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Generalized embedded-atom format for semiconductors

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A new type of total-energy functional for semiconductors is proposed, using a form based on an approximate quantum-mechanical analysis. Two new types of terms are included: pair terms giving a matrix description of an atom's local environment, and cluster terms describing the ring topology. The scheme reproduces both the covalent and metallic behavior of semiconductor materials in the appropriate limits. A parametrized form of the scheme is applied to Si.

Atomistic simulations of the materials properties of semiconductors are usually based on interatomic potentials which include angular forces. Several new types of interatomic potentials have been developed recently, particularly for Si.[1,2] However, the angular dependence of the forces has not been based on systematic quantum-mechanical analyses, but rather on physically motivated guesses. This has led to enormous variations in the depth and shape of the potentials,[2] and to poor results for some physical properties.[3] In this Rapid Communication, we present a format for total energies in semiconductors in which the angular dependence of the forces is derived quantum mechanically. This scheme is sufficiently general to treat both covalent bonding at low coordination numbers, and metallic bonding at high coordination numbers. It generalizes the "embedded-atom" format for metals[4,5] by including two new types of energy terms: (i) an energy associated with the nonspherical components of the local atomic environment, and (ii) cluster terms which include information about the ring topology. As in some other recent methods,[6-8] the total energy is not precisely given as a sum of interatomic potentials. We believe that ours is the most complete quantum-mechanical treatment suitable for atomistic simulations.[9]

The derivation of our energy functional utilizes a treatment of the electronic band energy

$$E_{\mathrm{el}}=\int_{-\infty}^{\varepsilon_F} E\rho(E)\,dE=\sum_i E_{\mathrm{el}}(i)=\sum_i \int_{-\infty}^{\varepsilon_F} E\rho_i(E)\,dE \tag{1}$$

based on low-order moments of the electronic density of states $\rho(E)$ in a one-electron tight-binding model with interatomic couplings $h_{ij}^{\alpha\beta}$, where i,j denote atomic positions, α,β are sp^3 orbital indices, and $\rho_i(E)$ is the site-projected density of states (DOS). The $h_{ij}^{\alpha,\beta}$ are assumed to have a two-center form with angular dependences given by the Slater-Koster relations.[10] The central quantity of the local environment correction is the second-moment matrix[11] $\hat{\mu}_2(i)$, given, for a particular site i, as a sum of pair terms:

$$\mu_2^{\alpha\beta}(i)=\langle i,\alpha\,|\,H^2\,|\,i,\beta\rangle=\sum_{j,\gamma} h_{ij}^{\alpha\gamma}h_{ji}^{\gamma\beta}\,. \tag{2}$$

"Embedded-atom" type schemes for metals have been derived[4] from the *scalar* second moment $\mu_2(i)=\mathrm{Tr}\hat{\mu}_2(i)$. Significantly more information is contained in $\hat{\mu}_2(i)$. For example, $\mu_2^{s,p_x}\neq 0$ only if the environment of atom i lacks x-inversion symmetry, as at a (100) surface. The vector $\boldsymbol{\mu}_2^{sp}=(\mu_2^{s,p_x},\mu_2^{s,p_y},\mu_2^{s,p_z})$ is analogous to the "dangling-bond vector" defined in Ref. 8.

Our method for obtaining the pair contribution $E_{\mathrm{el}}^{(2)}(i)$ to $E_{\mathrm{el}}(i)$ from $\hat{\mu}_2(i)$ is a matrix generalization of the scalar second-moment treatments.[4] The scalar treatments obtain $E_{\mathrm{el}}(i)\propto -[\hat{\mu}_2(i)]^{1/2}$. In our treatment this is replaced[12] by

$$E_{\mathrm{el}}^{(2)}=\sum_i E_{\mathrm{el}}^{(2)}(i)=-\sum_i \mathrm{Tr}[\hat{\mu}_2(i)]^{1/2}\,, \tag{3}$$

for materials with half-filled valence-band complexes. Justification for this functional form is obtained from an approximate electronic density of states generated by the recursion method. In the matrix version of this method,[13] the one-electron Green's-function matrix for the site i takes the form $\hat{G}_i(E)=[E-\hat{\mu}_2(i)/E]^{-1}$, where we have truncated the continued fraction at the first level. The corresponding density of states has δ-function peaks at $\pm\varepsilon_\mu$, where the ε_μ are the eigenvalues of $[\hat{\mu}_2(i)]^{1/2}$. Equation (3) then follows from Eq. (1), if the valence band is half-filled.

The form (3) for $E_{\mathrm{el}}^{(2)}$ can result in either covalent or metallic behavior in the appropriate limits:

(i) Covalent limit. In the diamond structure, if only nearest-neighbor sp^3 hybrids interact, $\hat{\mu}_2(i)$ has four degenerate eigenvalues equal to the bulk bond strength. When bonds are broken by, for example, creating a vacancy, each broken bond results in a zero eigenvalue on a neighboring atom. Thus the bond strengths are additive in this limit.

(ii) Metallic limit. If the number of neighbors is large, then the fractional change in the eigenvalues of $\hat{\mu}_2(i)$ resulting from breaking a single bond is small. One can show that $E_{\mathrm{el}}^{(2)}(i)$ is roughly proportional to the square root of the coordination number, in agreement with the scalar second moment treatments[4] for metals.

We have found that the fit to known values of defect energies in Si is improved by including an additional local environment term in the total energy. This term contains the self-energy of the electrostatic dipole that is created when an atom is placed in an environment lacking inversion symmetry. This dipole is roughly proportional to the asymmetry of the potential resulting from the local environment. This asymmetry, in turn, is measured by the *s-p* part of $\hat{\mu}_2(i)$. For example, if an atom in the $+x$ direction is displaced a small distance toward atom i and one in the $-x$ direction moves the same distance away from atom i, the vector $\mu_2^{s\text{-}p}$ points in the x direction and is linear in the displacement. Thus, since the dipole self-energy is proportional to the square of the dipole strength, we take this energy to have the form $E_{\text{dip}} = B \sum_i |\mu_2^{s\text{-}p}(i)|^2$, where B is an adjustable constant.

The cluster contributions $E_{\text{el}}^{(4)}(i)$ to $E_{\text{el}}(i)$ are based on the fourth moment $\mu_4(i)$ of $\rho_i(E)$. Methods based on $\mu_4(i)$ have previously been used for structural and defect properties of transition metals.[14,15] Our method differs from these through the use of the matrix $\hat{\mu}_2(i)$; in addition, we simplify the dependence of $E_{\text{el}}^{(4)}$ on $\mu_4(i)$. We have not included terms involving $\mu_3(i)$, because to first order these do not affect the bonding energies in systems, such as diamond structure semiconductors, which have half-filled *s-p* complexes.[16] Furthermore, the second-order contributions obtained by calculations[17] with model state densities are small. One has, rigorously,[18]

$$\mu_4(i) = \sum_{jkl} \sum_{\alpha\beta\gamma\delta} h_{ij}^{\alpha\beta} h_{jk}^{\beta\gamma} h_{kl}^{\gamma\delta} h_{li}^{\delta\alpha} \tag{4}$$

as a sum of two-, three-, and four-body paths. A small value of $\mu_4(i)/\mu_2(i)^2$ results from a DOS with two peaks surrounding a gap at roughly the center of the band. For larger values of $\mu_4(i)$, the gap fills in and the density of states has a metallic form.[2] Our prescription for including the effects of $\mu_4(i)$ is based on the idea that a gap in or lowering of the DOS at the Fermi level enhances the stability of a semiconductor.[19] This corresponds to reduced values of $\mu_4(i)$. We thus take

$$E_{\text{el}}^{(4)} = C \sum_i [\mu_4(i) - \mu_4^{(2)}(i)]/\mu_2(i)^{3/2} . \tag{5}$$

Here C is a positive constant, and $\mu_4^{(2)}(i) = \text{Tr}[\hat{\mu}_2(i)]^2$ is the contribution to μ_4 from paths in Eq. (4) with $i = k$. This part of $\mu_4(i)$ is subtracted off because the energy from it is already included in $E_{\text{el}}^{(2)}$. [For example, in a geometry such that all paths have $i = k$, the density of states $\rho_i(E)$ generated from $\hat{\mu}_2(i)$ already has the correct value of μ_4, and additional μ_4 terms would be double counted.] The normalizing factor of $\mu_2(i)^{3/2}$ is obtained from a quantum-mechanical analysis.[17]

Since the electronic contribution to the bonding energy is purely attractive, it is necessary to supplement the electronic terms by a repulsive term describing the Pauli repulsion at high densities. This we approximate by a pair potential V_2^{rep}, obtaining

$$E = \tfrac{1}{2} \sum_{i,j} V_2^{\text{rep}}(i,j) + E_{\text{el}}^{(2)} + E_{\text{dip}} + E_{\text{el}}^{(4)} . \tag{6}$$

As mentioned above, Eq. (6) is not precisely in the form of an interatomic potential series. However, since the various quantities entering the energy functional are sums of cluster terms, it is possible to define effective potentials, which describe the energy in a limited range of configuration space and are useful interpretive tools. We obtain these potentials via a straightforward matrix generalization of methods previously developed for the scalar case.[4,20-22] E is expanded in powers of the deviations of $\hat{\mu}_2(i)$ and $\mu_4(i)$ from their values in a uniform "reference environment." The three-body potential thus obtained, by a second-order treatment, has a separable form similar to that used by Stillinger and Weber (SW).[23] The radial functions are given in terms of the interatomic couplings and the angular dependence contains $\cos(\theta)^l$ terms with $l \leq 2$. However, the potential contains prefactors determined by the values of $\hat{\mu}_2$ and μ_4 in the reference environment, which make the potentials strongly environmentally dependent.

We have used the functional form of Eq. (6) to generate a semiempirical angular force scheme for Si. By the Slater-Koster relations,[10] the couplings in H [cf. Eq. (2)] are completely determined by four radial functions: $h_{ss}(r)$, $h_{sp}(r)$, $h_{pp\sigma}(r)$, and $h_{pp\pi}(r)$. To reduce the number of parameters we make the free-electron approximation[10] $h_{pp\pi} = -\frac{1}{4} h_{pp\sigma}$ and assume that $h_{sp} = |h_{ss} h_{pp\sigma}|^{1/2}$. Then h_{ss}, and $h_{pp\sigma}$, as well as $V^{\text{rep}}(r)$, are assumed to have a radial dependence of the form

$$h(r) = A \int \int \exp(-kr^2) dr - a + b(r_{\max} - r) ,$$

for $r < r_{\max}$, and $j(r) = 0$ for $r > r_{\max}$. Here a and b are chosen to eliminate discontinuities in $h(r)$ and $h'(r)$ at $r_{\max}$. This form guarantees a monotonic and rapid radial decay of the couplings as well as their first and second derivatives. Because the $E_{\text{el}}^{(4)}$ term involves four-body paths whose number grows very rapidly with $r_{\max}$, we have used a shorter value $r_{\max}^{<}$ of $r_{\max}$ for this term than the value $r_{\max}^{>}$ used in the $E_{\text{el}}^{(2)}$ and E^{dip} terms. The radii $r_{\max}^{>}$ and $r_{\max}^{<}$ were chosen to be 6.0 and 4.4 Å, respectively, so that the $r_{\max}^{<}$ terms include only first and second neighbors in the diamond structure. The values of the remaining parameters were obtained by a weighted least-squares fit to *ab initio* density functional (DF) values for the cohesive energies,[24,25] lattice constants,[24,25] and bulk moduli[25-27] in the diamond, graphitic (ideal c/a ratio), simple cubic, and fcc structures; the elastic constant $C_{44}^{(0)}$ in the absence of internal strain;[26] and the unrelaxed vacancy formation energy[28-30] $\varepsilon_{\text{vac}}^{\text{unrel}}$. The experimental value[31] for the zone-boundary phonon frequency $\omega_{\text{TA}}(X)$ was used as well. The values of the resulting parameters are $A_{ss} = 2.7742$ eV, $A_{pp\sigma} = 12.2794$ eV, $A_{\text{rep}} = 168.013$ eV; $k_s = 0.3866$ Å^{-1}, $k_{pp\sigma} = 0.3950$ Å^{-1}, $k_{\text{rep}} = 0.7894$ Å^{-1}; $B = 1.6073$ eV^{-3}; and $C = 0.3197$. The input data base quantities are fitted to within 20% in most cases; the worst discrepancies are $+32\%$ for $C_{44}^{(0)}$, $+25\%$ for the graphite versus diamond energy difference, and -24% for $\varepsilon_{\text{vac}}^{\text{unrel}}$.

Figure 1 shows the effective three-body potential V_3^{eff} using the diamond structure as a reference environment, along with the SW potential[23] V_3^{SW} for comparison. The angular dependence of V_3^{eff} is similar to that of V_3^{SW}, with

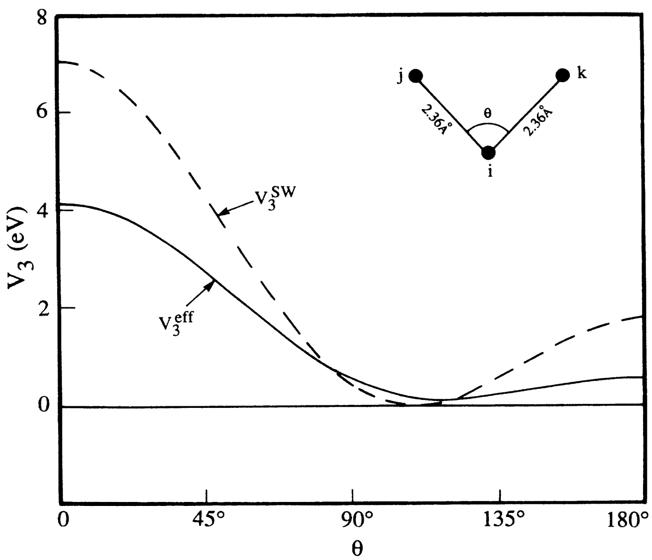

FIG. 1. Effective three-body potential V_3^{eff} obtained from our functional vs angle θ. Stillinger-Weber potential also included for comparison.

the minimum occurring at 118° vs 109° for the latter. The energy scale is roughly 50% smaller than that of V_3^{SW}. However, even this agreement can be considered to be fairly close; other types of empirical potentials that have been used often differ from V_3^{SW} by a factor of 5 or more.[2] The results to be presented below are obtained with the full energy functional rather than the potentials.

We have found that the angular terms are crucial in obtaining the correct values of both defect and bulk input properties. In the absence of these terms (using a scalar μ_2 treatment), we obtain $\varepsilon_{vac}^{unrel} = 1.5$ eV, only a third of the cohesive energy $|E_c^{dia}|$. The second-moment *matrix* terms raise this value to 3.5 eV, versus the DF value[28–30] of 4.5 eV. For the structural energy difference $\Delta E^{fcc\text{-}dia}$, both the scalar and matrix second-moment treatments give a negative value, but the cluster terms raise it to 0.57 eV (equal to the DF value). However, $|E_c^{dia}|$ is essentially unaffected by the angular terms.

We have not yet applied our total energy format to large-scale atomistic calculations. The results of some representative calibration tests for a structural energy, an elastic constant, and point defect properties are shown in Table I, and compared with results from DF calculations,[24,28,29,32] experiment,[33] the Stillinger-Weber potential,[3,7,34] the "Tersoff" format,[3,6,35,36] and the "Biswas-Hamann" format.[3,37,38] We choose the H-site interstitial because it perturbs the lattice more strongly than the T-site interstitial, and because the DF results for the relaxations are more consistent. For $\Delta E^{bcc\text{-}dia}$ and the interstitial properties, the present format gives agreement with the DF results equal to or better than than that of the other formats. We note that even obtaining the correct sign and rough magnitude of $\Delta E^{bcc\text{-}dia}$ and $\varepsilon_{I,H}^{f}$ is not guaranteed by the inclusion of plausible angular terms.[35–37] However, our value for C_{44} is more than 50% too low. This probably results from too large a value of the internal strain parameter η; we obtain $\eta = 0.98$ versus the experimental value[39] of 0.73. Since one expects elastic constants to be strongly influenced by long-range electrostatic interactions, it is not surprising that short-ranged schemes such as the present one have had difficulties obtaining them correctly.[3,6]

In summary, we have found that even a crude quan-

TABLE I. Calculated bulk and defect properties for Si; $\Delta r/r$ denotes fractional nearest-neighbor relaxations around hexagonal-site interstitial. Values in parentheses for Tersoff and Biswas-Hamann formats are obtained with initial versions of these.

	$\Delta E^{bcc\text{-}dia}$ (eV)	C_{44} (Mbar)	$\varepsilon_{I,H}^{f}$ (eV)	$\Delta r/r$ (%)
Present	0.65	0.36	3.9	8
DF or expt.	0.53 [a]	0.80 [b]	4–6 [c]	5–7 [d,e]
Stillinger-Weber	0.25 [f]	0.56 [g]	6.5 [h]	15 [h]
Tersoff	0.63 [i] (−1.0 [j])	0.10 [i] (0.39 [g])	4.5 [i] (∼0 [k])	(5 [k])
Biswas-Hamann	0.32 [l] (0.70 [m])	(0.92 [g])	5.1 [l] (1.3 [l])	

[a] Reference 24.

[b] Reference 33.

[c] Reference 28. We have included a margin of error of up to −2 eV on the basis of the DF results for the vacancy formation energy, which have dropped 1-2 eV since the publication of Ref. 28 [R. Car (private communication)].

[d] Reference 32.

[e] Reference 29.

[f] Reference 7.

[g] Reference 3.

[h] Reference 34.

[i] Reference 6.

[j] Reference 35.

[k] Reference 36.

[l] Reference 37.

[m] Reference 38.

tum-mechanical analysis yields a total-energy format which contains many of the features intuitively expected for angular forces in semiconductors, including a natural transition from covalent to metallic bonding. In addition to justifying some of the terms used in previous types of energy functionals, the format developed here has been shown to yield a total energy scheme for Si which is similar in accuracy to the best empirical energy functionals presently available.

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