives from the different electron wave functions. There is a variety of quantum mechanical methods that are currently used ranging from very accurate many electron *ab initio* methods, such as quantum Monte Carlo, through slightly less accurate single electron *ab initio* methods, such as the local density approximation (LDA) to density functional theory (DFT),[12] down to the semiempirical methods, such as tight binding (TB).[13,14] In general, the more accurate the method, the more computer intensive it is. However, the computationally least intensive method (TB) offers remarkable accuracy (given its simplicity) for many materials. Further, results obtained with it often allow clear insight into the nature of cohesion to be obtained, precisely because of its simplicity.[15] TB models have been applied successfully to metallic systems,[16–18] semiconducting systems,[19–26] including the liquid phase,[27–30] and strongly covalent systems.[31,32] Thus we see that TB satisfies all three criteria sufficiently well to be very interesting.

The TB model involves the construction of a Hamiltonian matrix, and the evaluation of the band energy and band forces from it. The most computationally demanding part of any implementation of TB is extracting the band energy and forces from the Hamiltonian. The appropriate numerical technique for performing this operation when a small number of atoms (fewer than 100) is being considered is direct diagonalization of the Hamiltonian matrix. However, the time to perform this operation typically scales as the third power of the number of atoms in the unit cell. For periodic systems, this statement has to be treated with caution. It is only true when one k point is being used. If many k points are used, then the scaling is still cubic in the number of atoms for each k point, but the number of k points needed to achieve a given level of accuracy scales as the inverse of the number of atoms. Thus the time to evaluate the energy and forces scales only as the square of the number of atoms in the unit cell when working at constant accuracy. However, this scaling is still disastrous for simulations of large numbers of atoms. Thus it is necessary to find methods that can extract the useful information from the Hamiltonian matrix to a given level of accuracy with a much better scaling, ideally linear scaling [O(N) methods].

Several O(N) methods suitable for atomistic simulations based on TB have been proposed recently.[33–35,8,36–40] They are all methods for finding the density matrix, and are based on a variety of observations about electronic structure: the density matrix is short ranged for systems with a band gap in the density of states; the band energy is minimized by the correct density matrix; the density matrix at finite electron temperature can be written down explicitly as the Fermi function of the Hamiltonian; the density of states can be reconstructed efficiently from the moments of the Hamiltonian. The way a method is constructed depends on which observation one begins with. For BOP, the view is taken that the most *flexible* approach is to work with moment expansions for the densities of states. Working with moments also has the advantage that it allows an interpretation of elec-

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tronic structure in terms of atomic structure,[43,44,1,45,15] which makes it possible to form a direct connection between this approach and the potentials of Finnis and Sinclair[46] and Tersoff.[47]

In the remainder of this paper we discuss in detail the various elements that make up the bond-order potential. We begin with a quick survey of the TB model, deriving important results that allow it to be applied to total energy calculations. Having introduced the concept of the density of states, we show how it can be determined very efficiently from a moments description. We show how Green's functions provide a very natural, and computationally stable, way of obtaining densities of states from moments. To evaluate forces we need the full density matrix. We present BOP as a method for evaluating the density matrix within a Green's function framework. Two versions of BOP are described: two-site BOP and one-site BOP. It is possible to derive a Tersoff-like expression for the bond order (the off-diagonal part of the density matrix) from just the first-order term of the two-site BOP. However, this formulation cannot provide a good description of close packed metals, and so we have to develop the one-site formulation. This requires the use of an auxiliary space, which is explained in detail. The one-site formulation is found to give good convergence.

II. TIGHT BINDING

There is already a sizeable literature concerning the use of the TB model for total energy calculations.[42,14,45,15] Here we just summarize the key elements that will be used in the development of BOP.

The model has its origins in the linear combination of atomic orbitals (LCAO) method pioneered by Slater and Koster,[13] although, more recently,[45] it has been justified by the Kohn-Sham formulation of the density functional theory of the electron gas.[12] The central equation in the TB model is an effective single particle Schrödinger equation that is solved self-consistently for the eigenstates:

$$\hat{H}\psi^{(n)}(\vec{r})=\epsilon^{(n)}\psi^{(n)}(\vec{r}),$$

$$\delta_{n,m}=\int d\vec{r}(\psi^{(n)}(\vec{r}))^{*}\psi^{(m)}(\vec{r}), \tag{1}$$

where $\epsilon^{(n)}$ is an eigenvalue, and $\psi^{(n)}(\vec{r})$ is the corresponding eigenfunction. In operator notation, the same equations can be written as

$$\hat{H}|n\rangle=\epsilon^{(n)}|n\rangle,$$

$$\delta_{n,m}=\langle n|m\rangle, \tag{2}$$

where $|n\rangle$ is an eigenstate, and $\psi(\vec{r})\equiv\langle\vec{r}|n\rangle$ is the usual Schrödinger wave function, and as such is the amplitude for finding an electron in the neighborhood of the point $\vec{r}$ when it is in state n. The total electron density is therefore given by

$$\rho(\vec{r})=2\sum_{n(occ)}|\psi^{(n)}(\vec{r})|^{2}, \tag{3}$$

where the factor 2 accounts for spin degeneracy.

In TB the single particle eigenfunctions are assumed to be expanded in a basis set that is an orthonormal set of *real* atomiclike orbitals $|i\alpha\rangle$, where i is a site index and α is an orbital index:

$$|n\rangle=\sum_{i\alpha}C_{i\alpha}^{(n)}|i\alpha\rangle. \tag{4}$$

The error in the energy due to a lack of orthogonality between orbitals is corrected in the pair potential (see below).

The Hamiltonian can be represented by the matrix $H_{i\alpha,j\beta}$ where

$$H_{i\alpha,j\beta}=\langle i\alpha|\hat{H}|j\beta\rangle=\int d\vec{r}\phi_{i\alpha}(\vec{r})\hat{H}\phi_{j\beta}(\vec{r}), \tag{5}$$

where $\hat{H}$ is the Hamiltonian operator, and $\phi_{i\alpha}(\vec{r})=\langle\vec{r}|i\alpha\rangle$. The on-site elements of the matrix are given the symbols $\varepsilon_{i\alpha}(=H_{i\alpha,i\alpha})$. The intersite elements are determined using the tables of Slater and Koster.[13] The important point is that the matrix elements are not independent of one another, but are related by symmetry. This means that the number of integrals needed to define the matrix can be greatly reduced. For two atoms with s orbitals assigned to them there is, of course, only one integral ($V_{ss\sigma}$). With two atoms (a_1 and a_2), one of which is assigned an s orbital and the other a p orbital, there are three possible integrals ($\langle a_1s|\hat{H}|a_2p_x\rangle$, $\langle a_1s|\hat{H}|a_2p_y\rangle$ and $\langle a_1s|\hat{H}|a_2p_x\rangle$). However, by symmetry, they can be reduced to one integral ($V_{sp\sigma}$) which corresponds to the spherical s orbital overlapping a p orbital end on to form a σ bond, multiplied by angular factors. If both atoms have p orbitals assigned to them then there are nine possible integrals ($\langle a_1p_x|\hat{H}|a_2p_x\rangle$, $\langle a_1p_x|\hat{H}|a_2p_y\rangle$, $\langle a_1p_x|\hat{H}|a_2p_x\rangle$, etc.). These can be reduced to two: $V_{pp\sigma}$, which corresponds to two p orbitals overlapping end-to-end to form a σ bond, and $V_{pp\pi}$, corresponding to two p orbitals lying parallel to one another to form a π bond. Again these are multiplied by angular factors.

Combining Eqs. (2), (4), and (5) we obtain the following matrix equation:

$$\sum_{j\beta}H_{i\alpha,j\beta}C_{j\beta}^{(n)}=\epsilon^{(n)}C_{i\alpha}^{(n)}, \tag{6}$$

where $C_{i\alpha}^{(n)}\equiv\langle i\alpha|n\rangle$ and hence

$$\sum_{i\alpha}C_{i\alpha}^{(n)}C_{i\alpha}^{(m)}\equiv\sum_{i\alpha}\langle n|i\alpha\rangle\langle i\alpha|m\rangle=\delta_{n,m}. \tag{7}$$

Note that because the atomic orbitals are real, the Hamiltonian will be real, and the eigenvectors $C_{i\alpha}^{(n)}$ can always be made real. This will be assumed from here on. The cohesive energy may then be written as[45]

$$\begin{aligned}U_{coh}&=U_{band}+U_{rep}-U_{atoms}\\&=2\sum_{n(occ)}\epsilon^{(n)}+\frac{1}{2}\sum_{i\neq j}\phi(r_{ij})-\sum_{i\alpha}N_{i\alpha}^{atom}\varepsilon_{i\alpha},\end{aligned} \tag{8}$$

where $\phi(r_{ij})$ is a repulsive pair potential, and $N_{i\alpha}^{atom}$ is the occupancy of an atomic state in the free atom. The pair potential accounts for the repulsion of the ionic cores at short range. It has contributions from electrostatics, and from the repulsion of overlapping orbitals due to Pauli's principle. Combining Eqs. (7) and (8) we get

$$U_{coh}=2\sum_{n(occ),i\alpha,j\beta} C^{(n)}_{i\alpha}H_{i\alpha,j\beta}C^{(n)}_{j\beta}+\frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) -\sum_{i\alpha} N^{atom}_{i\alpha}\varepsilon_{i\alpha}. \tag{9}$$

Using this equation, the band and atomic energies can be repartitioned into bond and promotion energies:

$$\begin{aligned} U_{band}-U_{atoms}&=2\sum_{n(occ),i\alpha,j\beta} C^{(n)}_{i\alpha}H_{i\alpha,j\beta}C^{(n)}_{j\beta}-\sum_{i\alpha} N^{atom}_{i\alpha}\varepsilon_{i\alpha}\\ &=2\sum_{i\alpha\neq j\beta}\sum_{n(occ)} C^{(n)}_{i\alpha}C^{(n)}_{j\beta}H_{i\alpha,j\beta}\\ &\quad+\sum_{i\alpha}\left[2\sum_{n(occ)} C^{(n)}_{i\alpha}C^{(n)}_{i\alpha}-N^{atom}_{i\alpha}\right]\varepsilon_{i\alpha}\\ &=U_{bond}+U_{prom}. \end{aligned} \tag{10}$$

The bond energy contains only off-diagonal elements of the Hamiltonian matrix, and the promotion energy contains only on-site elements.

The forces on the atoms ($\vec{F}_i$) are obtained by differentiating Eq. (9) with respect to atomic positions. Making use of the orthonormality of the eigenvectors we get

$$\begin{aligned} -\vec{F}_k&=\frac{\partial U_{coh}}{\partial \vec{r}_k}\\ &=2\sum_{n(occ),i\alpha,j\beta} C^{(n)}_{i\alpha}\frac{\partial H_{i\alpha,j\beta}}{\partial \vec{r}_k}C^{(n)}_{j\beta}+\frac{1}{2}\sum_{i\neq j}\frac{\partial \phi(r_{ij})}{\partial \vec{r}_k}. \end{aligned} \tag{11}$$

The first term is the Hellmann-Feynman force.[48,49] If we define the density matrix ($\rho_{i\alpha,j\beta}$) by

$$\rho_{i\alpha,j\beta}=\sum_{n(occ)} C^{(n)}_{j\beta}C^{(n)}_{i\alpha}, \tag{12}$$

then the cohesive energy and atomic forces can be expressed in a very compact form:

$$\begin{aligned} U_{coh}&=2\sum_{i\alpha\neq j\beta}\rho_{j\beta,i\alpha}H_{i\alpha,j\beta}+\frac{1}{2}\sum_{i\neq j}\phi(r_{ij})\\ &\quad+\sum_{i\alpha}[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}]\varepsilon_{i\alpha},\\ -\vec{F}_k&=2\sum_{i\alpha\neq j\beta}\rho_{j\beta,i\alpha}\frac{\partial H_{i\alpha,j\beta}}{\partial \vec{r}_k}+\frac{1}{2}\sum_{i\neq j}\frac{\partial \phi(r_{ij})}{\partial \vec{r}_k}\\ &\quad+\sum_{i\alpha}[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}]\frac{\partial \varepsilon_{i\alpha}}{\partial \vec{r}_k}. \end{aligned} \tag{13}$$

Note that there are two important limiting cases in which the diagonal contribution to the forces is zero. The first is when there is no self-consistency imposed, in which case the diagonal elements of the Hamiltonian are constants, and thus have zero derivative. The second is when *local charge neutrality* (LCN) is imposed, as in the tight binding bond model.[14] In this case, the condition $\Sigma_\alpha[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}]=0$ is imposed on each site by varying the on-site energies. The splittings between on-site energies on each site are kept fixed, but they are allowed to move together by an amount $\Delta\varepsilon_i$. That is, $\varepsilon_{i\alpha}=\varepsilon^{(0)}_{i\alpha}+\Delta\varepsilon_i$, where $\varepsilon^{(0)}_{i\alpha}$ is an on-site energy in some reference system. The promotion energy is then given by

$$\begin{aligned} U^{LCN}_{prom}&=\sum_{i\alpha}[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}]\varepsilon_{i\alpha}\\ &=\sum_{i\alpha}[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}](\varepsilon^{(0)}_{i\alpha}+\Delta\varepsilon_i)\\ &=\sum_{i\alpha}[2\rho_{i\alpha,i\alpha}-N^{atom}_{i\alpha}]\varepsilon^{(0)}_{i\alpha}. \end{aligned} \tag{14}$$

Note that to obtain the final expression, use has been made of the LCN condition. It is clear, then, that only the reference (and hence environment independent) on-site energies appear in the promotion energy when LCN is imposed. Their derivatives with respect to atomic coordinates are zero.

III. MOMENTS DESCRIPTION OF THE DENSITY OF STATES

For all that follows the concept of the *density of states* is fundamental. The *total* density of states $[n_{total}(E)]$ is defined by the following equation:

$$n_{total}(E)=\sum_{n}\delta(E-\epsilon^{(n)}). \tag{15}$$

The band energy [see Eq. (8)] can be rewritten in terms of the density of states in the following way:

$$U_{band}=2\int^{E_f} E\,n_{total}(E)\,dE, \tag{16}$$

where E_f is the Fermi energy, and has a value that lies between the energy of the highest occupied state and the lowest unoccupied state.

The total density of states is a *global* property of a system. We are principally interested in studying the behavior of systems by considering regions of the systems that are *localized* in space. A very useful and important quantity for characterizing the electronic properties in a local manner is the *local density of states*.[41] To derive an expression for this quantity, we need two results:

$$\begin{aligned} \langle n|\delta(E-\hat{H})|m\rangle&=\delta(E-\epsilon^{(n)})\delta_{n,m},\\ \hat{1}=\sum_{n}|n\rangle\langle n|&=\sum_{i\alpha}|i\alpha\rangle\langle i\alpha|. \end{aligned} \tag{17}$$

It is straightforward to check that $\hat{1}$ is the unit operator by showing that it satisfies $\hat{1}^2=\hat{1}$. We have defined functions of operators in the following way:

$$f(\hat{H})|n\rangle=f(\varepsilon^{(n)})|n\rangle. \tag{18}$$

This is easily justified by replacing the function with its Taylor expansion, inserting it into the left hand side of Eq. (18), and resumming to obtain the right hand side.

Inserting these results into Eq. (15), we obtain

$$\begin{aligned} n_{total}(E) &= \sum_n \langle n|\delta(E-\hat{H})|n\rangle \\ &= \sum_{n,m,i\alpha} \langle n|i\alpha\rangle\langle i\alpha|m\rangle\langle m|\delta(E-\hat{H})|n\rangle \\ &= \sum_{i\alpha} \left\{ \sum_n |\langle i\alpha|n\rangle|^2 \delta(E-\epsilon^{(n)}) \right\} \\ &= \sum_{i\alpha} n_{i\alpha}(E). \end{aligned} \tag{19}$$

Thus we see that the global density of states can be decomposed into a sum over local densities of states $[n_{i\alpha}(E)]$ projected onto the atomic orbitals, where

$$n_{i\alpha}(E) = \sum_n |\langle i\alpha|n\rangle|^2 \delta(E-\epsilon^{(n)}) = \langle i\alpha|\delta(E-\hat{H})|i\alpha\rangle, \tag{20}$$

where the second expression is obtained by using Eqs. (17) to remove the sum over n. The interpretation is straightforward. The probability of finding an electron in state $|n\rangle$ on orbital $|i\alpha\rangle$ is $|\langle i\alpha|n\rangle|^2$. Thus the local density of states projected onto an orbital is just the total density of states weighted by the probability of finding the electron on that orbital.

This decomposition into local densities of states also has the advantage that we can write the promotion and bond energies in terms of densities of states. From Eq. (4) we see that $C_{i\alpha}^{(n)} = \langle i\alpha|n\rangle$. Thus from Eq. (20) we have $n_{i\alpha}(E) = \Sigma_n |C_{i\alpha}^{(n)}|^2 \delta(E-\epsilon^{(n)})$. Substituting this equation into Eq. (10), and then using Eqs. (16) and (19) we get

$$\begin{aligned} U_{prom} &= \sum_{i\alpha} \left(2\int^{E_f} n_{i\alpha}(E)dE - N_{i\alpha}^{atom} \right) \varepsilon_{i\alpha}, \\ U_{bond} &= U_{band} - U_{atoms} - U_{prom} \\ &= 2\sum_{i\alpha} \int^{E_f} (E-\varepsilon_{i\alpha}) n_{i\alpha}(E)dE. \end{aligned} \tag{21}$$

Similarly, we can introduce the generalized density of electron states

$$n(E,\vec{r}) = \sum_n |\psi^{(n)}(\vec{r})|^2 \delta(E-\epsilon^{(n)}) \tag{22}$$

which follows from Eq. (15). The electron density and total density of states are then given by

$$\begin{aligned} \rho(\vec{r}) &= 2\int dE\, n(E,\vec{r}), \\ n_{total}(E) &= \int d\vec{r}\, n(E,\vec{r}). \end{aligned} \tag{23}$$

The generalized density of states has the physical meaning of being the energy-resolved spatial density of states and is frequently used for the analysis of electron distributions.

As already noted, the most demanding part of evaluating the cohesive energy is finding the band energy. In particular, diagonalizing the Hamiltonian matrix to find the eigenvalues and eigenvectors takes time on a computer that scales as the *cube* of the number of particles in the unit cell. We will now see how using a moments description for the density of states makes it possible to evaluate the energy in a time that scales *linearly* with the number of atoms in the unit cell.

From Eq. (16) it is clear that evaluating the band energy is straightforward once the density of states is known. The density of states is a distribution function of finite width (for finite basis set size), and thus can be characterized by the position of its center, its width, and its shape. These properties of the density of states can all be described by its *moments*. The pth moment $(\mu_{i\alpha}^{(p)})$ of the projected density of states $n_{i\alpha}(E)$ is given by

$$\mu_{i\alpha}^{(p)} = \int E^p n_{i\alpha}(E)dE. \tag{24}$$

The first moment $(\mu_{i\alpha}^{(1)})$ defines the center of gravity of the band, the second moment $(\mu_{i\alpha}^{(2)})$ its mean square width, the third moment $(\mu_{i\alpha}^{(3)})$ gives a measure of how skewed the band is, the fourth moment $(\mu_{i\alpha}^{(4)})$ determines whether the density of states is unimodal or bimodal, and so on,[42] as is illustrated in Fig. 1.

There is a useful identity[43] which follows directly from Eq. (20), which is that the pth moment of the density of states projected onto orbital $|i\alpha\rangle$ equals the pth moment of the Hamiltonian projected onto the same orbital:

$$\mu_{i\alpha}^{(p)} = \int E^p n_{i\alpha}(E)dE = \langle i\alpha|\hat{H}^p|i\alpha\rangle. \tag{25}$$

This allows us to evaluate the moments of the projected density of states from the Hamiltonian matrix. Substituting the Hamiltonian matrix for the operator in Eq. (25) we obtain

$$\mu_{i\alpha}^{(p)} = \sum_{j_1\beta_1 \cdots j_{p-1}\beta_{p-1}} H_{i\alpha,j_1\beta_1} H_{j_1\beta_1,j_2\beta_2} \cdots H_{j_{p-1}\beta_{p-1},i\alpha}. \tag{26}$$

This equation reveals a correspondence between the pth moment and a process of hopping around the lattice along closed paths of length p. Thus the first moment corresponds to a hop on a single site, the second to hops to nearest neighbors and back, and so on. Increasing the order of the moments by *two* corresponds to obtaining information about *one* extra shell of atoms since you have to hop out and back. This direct correspondence between electronic structure and the positions of atoms can give immediate insight into the nature of cohesion and structural stability, provided not too many moments are needed for an adequate description of the density of states.[15] Further, the increase in the number of shells with increasing numbers of moments means that when only a few moments are necessary to describe the density of states sufficiently accurately to give a good cohesive energy, then only a small cluster of atoms contributes to the density of states. The time to construct the local density of states for one site depends only on how many moments are needed, and not on the system size. If this time is t_M for M moments, then for a complete system with N sites, the time to construct

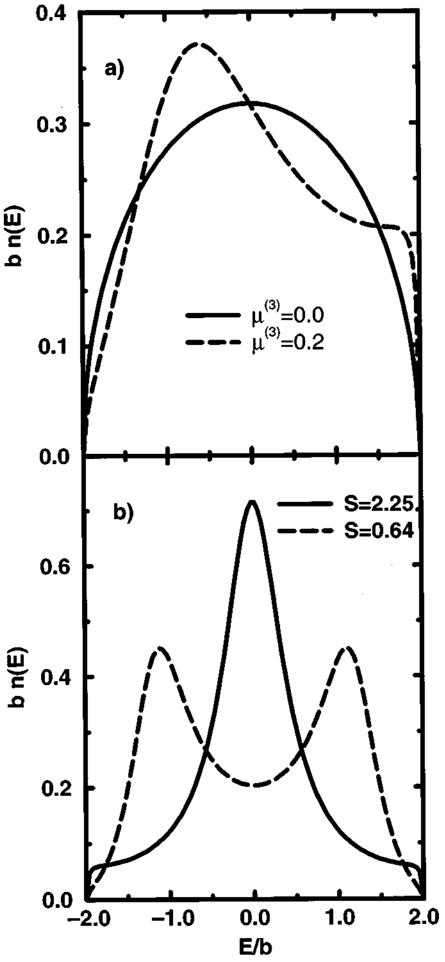

FIG. 1. The dependence of the shape of the density of states on the moments is illustrated here. The energy scale is given by the parameter b. Panel (a) shows how the third moment skews the density of states. When the shape factor $S = [\mu^{(4)}/(\mu^{(2)})^2 - 1]$ is less than 1, then a bimodal distribution results, whereas when it is greater than 1, a unimodal distribution is found, as shown in panel (b).

the total density of states is Nt_M, which is linear in the number of sites. Thus this is an O(N) method. The benefits of this are clear from Fig. 2.

IV. GREEN'S FUNCTIONS AND THE RECURSION METHOD

Although a function can in principle be reconstructed once its moments are known, care has to be taken to achieve this in a numerically stable way. The recursion method[44] is an optimal method for building densities of states from moments which makes use of Green's functions. It is straightforward to see why Green's functions are useful in this case. Consider the following expression for the δ function:

$$\delta(x) = -\frac{1}{\pi}\lim_{\eta\to 0} \mathrm{Im}\{[x + i\eta]^{-1}\}. \tag{27}$$

Combining Eqs. (20) and (27) we obtain

$$n_{i\alpha}(E) = -\frac{1}{\pi}\lim_{\eta\to 0} \mathrm{Im}\{\langle i\alpha|[E + i\eta - \hat{H}]^{-1}|i\alpha\rangle\}. \tag{28}$$

The one particle Green's function is defined by

$$\hat{G}(Z) = [Z - \hat{H}]^{-1}. \tag{29}$$

Substituting Eq. (29) into Eq. (28) we obtain

$$n_{i\alpha}(E) = -\frac{1}{\pi}\lim_{\eta\to 0} \mathrm{Im}\{G_{i\alpha,i\alpha}(E + i\eta)\}, \tag{30}$$

where we have introduced the notation $G_{i\alpha,j\beta}(Z) = \langle i\alpha|\hat{G}(Z)|j\beta\rangle$. The expression for the local density of states in terms of one of the diagonal matrix elements of the single particle Green's function is useful because it is possible to write down an explicit continued fraction expression for this element of the Green's function in terms of the elements of the tridiagonalized Hamiltonian,[44] as is explained below. First, though, we need to introduce the Lanczos algorithm.

The Lanczos algorithm[50] is an efficient scheme for tridiagonalizing a matrix. Let the diagonal elements of the tridi-

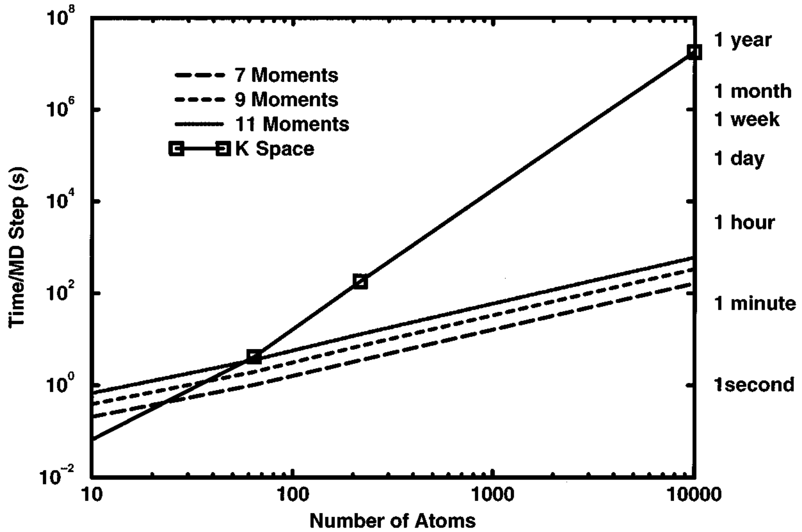

FIG. 2. The time to perform one molecular-dynamics step is shown here as a function of the number of atoms being considered. The calculations were all peformed on HP9000/735 workstations. The moments method is compared with direct diagonalization. The O(N^3) scaling of diagonalization makes this approach very inefficient for systems containing more than about 100 atoms.

agonal Hamiltonian be a_n and the off-diagonal ones be b_n. Let the states that tridiagonalize the Hamiltonian be $|U_n\rangle$. We then have

$$\langle U_m|\hat{H}|U_n\rangle=\begin{cases} a_n & \text{if } m=n, \\ b_n & \text{if } m=n-1, \\ b_{n+1} & \text{if } m=n+1, \\ 0 & \text{otherwise.} \end{cases} \quad (31)$$

The Lanczos algorithm for finding the tridiagonal matrix is based on the following recurrence relationship:

$$\hat{H}|U_n\rangle=a_n|U_n\rangle+b_n|U_{n-1}\rangle+b_{n+1}|U_{n+1}\rangle, \quad (32)$$

and the fact that the states $|U_n\rangle$ are orthonormal ($\langle U_n|U_m\rangle=\delta_{n,m}$). Starting with some arbitrary state $|U_0\rangle$, we can find a_0 from Eq. (31). From Eq. (32), we can then evaluate $b_1|U_1\rangle$ (since we know that $b_0=0$), and then from the normalization of $|U_1\rangle$ we can obtain b_1. Starting with $|U_1\rangle$ the process can be repeated to find a_1, b_2, and $|U_2\rangle$, and so on. Let us introduce the notation $G_{nm}(Z)=\langle U_n|\hat{G}(Z)|U_m\rangle$. The element of the Green's function $G_{00}(Z)$ can now be obtained from[44]

$$G_{00}(Z)=\cfrac{1}{Z-a_0-\cfrac{b_1^2}{Z-a_1-\cfrac{b_2^2}{Z-a_2-\cfrac{b_3^2}{\ddots}}}}. \quad (33)$$

In general, if element $G_{\psi,\psi}(Z)=\langle\psi|\hat{G}(Z)|\psi\rangle$ is to be calculated, then $|U_0\rangle$ is first set equal to $|\psi\rangle$, and then the above prescription is applied. Thus any diagonal element of the Green's function can be found in this way. In this work, $|\psi\rangle$ will always be either an atomic orbital ($|i\alpha\rangle$) or a linear combination of atomic orbitals.

Above it was stated that the recursion method is an optimal way of constructing a density of states from its moments. The connection between moments and recursion can be made explicit by writing the moments in terms of the elements of the tridiagonal Hamiltonian (which shall be called *recursion coefficients* from now on). This is easily accomplished by noting the following:

$$\begin{aligned}\mu_{i\alpha}^{(n)}&=\langle i\alpha|\hat{H}^n|i\alpha\rangle\\&=\langle U_0|\hat{H}^n|U_0\rangle\\&=\sum_{m_1\cdots m_{n-1}}\langle U_0|\hat{H}|U_{m_1}\rangle\\&\quad\times\langle U_{m_1}|\hat{H}|U_{m_2}\rangle\cdots\langle U_{m_{n-1}}|\hat{H}|U_0\rangle.\end{aligned} \quad (34)$$

The first few moments are

$$\begin{aligned}\mu_{i\alpha}^{(0)}&=1,\\ \mu_{i\alpha}^{(1)}&=a_0,\\ \mu_{i\alpha}^{(2)}&=a_0^2+b_1^2,\\ \mu_{i\alpha}^{(3)}&=a_0^3+2a_0b_1^2+a_1b_1^2,\\ \mu_{i\alpha}^{(4)}&=a_0^4+3a_0^2b_1^2+2a_0a_1b_1^2+a_1^2b_1^2+b_1^2b_2^2+b_1^4.\end{aligned} \quad (35)$$

These equations can be inverted to give the recursion coefficients in terms of the moments. Every extra moment allows one extra recursion coefficient to be evaluated. Inverting these equations numerically can be unstable. However, Eq. (32) always gives stable results.

For an infinite system, there could be an infinite number of levels in the continued fraction. It is often the case, however, that the exact values can be replaced by estimated values after a certain number of levels, without reducing the accuracy significantly. The simplest approximation is to take $a_n=a_\infty, b_n=b_\infty$ for $n>N$, where N is the number of exact levels, and a_∞ and b_∞ are constants defining the band center and bandwidth.[51] The constant terms can be summed exactly to form the square root terminator:

$$\begin{aligned}t(Z)&=\cfrac{1}{Z-a_\infty-\cfrac{b_\infty^2}{Z-a_\infty-\cfrac{b_\infty^2}{Z-a_\infty-\cfrac{b_\infty^2}{\ddots}}}}\\&=\frac{1}{b_\infty}\left[\left(\frac{Z-a_\infty}{2b_\infty}\right)-i\sqrt{1-\left(\frac{Z-a_\infty}{2b_\infty}\right)^2}\right].\end{aligned} \quad (36)$$

For the BOP derivation, we need to differentiate the Green's function $G_{00}(Z)$ with respect to the recursion coefficients. To do that we need to know the first-order change in the Green's function due to the small change in the Hamiltonian.[52] Let us make a simple derivation with the use of Eq. (29), which we write formally in the following form:

$$\hat{G}^{-1}(Z)=Z-\hat{H}=Z-\hat{H}_0-\delta\hat{H}. \quad (37)$$

Multiplying Eq. (37) by $\hat{G}_0(Z)=(Z-\hat{H}_0)^{-1}$ from the left and by $\hat{G}(Z)$ from the right, bearing in mind that $\hat{H}_0$ and δH may be noncommuting operators, we obtain, using $\hat{G}_0(Z)(Z-\hat{H}_0)=\hat{1}$, the well known Dyson equation

$$\begin{aligned}\hat{G}(Z)&=\hat{G}_0(Z)+\hat{G}_0(Z)\delta\hat{H}\hat{G}(Z)\\&=\hat{G}_0(Z)+\hat{G}_0(Z)\delta\hat{H}\hat{G}_0(Z)+\cdots.\end{aligned} \quad (38)$$

Therefore the variation in the Green's function to first order in $\delta\hat{H}$ is $\delta\hat{G}(Z)=\hat{G}(Z)\delta\hat{H}\hat{G}(Z)$. The corresponding matrix equation is $\delta G_{nm}(Z)=\Sigma_{kl}G_{nk}(Z)\delta H_{kl}G_{lm}(Z)$. Taking for the basis states the Lanczos vector space which is complete and tridiagonalizes the Hamiltonian [see Eq. (31)], we obtain the following derivatives:

$$\begin{aligned}\frac{\partial G_{00}(Z)}{\partial a_n}&=G_{0n}(Z)G_{n0}(Z),\\ \frac{\partial G_{00}(Z)}{\partial b_n}&=G_{0n}(Z)G_{(n-1)0}(Z)+G_{0(n-1)}(Z)G_{n0}(Z).\end{aligned} \quad (39)$$

The off-diagonal elements of the Green's function (with respect to the tridiagonalizing states) that appear in the derivative are evaluated by means of another recurrence relation. From Eq. (29) we have $(Z-\hat{H})\hat{G}(Z)=\hat{1}$. Inserting the tridiagonalizing states we obtain the following:

$$(Z-a_n)G_{nm}(Z)-b_nG_{n-1,m}(Z)-b_{n+1}G_{n+1,m}(Z)=\delta_{n,m}. \tag{40}$$

All elements $G_{0n}(Z)$ can be obtained from this equation, once $G_{00}(Z)$ has been evaluated, since $G_{0n}(Z)=G_{n0}(Z)$.

V. GREEN'S FUNCTIONS AND THE DENSITY MATRIX

In Eq. (13) we see that both the energy and forces can be evaluated very simply once the density matrix is known. In the preceding two sections we have seen how using moments, and especially the recursion method, allows us to perform an efficient evaluation of band energy which scales linearly with system size. We would like now to combine these two observations and find a moments based method for evaluating the density matrix.

Starting with Eq. (12) we can derive the following useful expression for the density matrix:

$$\begin{aligned}\rho_{i\alpha,j\beta}&=\sum_{n(occ)}C_{i\alpha}^{(n)}C_{j\beta}^{(n)}=\sum_{n}C_{i\alpha}^{(n)}\Theta(E_f-\epsilon^{(n)})C_{j\beta}^{(n)}\\&=\int^{E_f}dE\sum_{n}C_{i\alpha}^{(n)}\delta(E-\epsilon^{(n)})C_{j\beta}^{(n)}\\&=\int^{E_f}dE\sum_{n}\langle i\alpha|n\rangle\langle n|\delta(E-\hat{H})|n\rangle\langle n|j\beta\rangle\\&=\int^{E_f}dE\langle i\alpha|\delta(E-\hat{H})|j\beta\rangle\\&=-\frac{1}{\pi}\lim_{\eta\to 0}\mathrm{Im}\int^{E_f}dE\,G_{i\alpha,j\beta}(E+i\eta),\end{aligned} \tag{41}$$

where $\Theta(x)$ is the step function. Thus we see that to obtain the density matrix, we need the off-diagonal matrix elements of the Green's function. BOP is a method for evaluating these within a moments framework.

Since we know how to evaluate the diagonal matrix elements of the Green's function, we could evaluate the off-diagonal ones also if we could transform the off-diagonal problem into a diagonal one. There is a simple way to do this. Consider the states $|+\rangle=(1/\sqrt{2})(|i\alpha\rangle+|j\beta\rangle)$ (a bonding state) and $|-\rangle=(1/\sqrt{2})(|i\alpha\rangle-|j\beta\rangle)$ (an antibonding state). We can easily calculate $G_{++}(Z)=\langle+|\hat{G}(Z)|+\rangle$ and $G_{--}(Z)=\langle-|\hat{G}(Z)|-\rangle$ using recursion. If we expand out the bonding and antibonding states in terms of the atomic states, and then take the difference between $G_{++}(Z)$ and $G_{--}(Z)$, we obtain the following expression for the off-diagonal Green's function:

$$G_{i\alpha,j\beta}(Z)=\frac{1}{2}[G_{++}(Z)-G_{--}(Z)]. \tag{42}$$

This expression can be considered the central one for BOP. The developments that follow can be considered variations on this theme.

The bond order ($\Theta_{i\alpha,j\beta}$) is defined by

$$\Theta_{i\alpha,j\beta}=2\rho_{i\alpha,j\beta}\quad(i\neq j). \tag{43}$$

The factor of 2 is a result of spin degeneracy. Combining Eqs. (41), (42), and (43) we get

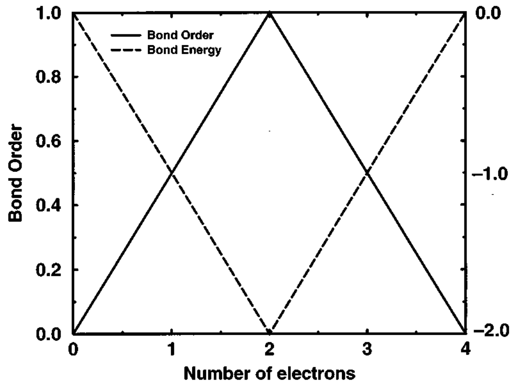

FIG. 3. The variation of the bond order (solid line) and the bond energy (dashed line) as a function of band filling for the *s*-valent dimer.

$$\begin{aligned}\Theta_{i\alpha,j\beta}&=-\frac{1}{\pi}\lim_{\eta\to 0}\mathrm{Im}\int^{E_f}dE[G_{++}(E+i\eta)-G_{--}(E+i\eta)]\\&=\frac{1}{2}[N_+-N_-],\end{aligned} \tag{44}$$

where N_+ and N_- are the number of electrons in the bonding and antibonding states. This provides us with a simple picture to illuminate what is meant by a bond order (and hence density matrix). This can be illustrated by the s-valent dimer. Each s-valent atom is assumed to have one s orbital, which we shall label $|1\rangle$ and $|2\rangle$. The TB Hamiltonian matrix for the dimer can then be written as

$$H=\begin{pmatrix}\varepsilon & v\\ v & \varepsilon\end{pmatrix}, \tag{45}$$

where ε is the on-site energy, and v is the hopping integral between the two orbitals and is negative. On diagonalizing this matrix we obtain two eigenstates, one of which is the bonding state, and the other of which is the antibonding state. The eigenstates are $|+\rangle=(|1\rangle+|2\rangle)/\sqrt{2}$ and $|-\rangle=(|1\rangle-|2\rangle)/\sqrt{2}$. The eigenvalues are $\epsilon_+=\varepsilon-|v|$ and $\epsilon_-=\varepsilon+|v|$. Using Eqs. (41) and (43) we easily find the bond order for the dimer as a function of a number of electrons N_{dimer}:

$$\Theta_{12}=\begin{cases}\dfrac{N_{dimer}}{2} & \text{if } N_{dimer}<2,\\[2ex] 2-\dfrac{N_{dimer}}{2} & \text{if } 2<N_{dimer}<4.\end{cases} \tag{46}$$

In Fig. 3 we present the variation of the bond order and the bond energy with the number of electrons as given by Eqs. (44) and (10). The bond order has a maximum value of 1 when there are two electrons present, both in the bonding state. This is also the point at which the bond is strongest. The bond order is then seen to be a measure of the bond charge density.

VI. THE TWO-SITE BOND-ORDER POTENTIAL EXPANSION

Although Eq. (42) is formally exact, it is very slowly convergent. That is, many levels are required in order to obtain an accurate bond order. We now show how we may obtain a more rapidly convergent expansion.[3]

Consider the following linear combination of atomic orbitals:

$$|U_0^\lambda\rangle = \frac{1}{\sqrt{2}}[|i\alpha\rangle + e^{i\theta}|j\beta\rangle], \tag{47}$$

where $\theta = \cos^{-1}(\lambda)$ and $-1 \leqslant \lambda \leqslant 1$. This choice is a simple generalization of the bonding and antibonding orbitals used in the preceding section. They are given by $|+\rangle = |U_0^1\rangle$ and $|-\rangle = |U_0^{-1}\rangle$. The matrix element of the Green's function with respect to this state expands out to give

$$G_{00}^\lambda(Z) = \langle U_0^\lambda|\hat{G}(Z)|U_0^\lambda\rangle = \frac{1}{2}[\langle i\alpha|\hat{G}(Z)|i\alpha\rangle + \langle j\beta|\hat{G}(Z)|j\beta\rangle] + \lambda\langle i\alpha|\hat{G}(Z)|j\beta\rangle, \tag{48}$$

where to obtain the second term we have used the fact that the tight-binding Hamiltonian $H_{i\alpha,j\beta}$ is real and symmetric, which follows from the choice of real atomic orbitals. The off-diagonal elements of the Green's function can now be obtained by considering two values of λ:

$$G_{i\alpha,j\beta}(Z) = \frac{G_{00}^{\lambda_1}(Z) - G_{00}^{\lambda_2}}{\lambda_1 - \lambda_2}. \tag{49}$$

This is a straight generalization of Eq. (42). In general, this requires the use of two Green's functions, and it is this that leads to the poor convergence. However, by taking the limit $\lambda_1 \rightarrow \lambda_2$, we obtain the off-diagonal Green's function as the derivative of a *single* Green's function:

$$G_{i\alpha,j\beta}(Z) = \frac{\partial G_{00}^\lambda(Z)}{\partial \lambda}. \tag{50}$$

Combining Eqs. (41), (43), and (50) we get

$$\Theta_{i\alpha,j\beta} = \frac{\partial N^\lambda}{\partial \lambda}, \tag{51}$$

where

$$N^\lambda = -\frac{2}{\pi}\lim_{\eta\rightarrow 0}\mathrm{Im}\int^{E_f} dE\, G_{00}^\lambda(E+i\eta). \tag{52}$$

N^λ is the number of electrons in the state $|U_0^\lambda\rangle$. Equation (51) is similar to Eq. (44), but gives better convergence.[4]

As was explained above, the diagonal Green's function may be written as a continued fraction [Eq. (33)] and hence the dependence of $G_{00}^\lambda(Z)$ on λ is through the recursion coefficients $a_0^\lambda, b_1^\lambda, \ldots$. Applying the chain rule for partial differentiation to Eq. (50), we obtain the following expression:

$$G_{i\alpha,j\beta}(Z) = \sum_{n=0}^{\infty}\frac{\partial G_{00}^\lambda}{\partial a_n^\lambda}\delta a_n^\lambda + \sum_{n=1}^{\infty}\frac{\partial G_{00}^\lambda}{\partial b_n^\lambda}\delta b_n^\lambda, \tag{53}$$

where

$$\delta a_n^\lambda = \frac{\partial a_n^\lambda}{\partial \lambda} \quad \text{and} \quad \delta b_n^\lambda = \frac{\partial b_n^\lambda}{\partial \lambda}. \tag{54}$$

Substituting Eqs. (53), (52), (39), and (41) into Eq. (43), we obtain the following exact series expansion for the bond order:

$$\begin{aligned}\Theta_{i\alpha,j\beta} &= \sum_{n=0}^{\infty}\frac{\partial N^\lambda}{\partial a_n^\lambda}\delta a_n^\lambda + \sum_{n=1}^{\infty}\frac{\partial N^\lambda}{\partial b_n^\lambda}\delta b_n^\lambda \\ &= -2\left[\sum_{n=0}^{\infty}\chi_{0n,n0}(E_f)\delta a_n^\lambda + \sum_{n=1}^{\infty}\chi_{0(n-1),n0}(E_f)2\delta b_n^\lambda\right],\end{aligned} \tag{55}$$

where the response functions $\chi_{0m,n0}(E_f)$ are defined by

$$\chi_{0m,n0}(E_f) = \frac{1}{\pi}\lim_{\eta\rightarrow 0}\mathrm{Im}\int^{E_f} G_{0m}^\lambda(E+\mathrm{i}\eta)G_{n0}^\lambda(E+i\eta)dE \tag{56}$$

and $G_{0m}^\lambda(Z)$ is calculated from Eq. (40).

Let us take a look at the expansion for the bond order, to understand what the terms mean. The expansion consists of the sum of the product of two types of term: the response functions $\chi_{0m,n0}(E_f)$ and the derivatives of the recursion coefficients δa_n^λ and δb_n^λ. All the dependence of the bond order on the number of electrons appears in the response functions. However, they have a fairly weak dependence on atomic coordination, whereas the derivatives of the recursion coefficients are very sensitive to the local atomic arrangement. This last point becomes apparent when the derivatives of the recursion coefficients are expanded in terms of derivatives with respect to moments:

$$\delta a_n^\lambda = \frac{\partial a_n^\lambda}{\partial \lambda} = \sum_{r=1}^{2n+1}\frac{\partial a_n^\lambda}{\partial \mu_\lambda^{(r)}}\frac{\partial \mu_\lambda^{(r)}}{\partial \lambda} = \sum_{r=1}^{2n+1}\frac{\partial a_n^\lambda}{\partial \mu_\lambda^{(r)}}\zeta_{i\alpha,j\beta}^{(r+1)},$$

$$\delta b_n^\lambda = \frac{\partial b_n^\lambda}{\partial \lambda} = \sum_{r=1}^{2n}\frac{\partial b_n^\lambda}{\partial \mu_\lambda^{(r)}}\frac{\partial \mu_\lambda^{(r)}}{\partial \lambda} = \sum_{r=1}^{2n}\frac{\partial b_n^\lambda}{\partial \mu_\lambda^{(r)}}\zeta_{i\alpha,j\beta}^{(r+1)}, \tag{57}$$

where $\mu_\lambda^{(r)} = \langle U_0^\lambda|\hat{H}^r|U_0^\lambda\rangle$ and $\zeta_{i\alpha,j\beta}^{(r+1)} = \langle i\alpha|\hat{H}^r|j\beta\rangle$. The quantities $\zeta_{i\alpha,j\beta}^{(r+1)}$ are called interference terms (see Fig. 2 of Ref. 3), and are similar to moments, except that they link two sites, rather than one. The derivatives of the first two recursion coefficients are thus given by

$$\delta a_0^\lambda = H_{i\alpha,j\beta},$$

$$\delta b_1^\lambda = \frac{1}{2b_1^\lambda}[\zeta_{i\alpha,j\beta}^{(3)} + a_0^\lambda H_{i\alpha,j\beta}], \tag{58}$$

where Eq. (35) has been inverted to find derivatives of the recursion coefficients with respect to the moments. Thus, the response functions determine to what extent each derivative of the recursion coefficients does or does not contribute to the bond order, based on band filling, and the derivatives of the recursion coefficients determine the dependence of the bond order on atomic arrangement.

To illustrate the dependence of the response functions on band filling, we now consider the case in which the recursion coefficients have constant values:[1] $a_n=0, b_n=b$. From Eq. (40) we can easily find the off-diagonal Green's function for the constant linear chain:

$$G_{0n}(Z)=\frac{1}{b}e^{i(n+1)\theta}, \tag{59}$$

where θ is defined by $\cos(\theta)=(Z-a)/(2b)$. We can then write analytic expressions for both the number of electrons and the response functions as a function of the Fermi energy with the use of Eq. (56):

$$N=\frac{2\phi_f}{\pi}\left[1-\frac{\sin(2\phi_f)}{2\phi_f}\right]$$

$$b\chi_{0m,n0}(E_f)=\frac{1}{\pi}\left[\frac{\sin((m+n+1)\phi_f)}{m+n+1}-\frac{\sin((m+n+3)\phi_f)}{m+n+3}\right], \tag{60}$$

where $\cos(\phi_f)=E_f/(2b)$. There are two important features of the response functions that can be seen from Fig. 4. The first is that a new node appears for each new response function, and the second is that the amplitudes decay with increasing order. It can be seen from Eq. (60) that the amplitude decays as

$$\chi_{0m,n0}(E_f)\approx\frac{2}{(m+n+2)^2}[\sin((m+n+2)\phi_f)-(m+n+2)\phi_f]\propto\frac{2\phi_f}{m+n+2}$$

with increasing $m+n$.

VII. CONNECTION WITH EMPIRICAL POTENTIALS

We will now show how the lowest-order term in the BOP expansion for systems containing s and p orbitals allows us to derive in a systematic manner[2] a potential with properties very similar to those of the empirical potential of Tersoff.[47]

The individual contribution of the bond joining sites i and j to the bond energy U_{bond} is

$$U_{i,j}=2\sum_{\alpha,\beta}\Theta_{i\alpha,j\beta}H_{j\beta,i\alpha}. \tag{61}$$

By rotating the axes such that the quantization axis lies along the bond, and by making the assumption that $V_{sp\sigma}(r_{ij})=\sqrt{|V_{ss\sigma}(r_{ij})|V_{pp\sigma}(r_{ij})}$, the 2×2 σ block of the Hamiltonian matrix linking the two sites may be diagonalized with diagonal elements of $V_{ss\sigma}(r_{i,j})-V_{pp\sigma}(r_{ij})$ and 0, respectively.[2] The energy of the bond thus reduces to the form

$$U_{i,j}=[V_{ss\sigma}(r_{ij})-V_{pp\sigma}(r_{ij})]\Theta_{i\sigma,j\sigma}+2V_{pp\pi}(r_{ij})\Theta_{i\pi,j\pi}, \tag{62}$$

where the normalized orbitals $|i\sigma\rangle$ and $|j\sigma\rangle$ are defined by

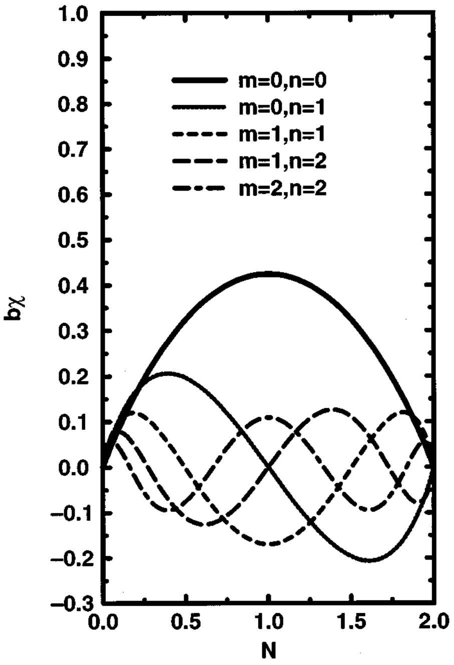

FIG. 4. The variation of the first few response functions for the simple constant linear chain model as a function of band filling. The number of nodes increases and the amplitude decreases as the order of the response function increases.

$$\begin{aligned}|i\sigma\rangle&=[\sqrt{|V_{ss\sigma}(r_{ij})|}|is\rangle\\&\quad+\sqrt{V_{pp\sigma}(r_{ij})}|iz\rangle]/\sqrt{|V_{ss\sigma}(r_{ij})|+V_{pp\sigma}(r_{ij})},\\|j\sigma\rangle&=[\sqrt{|V_{ss\sigma}(r_{ij})|}|js\rangle\\&\quad-\sqrt{V_{pp\sigma}(r_{ij})}|jz\rangle]/\sqrt{|V_{ss\sigma}(r_{ij})|+V_{pp\sigma}(r_{ij})},\end{aligned} \tag{63}$$

and $\Theta_{i\pi,j\pi}=\frac{1}{2}[\Theta_{ip_x,jp_x}+\Theta_{ip_y,jp_y}]$. From Eq. (55) the bond order may be written to lowest order as

$$\Theta_{i\alpha,j\beta}=-2\hat{\chi}_{00,00}(E_f)\frac{H_{i\alpha,j\beta}}{b_1}, \tag{64}$$

where $\hat{\chi}_{00,00}$ is the normalized response function, $b_1\hat{\chi}_{00,00}$ [see Eq. (60)]. Since $b=b_1$ is given by the second moment [see Eq. (35)] we can write the σ and π bond orders explicitly as

$$\Theta_{i\sigma,j\sigma}=\frac{-2\hat{\chi}_{00,00}(E_f)H_{i\sigma,j\sigma}}{\sqrt{\frac{1}{2}(\mu^{(2)}_{i\sigma}+\mu^{(2)}_{j\sigma})}},$$

$$\Theta_{i\pi,j\pi}=\frac{-2\hat{\chi}_{00,00}(E_f)H_{i\pi,j\pi}}{\sqrt{\frac{1}{2}(\mu^{(2)}_{i\pi}+\mu^{(2)}_{j\pi})}}, \tag{65}$$

where $\mu^{(2)}_{i\pi}=\frac{1}{2}(\mu^{(2)}_{ip_x}+\mu^{(2)}_{ip_y})$, $\mu^{(2)}_{j\pi}=\frac{1}{2}(\mu^{(2)}_{jp_x}+\mu^{(2)}_{jp_y})$, $\mu^{(2)}_{i\sigma}=\langle i\sigma|\hat{H}^2|i\sigma\rangle$, and $\mu^{(2)}_{j\sigma}=\langle j\sigma|\hat{H}^2|j\sigma\rangle$. The moments can be evaluated explicitly in terms of hopping integrals and bond angles, giving

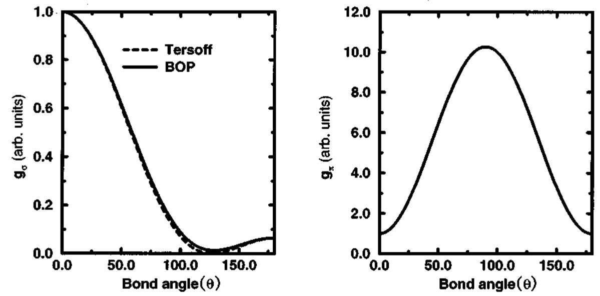

FIG. 5. The angular character of the σ and π bonds for an sp-bonded system within the second moment approximation. The predicted σ bond behavior from BOP (full curve) is compared to that from the empirical Tersoff potential (dashed curve).

$$\mu^{(2)}_{j\sigma}=\sum_{k\neq i,j}[V_{ss\sigma}(r_{jk})-V_{pp\sigma}(r_{jk})]^2 g_{\sigma}(\theta)+[V_{ss\sigma}(r_{ij})-V_{pp\sigma}(r_{ij})]^2,$$

$$\mu^{(2)}_{j\pi}=\sum_{k\neq i,j}V^2_{pp\pi}(r_{jk})g_{\pi}(\theta)+V^2_{pp\pi}(r_{ij}), \tag{66}$$

where the angular functions have the form $g_{\sigma}(\theta)=\tilde{a}+\tilde{b}\cos\theta+\tilde{c}\cos2\theta$ and $g_{\pi}(\theta)=\tilde{d}+\tilde{e}\cos2\theta$, and $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, $\tilde{d}$, and $\tilde{e}$ are constants given by ratios of the hopping integrals.[2]

The angular functions $g_{\sigma}(\theta)$ and $g_{\pi}(\theta)$ are shown in Fig. 5 using the Goodwin *et al.* parameter set for silicon.[20] The angular dependence of the empirical potential of Tersoff[47] is also plotted alongside $g_{\sigma}(\theta)$ in Fig. 5 for comparison. For the σ term there is remarkable agreement, which explains why the potential of Tersoff is successful. However, we also note that the potential of Tersoff does not include the π bonding contribution.

From Fig. 5 we see that the σ bond angular function is small (less than 0.1) for all bond angles $\theta>100°$ and has a minimum around 130°. Thus, atoms may be added which create bond angles in the range 100°–180° without greatly affecting the strength of the original σ bond (it can remain saturated). The π bond, on the other hand, shows completely different behavior. Its angular function is an order of magnitude larger than g_{σ} at its maximum which occurs at 90°. Thus, any neighbor will drastically reduce the strength of the original π bond by making it unsaturated. This is consistent with the fact that the π bond has lobes extending perpendicular to the bond axis.

VIII. PROBLEMS WITH THE TWO-SITE FORMALISM

It should be noted that the second-moment approximation used to derive this potential has limitations. For instance, it is unable to produce the buckling of dimers on the (100) surface of silicon[22] stabilized by a Jahn-Teller distortion. Further, it does not reproduce the correct structural energy difference between diamond, simple cubic, and face centered cubic structures.[9] Thus we need to add more moments. Unfortunately, adding more moments introduces its own problems. For simulations involving forces we need the derivatives of the energy. In the second-moment approximation we can do this explicitly. As more moments are added, this rapidly ceases to be an option, and so we must exploit the Hellmann-Feynman theorem [see Eq. (11)]. For the Hellmann-Feynman forces to be equal to the numerical derivatives of the energy, a very high level of convergence for the bond orders is needed. Thus, the question of improving the energy convergence cannot be addressed without also considering force convergence, and thus they will both be considered from here on. (In Appendix B an alternative approach[59] is described in which the energy can always be exactly differentiated. However, the price that has to be paid is that the energy convergence is slower.)

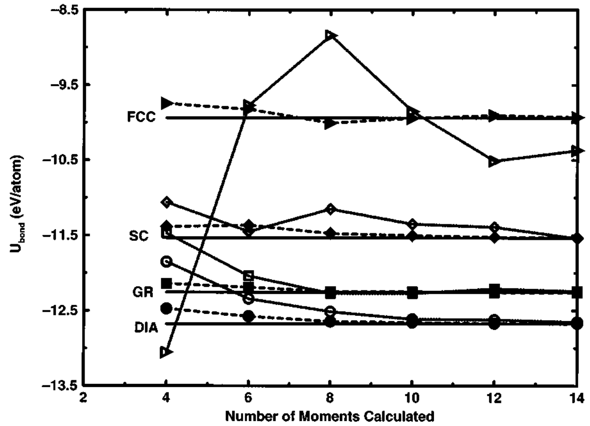

FIG. 6. The bond energy for silicon as a function of the number of recursion levels found using two-site BOP (open symbols), and single-site recursion (filled symbols). The exact results are represented by the horizontal lines without symbols.

Although the two-site BOP expansion that has just been derived gives rather better convergence than Eq. (42), it has two definite shortcomings: the promotion energy (a single-site quantity) is not easily defined in a consistent manner with the bond energy, and the convergence of the bond energy as compared with single-site recursion is worse than for single site recursion (see Fig. 6), most especially for close packed metals. As was discussed above, when more moments need to be added to improve energy convergence, moving to complete convergence becomes essential for the forces. Thus there is a strong motivation to improve the convergence still more. Both of these considerations point to the need to reformulate BOP in such a way that it operates one site at a time. This we now do. The price we have to pay, though, is an increase in complexity of the algebra, which requires the introduction of an *auxiliary space.*

IX. AUXILIARY SPACE

To formulate BOP one site at a time we need a simple generalization of the procedure used in Sec. VI: that is, we get $G_{i\alpha,j\beta}(Z)$ by differentiating $G_{00}(Z)$ with respect to an infinitesimal parameter $\Lambda_{i\alpha,j\beta}$ analogous to the parameter λ used in the two-site formalism.[8] To do this for all bonds in a system we have to assign a factor to every orbital on each site, analogous to the $\exp(i\theta)$ used in the two-site formalism. The list of these factors can be viewed as a vector. The set of these lists we call the *auxiliary* vector space. This auxiliary space has nothing to do with the physical wave functions constructed from the on-site atomic orbitals and, hence, the Hamiltonian does not operate on it. The formalism also allows us to find out the important *sum rules* for the Green's functions and formulate a numerically stable computational scheme.

We set the following rules for the auxiliary space. It is a vector space, spanned by the orthonormal unit vectors $|e^0_\nu)$. Thus

$$(e^0_\nu|e^0_{\nu'})=\delta_{\nu,\nu'}. \tag{67}$$

All other vectors in this space can be represented as a linear combination of these vectors. In particular, in order to formulate a single-site version of BOP we will need to consider the following vectors:

$$|e^\Lambda_{i\alpha})=\sum_\nu E^\Lambda_{i\alpha,\nu}|e^0_\nu). \tag{68}$$

The inner product between two of these vectors is given by

$$(e^\Lambda_{j\beta}|e^\Lambda_{i\alpha})=\sum_{\nu,\nu'}(e^0_\nu|[E^\Lambda_{j\beta,\nu}]^*E^\Lambda_{i\alpha,\nu'}|e^0_{\nu'})=\sum_\nu [E^\Lambda_{j\beta,\nu}]^*E^\Lambda_{i\alpha,\nu}$$
$$=\Lambda_{j\beta,i\alpha}. \tag{69}$$

Note that $\Lambda_{j\beta,i\alpha}$ has no physical meaning. It just allows us to label bonds between atomic orbitals.

As the single particle Hamiltonian $\hat{H}$ does not operate in this space, $\hat{H}|e^\Lambda_{i\alpha})=|e^\Lambda_{i\alpha})\hat{H}$. Consider the following expression: $(e^\Lambda_{i\alpha}|\hat{H}|e^\Lambda_{j\beta})$. Using Eq. (69), this simplifies to $\Lambda_{i\alpha,j\beta}\hat{H}$. Similarly, if we consider some function of the Hamiltonian $f(\hat{H})$, then we will have the corresponding result $(e^\Lambda_{i\alpha}|f(\hat{H})|e^\Lambda_{j\beta})=\Lambda_{i\alpha,j\beta}f(\hat{H})$.

The auxiliary space will always appear in conjunction with the atomic orbitals $|i\alpha\rangle$ used to expand the eigenstates of the Hamiltonian. Let matrix elements of the function f of the Hamiltonian be given by $f_{i\alpha,j\beta}=\langle i\alpha|f(\hat{H})|j\beta\rangle$. We can now evaluate the following useful matrix element:

$$(e^\Lambda_{i\alpha}|\langle i\alpha|f(\hat{H})|j\beta\rangle|e^\Lambda_{j\beta})=\Lambda_{i\alpha,j\beta}f_{i\alpha,j\beta}. \tag{70}$$

For the derivation of the one-site BOP expansion, we will use composite vectors of the form

$$|W^\Lambda_0\}=\sum_{i\alpha}|e^\Lambda_{i\alpha})|i\alpha\rangle. \tag{71}$$

This is a logical extension of the vector $|U^\lambda_0\rangle=[|i\alpha\rangle+\exp(i\theta)|j\beta\rangle]/\sqrt{2}$ used to derive the two center BOP expansion. Expectation values of functions of the Hamiltonian with respect to this composite vector are given by

$$\frac{\{W^\Lambda_0|f(\hat{H})|W^\Lambda_0\}}{\{W^\Lambda_0|W^\Lambda_0\}}=\frac{\sum_{i\alpha,j\beta}(e^\Lambda_{i\alpha}|\langle i\alpha|f(\hat{H})|j\beta\rangle|e^\Lambda_{j\beta})}{\sum_{i\alpha,j\beta}(e^\Lambda_{i\alpha}|\langle i\alpha|j\beta\rangle|e^\Lambda_{j\beta})}$$
$$=\frac{\sum_{i\alpha,j\beta}\Lambda_{i\alpha,j\beta}f_{i\alpha,j\beta}}{\sum_{i\alpha}\Lambda_{i\alpha,i\alpha}}, \tag{72}$$

where use has been made of Eq. (70).

X. THE SINGLE-SITE BOND-ORDER POTENTIAL EXPANSION

Following Eq. (72), we can define the following Green's function:

$$G^\Lambda_{00}(Z)=\frac{\{W^\Lambda_0|\hat{G}(Z)|W^\Lambda_0\}}{\{W^\Lambda_0|W^\Lambda_0\}}=\frac{\sum_{i\alpha,j\beta}G_{i\alpha,j\beta}(Z)\Lambda_{i\alpha,j\beta}}{\sum_{i\alpha}\Lambda_{i\alpha,i\alpha}}. \tag{73}$$

By direct analogy with Eq. (50), we differentiate this Green's function with respect to the parameters $\Lambda_{i\alpha,j\beta}$ to obtain

$$G_{i\alpha,j\beta}(Z)=\frac{\partial G^\Lambda_{00}(Z)}{\partial\Lambda_{i\alpha,j\beta}}+G^\Lambda_{00}(Z)\,\delta_{i,j}\,\delta_{\alpha,\beta}, \tag{74}$$

where we have now taken $\Sigma_{i\alpha}\Lambda_{i\alpha,i\alpha}=1$ (that is, the composite vector is normalized to 1). This expression is a much more general one than the two-site one, though the two-site one can be derived from it as a special case.

The sole reason for introducing the extra complications of this more general formalism is so that we can work one site at a time. If $\Lambda_{j\beta,k\gamma}=\delta_{i,j}\delta_{i,k}\delta_{\alpha,\beta}\delta_{\alpha,\gamma}$, then from Eq. (73) we have $G^\Lambda_{00}(Z)=G_{i\alpha,i\alpha}(Z)$. Thus we obtain a single-site quantity, which we know gives rapid energy convergence even for close packed metals, and which allows the promotion energy to be defined in a way that is completely consistent with the bond energy [see Eq. (21)]. Note that we need a separate Λ for every orbital in the system in order to calculate the energies in a strictly single-site manner. This can be reduced by using averaged moments as described at the end of this section. The problem now is how to obtain the bond orders. The solution is to use

$$\Lambda_{j\beta,k\gamma}=\delta_{i,j}\delta_{i,k}\delta_{\alpha,\beta}\delta_{\alpha,\gamma}+\eta_{j\beta,k\gamma}, \tag{75}$$

where i is the site whose energy is to be evaluated, α is the index for the orbitals on that site, and $\eta_{j\beta,k\gamma}$ is an infinitesimal quantity. This allows us to keep $G^\Lambda_{00}(Z)$ as a single-site quantity, while still enabling us to differentiate it to obtain the off-diagonal matrix elements of the Green's function. This is a purely formal result. We never need know the values of $\eta_{j\beta,k\gamma}$.

Clearly $G^\Lambda_{00}(Z)$ can be expressed in terms of the continued fraction given in Eq. (33), thus Eq. (74) can be cast in the form of Eq. (53):

$$G_{i\alpha,j\beta}(Z)=\sum_{n=0}^{\infty}G^\Lambda_{0n}(Z)G^\Lambda_{n0}(Z)\frac{\partial a^\Lambda_n}{\partial\Lambda_{i\alpha,j\beta}}$$
$$+2\sum_{n=1}^{\infty}G^\Lambda_{0(n-1)}(Z)G^\Lambda_{n0}(Z)\frac{\partial b^\Lambda_n}{\partial\Lambda_{i\alpha,j\beta}}$$
$$+G^\Lambda_{00}(Z)\,\delta_{i,j}\,\delta_{\alpha,\beta}. \tag{76}$$

Hence the expansion for the bond order can be cast in a form essentially identical with Eq. (55):

$$\Theta_{i\alpha,j\beta}=-2\left[\sum_{n=0}^{\infty}\chi^\Lambda_{0n,n0}\frac{\partial a^\Lambda_n}{\partial\Lambda_{i\alpha,j\beta}}+2\sum_{n=1}^{\infty}\chi^\Lambda_{0(n-1),n0}\frac{\partial b^\Lambda_n}{\partial\Lambda_{i\alpha,j\beta}}\right], \tag{77}$$

where $\chi^\Lambda_{0m,n0}$ is calculated from Eq. (56).

We now have to describe the procedure for evaluating the derivatives of the recursion coefficients. This is rather involved, and will require consideration of the new formalism in its full generality. The final result, though, is quite simple and can be evaluated in a stable manner.

The starting point is a simple generalization of the Lanczos algorithm to the compound vectors. The new recurrence relation is

$$\hat{H}|W_n^\Lambda\}=a_n^\Lambda|W_n^\Lambda\}+b_n^\Lambda|W_{n-1}^\Lambda\}+b_{n+1}^\Lambda|W_{n+1}^\Lambda\}, \tag{78}$$

with the condition

$$\{W_n^\Lambda|W_m^\Lambda\}=\delta_{m,n}. \tag{79}$$

The Green's function $G_{00}^\Lambda(Z)$ is given by the usual continued fraction, but with the recursion coefficients given by Eq. (78).

Let us define the orthogonal polynomials $P_n^\Lambda(x)$:

$$xP_n^\Lambda(x)=b_n^\Lambda P_{n-1}^\Lambda(x)+a_n^\Lambda P_n^\Lambda(x)+b_{n+1}^\Lambda P_{n+1}^\Lambda(x), \tag{80}$$

with $P_{-1}^\Lambda(x)=0$ and $P_0^\Lambda(x)=1$. The new recursion vectors can be written as

$$|W_n^\Lambda\}=P_n^\Lambda(\hat{H})|W_0^\Lambda\}=\sum_{i\alpha} P_n^\Lambda(\hat{H})|i\alpha\rangle|e_{i\alpha}^\Lambda). \tag{81}$$

Hence the recursion coefficients and orthonormality condition can be written as:

$$\delta_{m,n}=\{W_m^\Lambda|W_n^\Lambda\}=\sum_{i\alpha,j\beta}\langle i\alpha|P_m^\Lambda(\hat{H})P_n^\Lambda(\hat{H})|j\beta\rangle\Lambda_{i\alpha,j\beta},$$

$$a_n^\Lambda=\{W_n^\Lambda|\hat{H}|W_n^\Lambda\}=\sum_{i\alpha,j\beta}\langle i\alpha|P_n^\Lambda(\hat{H})\hat{H}P_n^\Lambda(\hat{H})|j\beta\rangle\Lambda_{i\alpha,j\beta},$$

$$\begin{aligned}b_n^\Lambda&=\{W_{n-1}^\Lambda|\hat{H}|W_n^\Lambda\}\\&=\sum_{i\alpha,j\beta}\langle i\alpha|P_{n-1}^\Lambda(\hat{H})\hat{H}P_n^\Lambda(\hat{H})|j\beta\rangle\Lambda_{i\alpha,j\beta}.\end{aligned} \tag{82}$$

If we now define the O matrix, which is given by

$$O_{i\alpha,j\beta}^{\Lambda,m,n}=\langle i\alpha|P_m^\Lambda(\hat{H})P_n^\Lambda(\hat{H})|j\beta\rangle, \tag{83}$$

then we can write the derivatives of Eqs. (82) as

$$0=O_{i\alpha,j\beta}^{\Lambda,m,n}+\left\{W_0^\Lambda\left|\frac{\partial P_m^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}P_n^\Lambda(\hat{H})\right|W_0^\Lambda\right\} \tag{84}$$

$$+\left\{W_0^\Lambda\left|P_m^\Lambda(\hat{H})\frac{\partial P_n^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}\right|W_0^\Lambda\right\},$$

$$\begin{aligned}\frac{\partial a_n^\Lambda}{\partial\Lambda_{i\alpha,j\beta}}&=\langle i\alpha|P_n^\Lambda(\hat{H})\hat{H}P_n^\Lambda(\hat{H})|j\beta\rangle\\&\quad+2\left\{W_0^\Lambda\left|\frac{\partial P_n^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}\hat{H}P_n^\Lambda(\hat{H})\right|W_0^\Lambda\right\},\end{aligned}$$

$$\begin{aligned}\frac{\partial b_n^\Lambda}{\partial\Lambda_{i\alpha,j\beta}}&=\langle i\alpha|P_{n-1}^\Lambda(\hat{H})\hat{H}P_n^\Lambda(\hat{H})|j\beta\rangle\\&\quad+\left\{W_0^\Lambda\left|\frac{\partial P_{n-1}^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}\hat{H}P_n^\Lambda(\hat{H})\right|W_0^\Lambda\right\}\\&\quad+\left\{W_0^\Lambda\left|P_{n-1}^\Lambda(\hat{H})\hat{H}\frac{\partial P_n^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}\right|W_0^\Lambda\right\}.\end{aligned}$$

Since $\partial P_n^\Lambda(x)/\partial\Lambda_{i\alpha,j\beta}$ is a polynomial of order less than or equal to m, it can be expressed as a linear combination of polynomials $P_r^\Lambda(x)$, with $r\leqslant m$. Consequently, the orthonormality condition given in Eq. (82) implies

$$\left\{W_0^\Lambda\left|\frac{\partial P_m^\Lambda(\hat{H})}{\partial\Lambda_{i\alpha,j\beta}}P_n^\Lambda(\hat{H})\right|W_0^\Lambda\right\}=0 \quad (\text{if } m<n). \tag{85}$$

Using Eq. (80) to eliminate $\hat{H}$ in Eq. (84), and then substituting in Eqs. (83) and (85), we get

$$\frac{\partial a_n^\Lambda}{\partial\Lambda_{i\alpha,j\beta}}=b_{n+1}^\Lambda O_{i\alpha,j\beta}^{\Lambda,n+1,n}-b_n^\Lambda O_{i\alpha,j\beta}^{\Lambda,n,n-1},$$

$$2\frac{\partial b_n^\Lambda}{\partial\Lambda_{i\alpha,j\beta}}=b_n^\Lambda(O_{i\alpha,j\beta}^{\Lambda,n,n}-O_{i\alpha,j\beta}^{\Lambda,n-1,n-1}). \tag{86}$$

Thus we have produced a simple final result for the derivatives of the recursion coefficients. We now give the algorithm for evaluating the derivatives in a stable manner. From the identity

$$\begin{aligned}&\langle i\alpha|P_{m-1}^\Lambda(\hat{H})(\hat{H}P_n^\Lambda(\hat{H}))|j\beta\rangle\\&\qquad=\langle i\alpha|(P_{m-1}^\Lambda(\hat{H})\hat{H})P_n^\Lambda(\hat{H})|j\beta\rangle,\end{aligned} \tag{87}$$

we obtain the following recursive relation for the O matrix:

$$\begin{aligned}&b_m^\Lambda O_{i\alpha,j\beta}^{\Lambda,m,n}+a_{m-1}^\Lambda O_{i\alpha,j\beta}^{\Lambda,m-1,n}+b_{m-1}^\Lambda O_{i\alpha,j\beta}^{\Lambda,m-2,n}\\&\quad=b_{n+1}^\Lambda O_{i\alpha,j\beta}^{\Lambda,m-1,n+1}+a_n^\Lambda O_{i\alpha,j\beta}^{\Lambda,m-1,n}+b_n^\Lambda O_{i\alpha,j\beta}^{\Lambda,m-1,n-1}.\end{aligned} \tag{88}$$

To apply this recursion relation, we need a set of starting matrices. The most natural choice is $O_{i\alpha,j\beta}^{\Lambda,n,0}=(e_{j\beta}|\langle i\alpha|W_n^\Lambda\}$. However, to generate $O_{i\alpha,j\beta}^{\Lambda,n,n}$, we need starting matrices up to $O_{i\alpha,j\beta}^{\Lambda,2n,0}$. This means that extra vectors $|W_n^\Lambda\}$ must be generated. This can be done using Eq. (78), but with arbitrary values of a_m^Λ and b_m^Λ for $m>n$, since the values of the derivatives of the recursion coefficients are independent of these values.

As mentioned earlier, it is often useful to use estimated recursion coefficients after the exact ones, as this can lead to greatly improved convergence. The square root terminator of Eq. (36) is generally found to give greatly improved energy convergence (though for strongly covalent systems we will not use it as many levels are needed to achieve force convergence, and it is no longer useful). This raises the question of how we can evaluate the derivatives of the estimated recursion coefficients, which we need for the BOP expansion. The answer is that we cannot evaluate the derivatives exactly, but we can make some guesses, and constrain them by sum rules to make sure certain properties are maintained.

There are two important sum rules[5,6] that follow from Eq. (86) that ensure that the two expressions for the bond energy [Eqs. (13) and (21)] give the same results. This equivalence corresponds to the following equation for the Green's function:

$$\begin{aligned}1&=\langle i\alpha|(Z-\hat{H})\hat{G}(Z)|i\alpha\rangle\\&=ZG_{i\alpha,i\alpha}(Z)-\sum_{j\beta}H_{i\alpha,j\beta}G_{j\beta,i\alpha}(Z).\end{aligned}\tag{89}$$

To use this for studying sum rules, we need the equivalent expression for $G_{00}^{\Lambda}(Z)$, namely

$$\begin{aligned}1&=\{W_0^{\Lambda}|(Z-\hat{H})\hat{G}(Z)|W_0^{\Lambda}\}\\&=ZG_{00}^{\Lambda}(Z)-\sum_{i\alpha,j\beta}\Lambda_{i\alpha,j\beta}\sum_{k\gamma}H_{i\alpha,k\gamma}G_{k\gamma,j\beta}(Z)\\&=ZG_{00}^{\Lambda}(Z)-\sum_{i\alpha,j\beta}\Lambda_{i\alpha,j\beta}\sum_{k\gamma}H_{i\alpha,k\gamma}\\&\quad\times\left[\sum_{n=0}^{\infty}G_{0n}^{\Lambda}(Z)G_{n0}^{\Lambda}(Z)\frac{\partial a_n^{\Lambda}}{\partial\Lambda_{k\gamma,j\beta}}\right.\\&\quad\left.+2\sum_{n=1}^{\infty}G_{0(n-1)}^{\Lambda}(Z)G_{n0}^{\Lambda}(Z)\frac{\partial b_n^{\Lambda}}{\partial\Lambda_{k\gamma,j\beta}}+G_{00}^{\Lambda}(Z)\delta_{k,j}\delta_{\gamma,\beta}\right],\end{aligned}\tag{90}$$

where we have substituted $G_{k\gamma,j\beta}(Z)$ from Eq. (76) in the square brackets. With the use of Eqs. (86) and (82) we obtain immediately the first sum rule:

$$\sum_{i\alpha,j\beta}\frac{\partial a_n^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}\Lambda_{i\alpha,j\beta}=b_{n+1}^{\Lambda}\{W_{n+1}^{\Lambda}|W_n^{\Lambda}\}-b_n^{\Lambda}\{W_n^{\Lambda}|W_{n-1}^{\Lambda}\}=0,$$

$$\sum_{i\alpha,j\beta}\frac{\partial b_n^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}\Lambda_{i\alpha,j\beta}=0.\tag{91}$$

This just ensures that the expansion for the bond order does not contribute to the on-site term. The second sum rule [which also follows from Eqs. (86) and (82)] is

$$\sum_{i\alpha,j\beta,k\gamma}\frac{\partial a_n^{\Lambda}}{\partial\Lambda_{i\alpha,k\gamma}}\Lambda_{i\alpha,j\beta}H_{k\gamma,j\beta}=(b_{n+1}^{\Lambda})^2-(b_n^{\Lambda})^2,$$

$$\sum_{i\alpha,j\beta,k\gamma}2\frac{\partial b_n^{\Lambda}}{\partial\Lambda_{i\alpha,k\gamma}}\Lambda_{i\alpha,j\beta}H_{k\gamma,j\beta}=b_n^{\Lambda}[a_n^{\Lambda}-a_{n-1}^{\Lambda}].\tag{92}$$

Applying this sum rule to Eq. (90) we get

$$\begin{aligned}1&=(Z-a_0^{\Lambda})G_{00}^{\Lambda}(Z)-\sum_{n=0}^{\infty}G_{0n}^{\Lambda}(Z)G_{n0}^{\Lambda}(Z)[(b_{n+1}^{\Lambda})^2-(b_n^{\Lambda})^2]\\&\quad-\sum_{n=1}^{\infty}G_{0n}^{\Lambda}(Z)G_{(n-1)0}^{\Lambda}(Z)b_n^{\Lambda}[a_n^{\Lambda}-a_{n-1}^{\Lambda}].\end{aligned}\tag{93}$$

This is an identity. Thus the on-site and intersite expressions for the bond energy are guaranteed to be equal at any level of approximation.

We are now in a position to evaluate the estimated derivatives of the terminating recursion coefficients. Assuming that we are using the square root terminator, the right hand sides of the first two sum rules [Eqs. (91) and (92)] are zero for $n\geqslant N+1$ for the derivatives of a_n^{Λ}, and for $n\geqslant N+2$ for the derivatives of b_n^{Λ}. Thus the simplest assumption is that the derivatives of the recursion coefficients are zero under these conditions, which makes the sums in Eq. (77) finite. Thus we need only find expressions for $\partial a_N^{\Lambda}/\partial\Lambda_{i\alpha,j\beta}$ and $\partial b_{N+1}^{\Lambda}/\partial\Lambda_{i\alpha,j\beta}$. If we assume that both $O_{i\alpha,j\beta}^{\Lambda,N+1,N}$ and $O_{i\alpha,j\beta}^{\Lambda,N+1,N+1}$ are linear in $\partial a_0^{\Lambda}/\partial\Lambda_{i\alpha,j\beta}$, then we obtain the following expressions by requiring that Eqs. (91) and (92) be satisfied:

$$\frac{\partial a_N^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}=\left(\frac{b_{\infty}^{\Lambda}}{b_1^{\Lambda}}\right)^2\frac{\partial a_0^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}-b_N^{\Lambda}O_{i\alpha,j\beta}^{\Lambda,N,N-1},$$

$$2\frac{\partial b_{N+1}^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}=b_{\infty}^{\Lambda}\delta_{i,j}\delta_{\alpha,\beta}+\frac{b_{\infty}^{\Lambda}(a_{\infty}^{\Lambda}-a_0^{\Lambda})}{(b_1^{\Lambda})^2}\frac{\partial a_0^{\Lambda}}{\partial\Lambda_{i\alpha,j\beta}}-b_{\infty}^{\Lambda}O_{i\alpha,j\beta}^{\Lambda,N,N}.\tag{94}$$

The energy convergence is now given by the single-site results in Fig. 6.

As formulated so far, BOP is not guaranteed to be rotationally invariant. That is, if the energy of a crystal is evaluated with the crystal oriented one way, and then evaluated again after it has been rotated, there is no guarantee that the two energies will be the same.[60] There is a way of overcoming this, which is to work with moments that involve traces over the magnetic quantum number (m) for a given angular momentum l. That is, we work with quantities of the form

$$\mu_{il}^{(n)}=\frac{1}{2l+1}\sum_{m=-l}^{l}\langle ilm|\hat{H}^n|ilm\rangle.\tag{95}$$

These are rotationally invariant, thus the recursion coefficients and the Green's function matrix element generated from them are rotationally invariant.

In many TB simulations, local charge neutrality (LCN) is imposed as the simplest form of self-consistency.[14] Within the BOP scheme, this can be applied very efficiently since we know the response functions. If the excess charge on site i is Q_i, then a good estimate of the shift that should be applied to the on-site energies is

$$\Delta_i=-Q_i/X_i,\tag{96}$$

where $X_i=-2\Sigma_{\alpha}\chi_{00,00}^{\Lambda}$, since $-2\chi_{00,00}^{\Lambda}=\partial N^{\Lambda}/\partial a_0^{\Lambda}$, and $a_0^{\Lambda}=\varepsilon_{i\alpha}$. Using this prescription, usually no more than three or four iterations are needed to achieve convergence.

XI. CONVERGENCE AND FINITE ELECTRON TEMPERATURE

Here we note a general way of accelerating the rate of convergence of the energy and (more importantly) the forces, though at the cost of some loss of accuracy, and demonstrate the convergence with results from molecular-dynamics simulations for silicon.

An increased rate of convergence can always be achieved by giving the electrons a finite temperature. This has the effect of reducing the range of the density matrix,[38] which means that fewer moments are necessary to describe it. Introducing a finite temperature for the electrons means that the electrons occupy single particle states according to the Fermi-Dirac distribution.[53] That is,

$$U_{band}(T)=2\sum_{n}\epsilon^{(n)}f(x^{(n)})=2\int dEn_{total}(E)f(x), \tag{97}$$

where $x^{(n)}=(\epsilon^{(n)}-\mu)/(k_BT)$, $x=(E-\mu)/(k_BT)$, μ is the chemical potential, k_B is Boltzmann's constant, T is the electron temperature, and $f(x)=1/(1+e^{x})$. Because electrons with energies near the chemical potential are free to move between states, there is an entropy term $[S_{band}(T)]$ which must be added to the band energy to produce a band free energy $[A_{band}(T)]$:

$$A_{band}(T)=U_{band}(T)-TS_{band}(T),$$

$$\begin{aligned}S_{band}(T)&=-2k_B\sum_{n}[f(x^{(n)})\ln(f(x^{(n)}))\\&\quad+(1-f(x^{(n)}))\ln(1-f(x^{(n)}))]\\&=-2k_B\int dEn_{total}(E)\sigma(x),\end{aligned} \tag{98}$$

where $\sigma(x)=[f(x)\ln(f(x))+(1-f(x))\ln(1-f(x))]$. The band energy and the forces [defined now as the negative gradient of the band free energy $A_{band}(T)$] are still given by the compact expressions of Eq. (13). It is interesting to note that the force expression *includes* the electron entropy contribution, provided the forces are evaluated at a constant number of electrons. The definition of the density matrix, however, is slightly changed, and is now given by

$$\begin{aligned}\rho_{i\alpha,j\beta}(T)&=\sum_{n}C_{i\alpha}^{(n)}C_{j\beta}^{(n)}f(x^{(n)})\\&=-\frac{1}{\pi}\lim_{\eta\to 0}\text{Im}\int dEG_{i\alpha,j\beta}(E+i\eta)f(x).\end{aligned} \tag{99}$$

Thus introducing finite electron temperature into BOP is straightforward. The entropy term has to be introduced, and integrals up to the Fermi energy are now replaced by integrals over all energy but with the Fermi function included as part of the integrand. The formalism for calculating the integrals is given in Appendix A.

To make explicit the reason for the increased rate of convergence when finite electron temperature is introduced, we shall look at the integrals for the response functions:

$$\chi_{0m,n0}^{\Lambda}(T)=\frac{1}{\pi}\lim_{\eta\to 0}\text{Im}\int G_{0m}^{\Lambda}(E+i\eta)G_{n0}^{\Lambda}(E+i\eta)f(x)dE. \tag{100}$$

Let us define the quantity

$$g_{mn}^{\Lambda}(E)=\frac{1}{\pi}\lim_{\eta\to 0}\text{Im}\{G_{0m}^{\Lambda}(E+i\eta)G_{n0}^{\Lambda}(E+i\eta)\}. \tag{101}$$

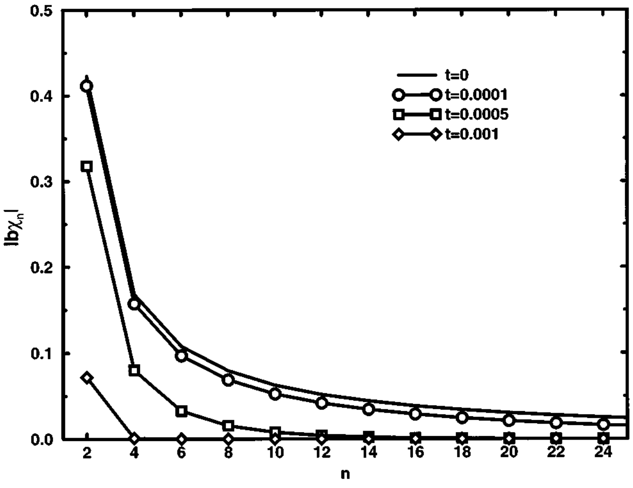

FIG. 7. The variation of convergence with electron temperature for the response functions for the semi-infinite constant linear chain with hopping integral b. $t=\pi k_BT/(2|b|)$.

The response functions are then given by

$$\chi_{0m,n0}^{\Lambda}(T)=\int g_{mn}^{\Lambda}(E)f(x)dE. \tag{102}$$

We saw earlier (for the constant linear chain) that $\chi_{0m,n0}^{\Lambda}(T=0)$ has $n+m$ nodes in it. Thus $g_{nm}^{\Lambda}(E)$ will have $n+m+1$ nodes in it. So for a band of width W, the period of oscillation is about $2W/(n+m+1)\approx W/n$ (as $|n-m|\leqslant 1$ for the response functions used in the BOP expansion). We can rewrite Eq. (102) in the following way to allow us to make use of this fact:

$$\chi_{0m,n0}^{\Lambda}(T)=\int_{-\infty}^{\mu}dE'\int_{-\infty}^{\infty}dEg_{mn}^{\Lambda}(E)\left(\frac{-1}{k_BT}\right)f'\left(\frac{E-E'}{k_BT}\right). \tag{103}$$

The function $f'(E-E'/k_BT)$ is a peaked function with a width of order $4k_BT$. Thus the inner integral *averages* $g_{mn}^{\Lambda}(E)$ over an energy range of $4k_BT$. This average will go to zero when the energy range over which the averaging is taking place is of the same order as the period of oscillation, which is when $4k_BT\approx W/n$. Thus the number of levels needed to reach convergence is given by $n_{max}\approx W/(4k_BT)$. Increasing T thus reduces the value of n_{max}. Since adding one extra recursion level involves adding another shell to the cluster, introducing finite electron temperature has the effect of limiting the size of the cluster that needs to be considered. This is equivalent to saying that the range of the density matrix is reduced. The increased rate of convergence for the linear chain can be seen in Fig. 7.

To test the degree of consistency between the energy and the forces, molecular-dynamics simulations have been performed for crystalline silicon with a real temperature of 500 K. If the forces on the atoms are all equal to the derivatives of the energy with respect to the atomic positions, then the total energy of the unit cell will be a constant as a function of time. One of the sources of the lack of consistency between the forces and the energy is the errors present in the approximations made for the derivatives of the terminating recursion

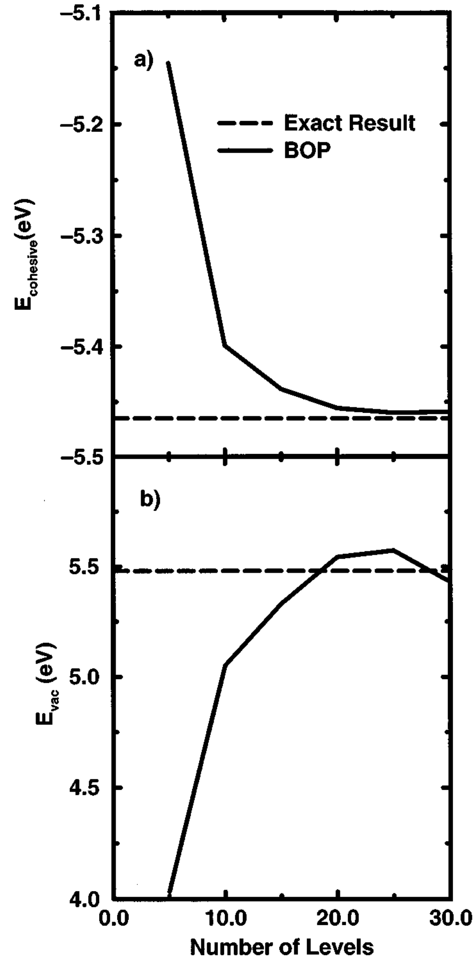

FIG. 8. The convergence of (a) the cohesive energy of bulk Si in the diamond structure, and (b) the formation energy of an unrelaxed vacancy, with respect to the number of levels used, for the case where a cluster of fixed size and no terminator is used. The size of the cluster is chosen to give the first five levels exactly.

coefficients. In the limit of a large number of exact coefficients or large electron temperature, these errors become unimportant.

For all the simulations, five levels of recursion and a square root terminator are used. The degree of force convergence is then controlled by the electron temperature. This is an adequate approach for molecular dynamics, and makes rapid simulations possible. However, if careful static calculations need to be performed that depend on the fine details of the electronic structure [for example, to obtain the buckling of the dimers at the (100) surface of Si], then a different approach is necessary. Thermal smearing is no longer acceptable since it averages out fine structure in the density of states, for which many moments are required. However, the short range of the density matrix for semiconductors and insulators means that we can take the moments inside a small cluster, rather than allowing the cluster to expand, making this approach computationally efficient. In Fig. 8 is shown the convergence of the cohesive energy for bulk silicon in the diamond structure, and the formation energy for an unrelaxed vacancy, using this approach. A cluster that allows the first five levels to be evaluated exactly has been used.

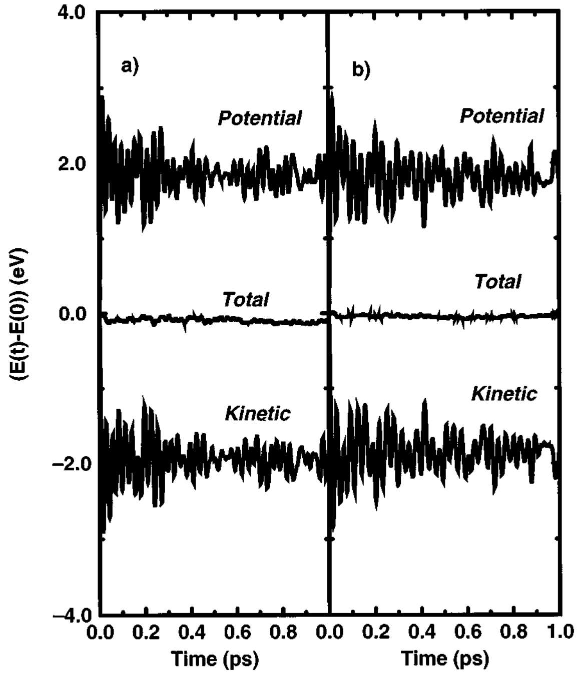

FIG. 9. The variation of the band structure (potential) energy, ionic kinetic energy, and total energy of a unit cell as a function of time for crystalline silicon at 500 K. In panel (a) the results are for an electron temperature of 0.1 eV, and in panel (b) they are for an electron temperature of 1.0 eV.

Good convergence is found for both quantities. The details of this approach, and a more complete survey of the convergence properties of BOP with respect to number of levels, are given elsewhere.[11]

In Fig. 9 the energy as a function of time is given for crystalline silicon at 500 K using electron temperatures of 0.1 eV and 1.0 eV. For both temperatures the energy is conserved very well, though there is a slight improvement on going from 0.1 eV to 1.0 eV. We have repeated the simulations with a vacancy present (so that there are undercoordinated Si atoms present, which lead to narrow features in the

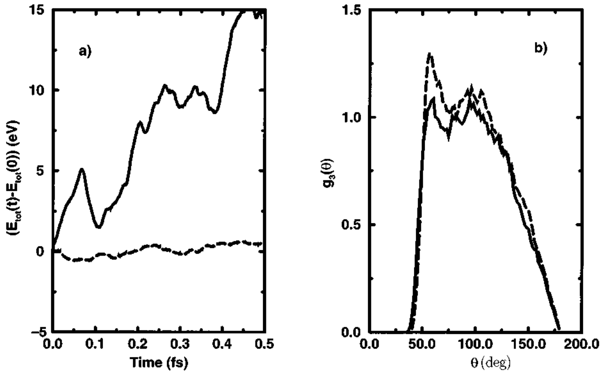

FIG. 10. In panel (a) is shown the variation of the total energy of a unit cell as a function of time for liquid silicon at 3000 K. The solid line is for an electron temperature of 0.3 eV, and the dashed line is for an electron temperature of 1.0 eV. In panel (b) is shown the pair correlation function for the two electron temperatures. The same line style convention is used as for panel (a).

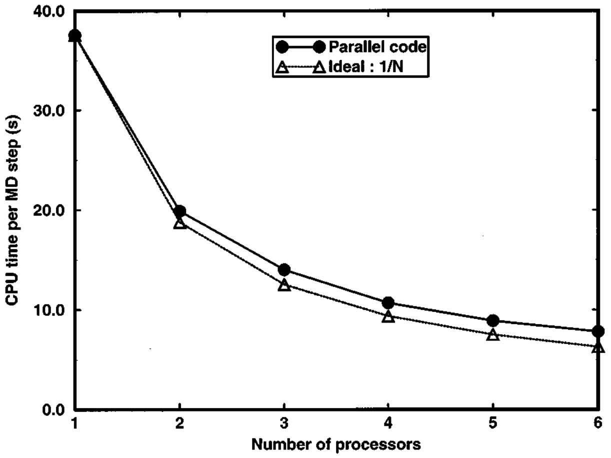

FIG. 11. The time taken to evaluate, in parallel, the energy and forces of a 768 atom silicon cell as a function of the number of processors. The benchmarks were performed on a cluster of HP9000/735 workstations using five exact recursion levels and a square root terminator.

density of states). Slightly greater fluctuations in the total energy are found, but the convergence is still good.

The final set of simulations was on silicon at 3000 K. At this temperature it is a liquid. Five levels and a square root terminator were again used, and in Fig. 10 the energy as a function of time is shown for $k_BT = 0.3$ eV and $k_BT = 1.0$ eV, as is the angular correlation function. The energy is not well conserved at the lower electron temperature (there is a systematic upward drift). However, raising the electron temperature to 1.0 eV leads to better energy conservation. Raising the temperature still further would improve the conservation of energy even more, but will eventually change the dynamics considerably. Thus it is better to add more moments if better conservation is needed. The angular correlation is also found to give better agreement with other calculations at the higher electron temperature.[28]

XII. THE IMPLEMENTATION OF BOND-ORDER POTENTIALS ON PARALLEL COMPUTERS

Parallel computation, in which a number of processors are employed simultaneously on a single problem, offers dramatic possibilities for performing large-scale and/or long-time atomistic molecular-dynamics simulations.[61] The BOP scheme described in this paper is naturally parallelizable since the evaluation of moments and recursion coefficients may be performed *one site at a time* independently. We have adopted a spatial decomposition strategy to parallelization[62] in which each processor of the parallel machine is assigned a region of real space within the simulation cell. Each processor is then responsible for calculating the energy of, and forces on, only those atoms within its assigned spatial region. A small amount of interprocessor communication is required in order to determine the global Fermi energy and in the evaluation of interatomic forces. In the latter case this is because an atom which resides near the boundary of a node's spatial region can exert a force on an atom calculated by a neighboring node. However, the overhead of these communications is small compared to the time taken to evaluate the recursion coefficients. The scaleability of the algorithm is demonstrated in Fig. 11, which shows the time required to evaluate the energy and forces of a 768 silicon-atom diamond cell as a function of the number of processors. A near ideal scaling is observed.

XIII. CONCLUSION

The bond-order potential is a numerically efficient scheme that works within the orthogonal tight binding framework. It allows the evaluation of the bond and promotion energies, and the corresponding forces, to be evaluated in a time which scales linearly with the number of particles for a given accuracy. It is a naturally parallel method, giving essentially ideal scaling of time with respect to the number of nodes on a parallel machine.

The details of the theory needed to derive both two-site and one-site BOP, and to implement one-site BOP as a computer code, has been given in a systematic manner. The fact that BOP can be represented as a moments expansion allows us to derive an expression for the bond energy that has the same properties as the potential of Tersoff. This is one example of how BOP can be used as an analytical tool to study the origins of cohesion, as well as a computational tool.

The question of convergence is studied by means of constant-energy molecular-dynamics simulations. The energy is found to be well conserved for crystalline and liquid silicon, even with a low electron temperature of 0.1 eV in the case of the solid.

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APPENDIX A

The calculation of energies and response functions at finite electron temperature requires integrals with the Fermi function. This is customarily carried out in the complex plane by summing up an infinite series over the Matsubara poles.[54] The convergence of this series is, however, *very* slow. A much more efficient scheme[55] is now described. It should be noted that another scheme exists also.[56]

It is possible to accelerate considerably the Matsubara summation by using the following approximant for the exponential function:

$$\exp(Z) \approx \left(1 + \frac{Z}{n}\right)^n \tag{A1}$$

which becomes *exact* as n tends to infinity. This gives the following very useful representation for the Fermi function:

$$f(E)=\frac{1}{\exp(\beta(E-\mu))+1}\approx\frac{1}{\left(1+\dfrac{\beta(E-\mu)}{2M}\right)^{2M}+1}, \tag{A2}$$

where $\beta=1/k_BT$, and μ is the chemical potential. This approximation (which becomes exact in the limit of large M) has $2M$ simple poles (E_p) located on a circle in the complex plane off the real axis

$$E_p=\mu+\frac{2M}{\beta}(z_p-1),$$

$$z_p=\exp(\mathrm{i}\pi(2p+1)/2M),\quad p=0,1,\ldots,2M-1 \tag{A3}$$

with residues $R_p=-z_p/\beta$.

Now we can write the equation for the bond energy of individual sites [see Eq. (21)] in the following simple form:

$$E_{bond}^{i\alpha}=\frac{4}{\beta}\mathrm{Re}\sum_{p=0}^{M-1} z_p(E_p-\varepsilon_{i\alpha})G_{i\alpha,i\alpha}(E_p), \tag{A4}$$

where $G_{00}^{i\alpha}(Z)=\langle i\alpha|(Z-\hat{H})^{-1}|i\alpha\rangle$. Analogously, we obtain the following expressions for the response functions [see Eq. (101)] and the number of electrons:

$$\chi_{0m,n0}^{i\alpha}=-\frac{2}{\beta}\mathrm{Re}\sum_{p=0}^{M-1} z_pG_{0m}^{i\alpha}(E_p)G_{n0}^{i\alpha}(E_p),$$

$$N^{i\alpha}=\frac{4}{\beta}\,\mathrm{Re}\sum_{p=0}^{M-1} z_pG_{00}^{i\alpha}(E_p). \tag{A5}$$

We find that typically 30 to 50 complex poles are enough to achieve convergence within about 12 digits. The present method is found to be much more stable than analytical integration.[57] Moreover, the method is very general and may be used with any terminator, such as that which describes band gaps.[58]

In the absence of any terminator, it is possible to perform the integrals exactly. Let ϵ_I^Λ be an eigenvalue of the tridiagonal Hamiltonian matrix ($\{W_n^\Lambda|\hat{H}|W_m^\Lambda\}$) formed from the recursion coefficients, and $|\Psi_I^\Lambda\}$ be the corresponding eigenvector. Then we can write

$$G_{nm}^\Lambda(Z)=\sum_I\frac{\{W_n^\Lambda|\Psi_I^\Lambda\}\{\Psi_I^\Lambda|W_m^\Lambda\}}{Z-\epsilon_I^\Lambda}. \tag{A6}$$

The number of electrons, the band energy, and the entropy are then given by

$$N^\Lambda(T)=2\sum_I f(x_I^\Lambda),$$

$$U_{band}^\Lambda(T)=2\sum_I \epsilon_I^\Lambda f(x_I^\Lambda),$$

$$S_{band}^\Lambda(T)=-k_B\sum_I [f(x_I^\Lambda)\ln(f(x_I^\Lambda))+(1-f(x_I^\Lambda))\ln(1-f(x_I^\Lambda))], \tag{A7}$$

where $x_I^\Lambda=(\epsilon_I^\Lambda-\mu)/(k_BT)$. The response functions are given by

$$\chi_{mn}^\Lambda(T)=\sum_{I,J}\{W_0^\Lambda|\Psi_I^\Lambda\}\{\Psi_I^\Lambda|W_m^\Lambda\}\{W_n^\Lambda|\Psi_J^\Lambda\}\{\Psi_J^\Lambda|W_0^\Lambda\}\times\left[\frac{f(x_I^\Lambda)-f(x_J^\Lambda)}{\epsilon_I^\Lambda-\epsilon_J^\Lambda}\right]. \tag{A8}$$

APPENDIX B

The starting point for the exactly differentiable energy approach is the free energy functional given by Eqs. (97) and (98):

$$A_{tot}=A_{band}+U_{rep},$$

$$A_{band}=2\int dEn_{tot}(E)[Ef(x)-k_BT\sigma(x)]. \tag{B1}$$

The chemical potential μ is found from the conservation of the number of electrons N_e:

$$N_e=2\int dEf(x)n_{tot}(E). \tag{B2}$$

The total density of states is found from $\overline{G_{00}}(Z)$, which is the average single particle Green's function for the *entire* system:

$$n_{tot}(E)=-\frac{2N_o}{\pi}\lim_{\eta\to0}\mathrm{Im}\{\overline{G_{00}}(E+\mathrm{i}\eta)\}, \tag{B3}$$

where N_o is the total number of orbitals in the system. The Green's function is expressed by the continued fraction given in Eq. (33), and the square root terminator is used [see Eq. (36)]. The coefficients $\overline{a_s}$ and $\overline{b_s}$ are found from the average moments ($\overline{\mu^{(s)}}$) of the density of states [see Eq. (35)], where

$$\overline{\mu^{(s)}}=\frac{1}{N_o}\sum_{i\alpha}\mu_{i\alpha}^{(s)}. \tag{B4}$$

The equations used to compute the coefficients $\overline{a_s}$ and $\overline{b_s}$ from the moments are as follows:

$$c_0^0=1,$$

$$c_j^s=0 \text{ if } j>s \text{ or } j<0 \text{ or } s<0,$$

$$\overline{b_{s+1}}c_j^{s+1}=c_{j-1}^s-\overline{a_s}c_j^s-\overline{b_s}c_j^{s-1},$$

$$1=\sum_{j=0}^{s}\sum_{l=0}^{s} c_j^sc_l^s\overline{\mu^{(j+l)}},$$

$$\overline{a_s}=\sum_{j=0}^{s}\sum_{l=0}^{s} c_j^sc_l^s\overline{\mu^{(j+l+1)}},$$

$$\overline{b_s}=\sum_{j=0}^{s}\sum_{l=0}^{s-1} c_j^sc_l^{s-1}\overline{\mu^{(j+l+1)}}. \tag{B5}$$

The quantities c_j^s are the coefficients for the expansion in powers of x of the orthogonal polynomials $P_r(x)$ used in the recursion algorithm.[44]

All the elements needed to construct the energy functional are now defined. The force $\vec{F}_k$ can be obtained by direct differentiation of Eq. (B1):

$$\vec{F}_k = -\frac{1}{2}\sum_{i\neq j} \phi'_{ij}(r_{ij})\frac{\partial r_{ij}}{\partial \vec{r}_k} + \frac{2N_o k_B T}{\pi}\lim_{\eta\to 0} \mathrm{Im}\int dE[xf(x) - \sigma(x)]\frac{\partial \overline{G_{00}}(E+i\eta)}{\partial \vec{r}_k}. \tag{B6}$$

To obtain this equation, use has been made of the fact that $\partial N_e/\partial \vec{r}_k = 0$. The derivative of the Green's function is given by [see Eq. (38)]

$$\frac{\partial \overline{G_{00}}(Z)}{\partial \vec{r}_k} = \sum_{s=0}^{m} \overline{G_{0s}}(Z)\overline{G_{s0}}(Z)\frac{\partial \overline{a_s}}{\partial \vec{r}_k} + 2\sum_{s=1}^{m} \overline{G_{0s}}(Z)\overline{G_{(s-1)0}}(Z)\frac{\partial \overline{b_s}}{\partial \vec{r}_k}, \tag{B7}$$

where $\overline{G_{0s}}(Z)$ is given by Eq. (40). The derivatives of the recursion coefficients can be obtained from Eq. (B5) in terms of the derivatives of the moments:

$$\frac{\partial \overline{a_s}}{\partial \vec{r}_k} = \overline{b_{s+1}}\sum_{j=0}^{s+1}\sum_{l=0}^{s} c_j^{s+1}c_l^s\frac{\partial \overline{\mu^{(l+j)}}}{\partial \vec{r}_k} - \overline{b_s}\sum_{j=0}^{s}\sum_{l=0}^{s-1} c_j^s c_l^{s-1}\frac{\partial \overline{\mu^{(l+j)}}}{\partial \vec{r}_k},$$

$$\frac{\partial \overline{b_s}}{\partial \vec{r}_k} = \frac{\overline{b_s}}{2}\left\{\sum_{j=0}^{s}\sum_{l=0}^{s} c_j^s c_l^s\frac{\partial \overline{\mu^{(l+j)}}}{\partial \vec{r}_k} - \sum_{j=0}^{s-1}\sum_{l=0}^{s-1} c_j^{s-1}c_l^{s-1}\frac{\partial \overline{\mu^{(l+j)}}}{\partial \vec{r}_k}\right\},$$

$$\frac{\partial \overline{\mu^{(s)}}}{\partial \vec{r}_k} = \frac{s}{N_o}\mathrm{Tr}\left\{\hat{H}^{s-1}\frac{\partial \hat{H}}{\partial \vec{r}_k}\right\}. \tag{B8}$$

This completes the formalism for the forces.

For some simulations it is necessary to know the charges on each site. These can be readily calculated from the local densities of states for each site. To obtain the local densities of states, we need the Green's functions projected onto each orbital $[G_{i\alpha,i\alpha}(Z)]$. These can be obtained from Eqs. (76) and (B8) with $\vec{r}_k$ replaced by $\Lambda_{i\alpha,i\alpha}$, where $\Lambda_{i\alpha,j\beta} = 1/N_o\delta_{i,j}\delta_{\alpha,\beta} + \eta_{i\alpha,j\beta}$ and $\partial\overline{\mu^{(s)}}/\partial\Lambda_{i\alpha,i\alpha} = \mu_{i\alpha}^{(s)} - \overline{\mu^{(s)}}$.

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[1] D.G. Pettifor, Phys. Rev. Lett. **63**, 2480 (1989).

[2] D.G. Pettifor, in *Many Atom Interactions in Solids*, edited by R.M. Nieminen, M.J. Puska, and M.J. Manninen, Springer Proceedings in Physics Vol. 48 (Springer-Verlag, Berlin, 1990), p. 64.

[3] D.G. Pettifor and M. Aoki, Philos. Trans. R. Soc. London Ser. A **334**, 439 (1991).

[4] M. Aoki and D.G. Pettifor, in *Physics of Trans. Metals*, edited by P.M. Oppeneer and J. Kübler (World Scientific, Singapore, 1993), p. 299.

[5] M. Aoki, P. Gumbsch, and D.G. Pettifor, in *Computer Aided Innovation of New Materials*, edited by M. Domaya, J. Kihara, M. Tanaka, and R. Yamamoto (North-Holland, Amsterdam, 1993).

[6] M. Aoki, P. Gumbsch, and D.G. Pettifor, in *Interatomic Potentials and Structural Stability*, edited by K. Terakura and H. Akai (Springer-Verlag, Berlin, 1993), p. 23.

[7] P. Alinaghian, P. Gumbsch, A.J. Skinner, and D.G. Pettifor, J. Phys. Condens. Matter **5**, 5795 (1993).

[8] M. Aoki, Phys. Rev. Lett. **71**, 3842 (1993).

[9] P. Alinaghian, S.R. Nishitani, and D.G. Pettifor, Philos. Mag. B **69**, 889 (1994).

[10] M. Aoki, A.P. Horsfield, and D.G. Pettifor (unpublished).

[11] A.P. Horsfield, A.M. Bratkovsky, D.G. Pettifor, and M. Aoki, Phys. Rev. B **53**, 1656 (1996).

[12] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[13] J.C. Slater and G.F. Koster, Phys. Rev. **94**, 1498 (1954).

[14] A.P. Sutton, M.W. Finnis, D.G. Pettifor, and Y. Ohta, J. Phys. C **21**, 35 (1988).

[15] D.G. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford University Press, Oxford, 1995).

[16] B. Legrand, Philos. Mag. B **49**, 171 (1984).

[17] B. Legrand, Philos. Mag. A **52**, 83 (1985).

[18] D.G. Pettifor, in *Electron Theory in Alloy Design*, edited by D.G. Pettifor and A.H. Cottrell (Institute of Materials, London, 1992), p. 81.

[19] P.B. Allen, J.Q. Broughton, and A.K. McMahan, Phys. Rev. B **34**, 859 (1986).

[20] L. Goodwin, A.J. Skinner, and D.G. Pettifor, Europhys. Lett. **9**, 701 (1989).

[21] J.L. Mercer and M.Y. Chou, Phys. Rev. B **47**, 9366 (1993).

[22] D.J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[23] F.S. Khan and J.Q. Broughton, Phys. Rev. B **39**, 3688 (1989).

[24] S. Sawada, in *Ordering at Surfaces and Interfaces*, edited by A. Yoshimori *et al.* (Springer-Verlag, Berlin, 1986), p. 129.

[25] B.J. Min, Y.H. Lee, C.Z. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. B **46**, 9677 (1992).

[26] C.Z. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. Lett. **66**, 189 (1991).

[27] P.B. Allen and J.Q. Broughton, J. Phys. Chem. **91**, 4964 (1987).

[28] C.Z. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. B **45**, 12 227 (1992).

[29] A.P. Horsfield and P. Clancy, Modelling Simul. Mater. Sci. Eng. **2**, 277 (1994).

[30] L. Colombo and G. Servalli, in *Materials Theory and Modelling*, edited by P. D. Bristowe *et al.* (Materials Research Society, Pittsburgh, 1993).

[31] C.H. Xu, C.Z. Wang, C.T. Chan, and K.M. Ho, J. Phys. Condens. Matter **4**, 6047 (1992).

[32] C.Z. Wang and K.M. Ho, Phys. Rev. B **50**, 12 429 (1994).

[33] G. Galli and M. Parrinello, Phys. Rev. Lett. **69**, 3547 (1992).

[34] F. Mauri, G. Galli, and R. Car, Phys. Rev. B **47**, 9973 (1993).

[35] P. Ordejon, D. Drabold, M. Grunbach, and R. Martin, Phys. Rev. B **48**, 14 646 (1993).

[36] X.-P. Li, R.W. Nunes, and D. Vanderbilt, Phys. Rev. B **47**, 10 891 (1993).

[37] M.S. Daw, Phys. Rev. B **47**, 10 895 (1993).

[38] S. Goedecker and L. Colombo, Phys. Rev. Lett. **73**, 122 (1994).

[39] E.B. Stechel, A.R. Williams, and P.J. Feibelman, Phys. Rev. B **49**, 10 088 (1994).

[40] J.D. Kress and A.F. Voter, Phys. Rev. B **52**, 8766 (1995).

[41] J. Friedel, Adv. Phys. **3**, 446 (1954).

[42] V. Heine, Solid State Phys. **35**, 1 (1980).

[43] F. Ducastelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids **31**, 1295 (1970).

[44] R. Haydock, Solid State Phys. **35**, 216 (1980).

[45] A.P. Sutton, *Electronic Structure of Materials* (Oxford University Press, Oxford, 1993).

[46] M.W. Finnis and J.E. Sinclair, Philos. Mag. A **50**, 45 (1984).

[47] J. Tersoff, Phys. Rev. B **38**, 9902 (1988).

[48] H. Hellmann, *Einfuhrung in die Quantumchemie* (Franz Deutsche, Leipzig, 1937).

[49] R.P. Feynman, Phys. Rev. **56**, 340 (1939).

[50] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 225 (1950).

[51] N. Beer and D.G. Pettifor, in *Structure and Phase Stability of Alloys*, edited by P. Phariseau and W. Temmerman (Plenum Press, New York, 1984).

[52] P. Turchi and F. Ducastelle, in *The Recursion Method and Its Applications*, edited by D.G. Pettifor and D.L. Weaire (Springer-Verlag, Berlin, 1985), p. 104.

[53] D.A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

[54] A.A. Abrikosov, L.P. Gorkov, and I.E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[55] D.M.C. Nicholson, G.M. Stocks, Y. Wang, W.A. Shelton, Z. Szotek, and W.M. Temmerman, Phys. Rev. B **50**, 14 686 (1994).

[56] S. Goedecker, Phys. Rev. B **48**, 17 573 (1993).

[57] G. Allan, M.C. Desjonqueres, and D. Spanjaard, Solid State Commun. **50**, 401 (1984).

[58] P. Turchi, F. Ducastelle, and G. Tréglia, J. Phys. C **15**, 2891 (1982).

[59] A.P. Horsfield (unpublished).

[60] J. Inoue and Y. Ohta, J. Phys. C **20**, 1947 (1987).

[61] D. Fincham, Mol. Simul. **1**, 1 (1987).

[62] M.R.S. Pinches, D.J. Tildesley, and W. Smith, Mol. Simul. **6**, 51 (1991).