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New Many-Body Potential for the Bond Order

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An analytic many-body potential is derived for the bond order of s-valent systems which allows the influence of the local atomic environment on the bond strength to be determined directly. The importance of the three-membered- and four-membered-ring terms on the topology of four-atom clusters is demonstrated. The simplicity of the potential's analytic form will allow the much used embedded-atom potentials to be extended to include explicit three-body and four-body terms.

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The last few years have seen rapid progress in the development of semiempirical many-body potentials for atomistic simulation.[1] The simplest, the embedded-atom potentials,[2,3] have been successful in modeling the fcc noble metals and aluminum, and their alloys.[4] The form of these embedding potentials may be justified either within effective-medium theory[5] or within the second-moment approximation to the local electronic density of states.[3] The modeling of open tetrahedrally coordinated semiconductors requires the inclusion of *explicit* three-body[6] and four-body[7] terms. The analytic behavior of these many-body terms for semiconductors and transition metals has been studied[8] using a moment expansion within a localized tight-binding basis. However, since this N-body expansion of the total energy is derived perturbatively with respect to some reference medium, many-body potentials which are fitted to *bulk* properties may lead to very poor predictions[9] for the binding and topology of small atomic *clusters.*

Recently Chelikowsky *et al.*[10] have shown that it is possible to fit both the bulk and cluster geometries of silicon with a suitably chosen bond-order potential. Bond-order potentials are similar in spirit to embedding potentials in that the bond between the given pair of atoms is considered embedded in and dependent upon the surrounding matrix.[11] In this Letter an explicit many-body potential for the bond order between valence s orbitals is derived theoretically for the first time, and the importance of the three-body and four-body contributions to the topology of four-atom clusters demonstrated.

The total binding energy of a collection of s-valent atoms may be written in the form[12,13]

$$U=\tfrac{1}{2}\sum_{i,j\neq i}\Phi(R_{ij})+\tfrac{1}{2}\sum_{i,j\neq i}h(R_{ij})\Theta_{ij}\,, \tag{1}$$

where $\Phi(R_{ij})$ is the repulsive interaction energy and $h(R_{ij})\Theta_{ij}$ is the attractive covalent bond energy between atoms i and j. h is the $ss\sigma$ bond or hopping integral and Θ_{ij} is the bond order which is defined to be the difference between the number of electrons in the bonding $(1/\sqrt{2})\,|\phi_i+\phi_j\rangle$ and antibonding $(1/\sqrt{2})\,|\phi_i-\phi_j\rangle$ states. For the isolated dimer with one valence electron per atom the bond order of the singlet state is clearly 2. However, as we will see, the bond order will be reduced if the isolated dimer is embedded in a surrounding atomic matrix.

Tersoff[11] and Chelikowsky *et al.*[10] assumed particular forms for the bond-order dependence on the neighboring atomic environment. Here we will derive its analytic dependence explicitly by using the recursion method[14] to write the bond order as an integral over the difference of two continued fractions:

$$\Theta_{ij}=-\frac{2}{\pi}\,\mathrm{Im}\int^{E_F}[G_{00}^{+}(E)-G_{00}^{-}(E)]\,dE\,, \tag{2}$$

where the factor 2 outside the integral sign accounts for spin degeneracy. Im is the imaginary part of the bonding and antibonding Green's functions which are given by

$$\begin{aligned}G_{00}^{\pm}(E)&=\langle u_0^{\pm}\,|\,(E-H)^{-1}\,|\,u_0^{\pm}\rangle\\&=\cfrac{1}{(E-a_0^{\pm})-\cfrac{(b_1^{\pm})^2}{(E-a_1^{\pm})-\cdots}}\,,\end{aligned} \tag{3}$$

where $|u_0^{\pm}\rangle=(1/\sqrt{2})\,|\phi_i\pm\phi_j\rangle$. The coefficients are determined by the Lanczos[15] recursion algorithm, namely

$$b_{n+1}^{\pm}\,|u_{n+1}^{\pm}\rangle=H\,|u_n^{\pm}\rangle-a_n^{\pm}\,|u_n^{\pm}\rangle-b_n^{\pm}\,|u_{n-1}^{\pm}\rangle\,, \tag{4}$$

with the boundary condition that $|u_{-1}^{\pm}\rangle$ vanishes. The Hamiltonian H is, therefore, *tridiagonal* with respect to the recursion basis $|u_n^{\pm}\rangle$, having nonzero elements

$$\langle u_n^{\pm}\,|H|\,u_n^{\pm}\rangle=a_n^{\pm} \tag{5}$$

and

$$\langle u_{n+1}^{\pm}\,|H|\,u_n^{\pm}\rangle=b_{n+1}^{\pm}\,. \tag{6}$$

Thus, the Hamiltonian with respect to the bonding and antibonding recursion basis may be characterized by the semi-infinite linear chain[14] with site diagonal elements $a_n^{\pm}$ and intersite hopping matrix elements $b_{n+1}^{\pm}$, namely

$$\begin{array}{ccccccccccccc} a_0^{\pm} & & a_1^{\pm} & & a_2^{\pm} & & & & a_{n-1}^{\pm} & & a_n^{\pm} & & \\ \cdot & -b_1^{\pm}- & \cdot & -b_2^{\pm}- & \cdot & - & \cdots & - & \cdot & -b_n^{\pm}- & \cdot & - & \cdots\,. \\ 0 & & 1 & & 2 & & & & n-1 & & n & & \end{array}$$

From Eqs. (4)–(6) the first three recursion coefficients take the values

$$a_0^{\pm} = \pm h(R_{ij}) , \tag{7}$$

$$(b_1^{\pm})^2 = \tfrac{1}{2}(\hat{\mu}_2^i + \hat{\mu}_2^j) \pm \sum_{k \neq i,j} h(R_{ik}) h(R_{kj}) , \tag{8}$$

$$(b_1^{\pm})^2 a_1^{\pm} = \tfrac{1}{2}(\hat{\mu}_3^i + \hat{\mu}_3^j) + \sum_{k,l \neq i,j} h(R_{ik}) h(R_{kl}) h(R_{lj}) , \tag{9}$$

where $\hat{\mu}_2^{i(j)}$ and $\hat{\mu}_3^{i(j)}$ correspond to the second and third moments about the site i (j) in which the direct path linking the bond ij is excluded from the path-counting summation.

The first level of the continued fraction (3), namely $1/(E - a_0^{\pm})$, corresponds to the bonding and antibonding Green's functions for an isolated dimer which has eigenvalues of $\pm h(R_{ij})$ with respect to the free atomic energy level.[16] The second level of the continued fraction begins to reflect the influence of the first shell of neighbors about the bond on the bonding and antibonding Green's functions. We see that the three-membered- and four-membered-*ring* contributions are solely responsible for the differences between the bonding and antibonding recursion coefficients given by Eqs. (8) and (9).

A many-body form for the bond order may be derived by using perturbation theory to expand the bonding and antibonding Green's functions $G^{\pm}$ about the average Green's function $G^0 = \frac{1}{2}(G^+ + G^-)$. The Hamiltonian for the latter may be characterized by the semi-infinite linear chain

$$\begin{array}{ccccccccccc} a_0^0 & & a_1^0 & & a_2^0 & & & a_{n-1}^0 & & a_n^0 & \\ \cdot & -b_1^0- & \cdot & -b_2^0- & \cdot & - \cdots - & & \cdot & -b_n^0- & \cdot & - \cdots , \\ 0 & & 1 & & 2 & & & n-1 & & n & \end{array}$$

where a_n^0, b_n^0 are the continued-fraction coefficients of the average Green's function G_{00}^0. Therefore, comparing the semi-infinite linear chain corresponding to the bonding and antibonding recursion basis with this reference, we have[17] from the first-order Dyson equation

$$G_{00}^{\pm} = G_{00}^0 + \sum_{n=0}^{\infty} (\delta a_n \pm \delta \alpha_n) G_{0n}^0 G_{n0}^0 + 2 \sum_{n=1}^{\infty} (\delta b_n \pm \delta \beta_n) G_{0(n-1)}^0 G_{n0}^0 , \tag{10}$$

where $a_n^{\pm} = a_n^0 + \delta a_n \pm \delta \alpha_n$, $b_n = b_n^0 + \delta b_n \pm \delta \beta_n$. It should be noted that the recursion coefficients a_n^0, b_n^0 of the average Green's function are not in general equal to the average recursion coefficients $(a_n^+ + a_n^-)/2$, $(b_n^+ + b_n^-)/2$. Thus, δa_n and δb_n represent the degree to which the coefficients are not equal to the average coefficients. Substituting into Eq. (2), the bond order becomes

$$\Theta = -4 \left[\sum_{n=0}^{\infty} \chi_{0n,n0}(E_F) \delta \alpha_n + 2 \sum_{n=1}^{\infty} \chi_{0(n-1),n0}(E_F) \delta \beta_n \right] , \tag{11}$$

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

$$\chi_{0m,n0}(E_F) = \frac{1}{\pi} \operatorname{Im} \int^{E_F} G_{0m}^0(E) G_{n0}^0(E) dE . \tag{12}$$

The response functions are those for the reference semi-infinite linear chain with coefficients a_n^0, b_n^0. An analytic expression for them may be derived by taking the reference linear chain as that with zero on-site energies $a_n^0 = 0$ and constant hopping elements $b_n^0 = b_1^0 = b$, say. This will lead to errors of first order in a_n^0/b, $(b_n^0 - b)/b$ in the response function Eq. (12), and hence errors of only second order in the bond order Eq. (11). It follows from the Lanczos recursion algorithm Eq. (4) that

$$b = \left\{ \left[\sum_{k \neq i} h^2(R_{ik}) + \sum_{k \neq j} h^2(R_{jk}) \right] / 2 \right\}^{1/2} , \tag{13}$$

where b is taken to be the negative square root corresponding to $h = ss\sigma < 0$. The semi-infinite linear chain with constant hopping matrix elements b has Green's-function matrix elements given by[17]

$$b G_{0n}^0 = \exp[i(n+1)\phi] , \tag{14}$$

where $\cos\phi = E/2b$. Therefore substituting Eq. (14) into Eq. (12), we have $\chi_{0m,n0} = \hat{\chi}_{0m,n0}/|b|$ where the reduced susceptibility

$$\hat{\chi}_{0m,n0}(N) = \frac{1}{\pi} \left[\frac{\sin(m+n+1)\phi_F}{m+n+1} - \frac{\sin(m+n+3)\phi_F}{m+n+3} \right] , \tag{15}$$

with $\phi_F = \cos^{-1}(E_F/2b)$. ϕ_F is fixed by the number of electrons per atom N through[13]

$$N = (2\phi_F/\pi)[1 - (\sin 2\phi_F)/2\phi_F] . \tag{16}$$

Figure 1 shows the behavior of the first three reduced response functions $\hat{\chi}$ as a function of the number of elec-

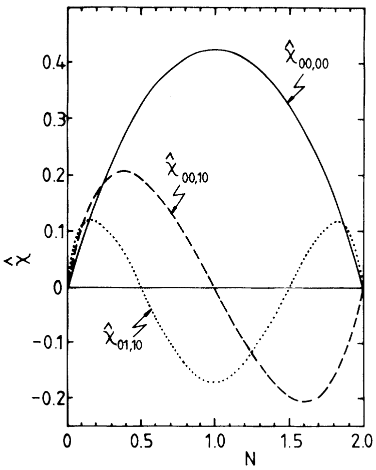

FIG. 1. The reduced susceptibilities as a function of the number of electrons per atom.

trons per atom N.

Finally, the many-body character of the bond order may be displayed explicitly by substituting the values of $\delta\alpha_0$, $\delta\alpha_1$, and $\delta\beta_1$ from Eqs. (7)–(9) into Eq. (11). To first order, using $\mu_3/\mu_2^{3/2} \ll 1$, we find

$$\Theta_{ij} = 4\left\{\hat{\chi}_{00,00}(N)[h(R_{ij})]/b + \hat{\chi}_{00,10}(N)\left[\sum_{k\neq i,j} h(R_{ik})h(R_{kj})\right]/b^2 + \hat{\chi}_{01,10}(N)\left[\sum_{k,l\neq i,j} h(R_{ik})h(R_{kl})h(R_{lj})\right]/b^3 + \cdots\right\}. \tag{17}$$

This is the *central result* of the Letter. The first term is similar to the embedding potentials of Daw and Baskes[2] and Finnis and Sinclair,[3] in that this contribution to the bond order may be written

$$\Theta_{ij}^{(2)} = 4\hat{\chi}_{00,00}(N)h(R_{ij})F((\rho_i+\rho_j)/2), \tag{18}$$

where the embedding function $F(\rho) = \rho^{-1/2}$ with the local "charge density" or "second moment" given by $\rho_i = \sum_{k\neq i} h^2(R_{ik})$. For nearest-neighbor interactions only, $\Theta_{ij}^{(2)} \propto 1/\sqrt{z}$, where z is the local coordination number, a well-known result within the second-moment approximation.[12] It accounts naturally for the back-bond strengthening factor which Chelikowsky *et al.*[10] found necessary to include for an accurate representation of both bulk and cluster silicon geometries.

$\Theta_{ij}^{(2)}$ involves only explicit two-body sums. We now demonstrate the importance of the three-body and four-body contributions to the bond order by considering the topology of a four-atom s-valent cluster. The total bond energies of the one-dimensional linear (l), two-dimensional square (s), and three-dimensional tetrahedral (t) clusters are shown in the left-hand panel of Fig. 2 as a function of the total number of valence electrons. The bond energies were obtained by diagonalizing the two-center Hückel secular equation with nearest-neighbor interactions only. The relative strengths of the hopping integrals $h_l{:}h_s{:}h_t$ were set by assuming that the equilibrium bond lengths of the individual clusters are such as to give identical second moments in the spirit of the structural-energy-difference theorem.[18] That is, $\mu_2 = 6h_l^2 = 8h_s^2 = 12h_t^2$ or $h_t = h/\sqrt{2}$, $h_s = \sqrt{3}h/2$, $h_l = h$. We see that the curves predict a change in structural stability from tetrahedral to linear to square as the total number of electrons in the cluster increases. The evaluation of the bond order directly using the appropriate recursion coefficients in Eq. (3) would, of course, give identical curves.

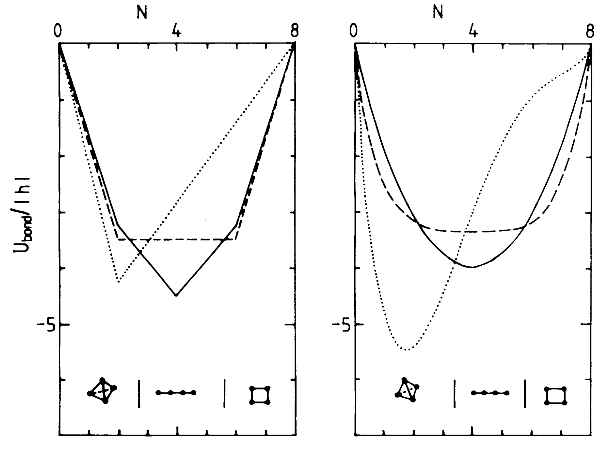

FIG. 2. The total bond energy as a function of the total number of electrons for a linear (full curves), square (dashed curves), and tetrahedral (dotted curves) cluster of four atoms. The left-hand panel gives the molecular-orbital result, whereas the right-hand panel shows the predictions of the many-body potential for the bond order.

The right-hand panel of Fig. 2 shows the predictions of the many-body potential approximation to the bond order. The linear cluster has no three-membered or four-membered rings, so that its behavior is controlled by the response function $\hat{\chi}_{00,00}$ in Fig. 1. However, each bond in the square cluster is associated with one four-membered ring so that there is an additional contribution from $\hat{\chi}_{01,10}$. This leads to the oscillatory behavior of the stability from square to linear to square observed in Fig. 2. On the other hand, each bond in the tetrahedral cluster is associated with two three-membered rings and two four-membered rings. The three-membered rings introduce the $\hat{\chi}_{00,10}$ response function which skews the binding curve towards small values of the electron number. It is the presence of these three-membered rings which favors the close-packed structures over the more open structures for monovalent, divalent, and trivalent sp-bonded elements.[19]

Thus, we see that the three-atom and four-atom contributions are essential for the correct prediction of the structural trends in Fig. 2. The perturbation theory has been performed with respect to a *continuum*-average Green's function so that it is not surprising that the agreement with the exact *cluster* results is only approximate. Chelikowsky *et al.*[10] has already found that their empirical bond-order predictions became progressively worse the smaller the cluster, the approximate and molecular-orbital binding energies differing by nearly a factor of 2 for a four-atom silicon cluster. Nevertheless the beauty of Eq. (17) is that it allows the bonds to be modeled reasonably accurately in *all* environments, from small clusters through to the infinite bulk, with the reduced response functions $\hat{\chi}$ being constants[20] independent of the bond environment. This could be a decisive advantage of this bond-order potential over other theoretically derived N-body potentials.[8]

In conclusion, a many-body potential has been derived for the bond order of s-valent systems. The importance of the three-body and four-body terms has been demonstrated. The simplicity of the potential's analytic form will allow the current use of embedded-atom potentials to be extended to include three-body and four-body terms. These could help remove problems in the accurate fitting of the surface energy, vacancy formation energy, and elastic anisotropy of fcc metals.[21] These potentials may be generalized to the case of sp-valent elements such as silicon or sd-valent elements such as molybdenum. The form of Eq. (17) remains unchanged except that the σ and π bond orders display explicit bond-angle dependence not only through the ring terms but also through the b defining the reference medium.[22] Results for sp-bonded systems will be presented elsewhere.[23]

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