Analytic Environment-Dependent Tight-Binding Bond Integrals: Application to MoSi$_2$

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We present the first derivation of explicit analytic expressions for the environmental dependence of the σ, π, and δ bond integrals within the orthogonal two-center tight-binding approximation by using the recently developed bond-order potential theory to invert the nonorthogonality matrix. We illustrate the power of this new formalism by showing that it not only captures the transferability of the bond integrals between elemental bcc Mo and Si and binary $C11_b$ MoSi$_2$ but also predicts the absence of any discontinuity between first and second nearest neighbors for the $dd\sigma$ bond integral even though large discontinuities exist for $pp\sigma$, $pp\pi$, and $dd\pi$.

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The past decade has witnessed an explosion in the number of applications of the tight-binding (TB) model to simulating the structural and cohesive properties of materials [1]. This is due to the TB model being the simplest scheme that includes correctly the underlying quantum mechanical character of the covalent bond. However, although the *semiempirical* TB method is 2 to 3 orders of magnitude faster than *ab initio* density functional methods, it suffers from the uncertainty of how best to choose the TB parameters that enter the scheme. In particular, it is now realized that an orthogonal TB model, which is robust and transferable to various different situations, requires the two-center TB parameters [2] to be environment dependent [3–13]. This unfortunately leads to the introduction of many additional fitting parameters, so that the application of an environmentally dependent TB method to multicomponent systems becomes formidable. Thus, to date no applications have been made in technologically important areas such as the CVD growth of diamond films or the mechanical properties of high-temperature intermetallics.

In this Letter, we show that it is possible to derive an analytic expression for this environmental dependence by starting from the nonorthogonal two-center TB representation and using our recently developed bond-order potential (BOP) theory [14] to invert the nonorthogonality matrix. We will see that the angular character of the bond that is being screened plays a key role in the functional form of the resultant environmental dependence. We will illustrate the technique by considering the transferability of the bond integrals between elemental bcc Mo and Si and binary MoSi$_2$, the latter being an important high-temperature intermetallic [15].

The most successful *ad hoc* scheme for introducing environmental dependence into the TB parameters is that of the Ames group [10–13]. They write the screened two-center bond integrals between a given pair of atoms i and j, a distance R_{ij} apart, in the form

$$\tilde{\beta}_{ll'\tau}^{ij} = \beta_{ll'\tau}(\kappa R_{ij})(1 - S_{ll'\tau}^{ij}), \qquad (1)$$

where the screening function $S_{ll'\tau}^{ij}$ is a hyperbolic tangent with argument $\xi_{ll'\tau}^{ij}$ given by

$$\xi_{ll'\tau}^{ij} = A_{ll'\tau} \sum_{k \neq i,j} \exp\left[-\lambda_{ll'\tau}\left(\frac{R_{ik} + R_{kj}}{R_{ij}} \right)^{\eta_{ll'\tau}} \right], \quad (2)$$

with $l, l' = s$, p, or d, $\tau = \sigma$, π, or δ, and A, λ, and η as fitting parameters. $\beta(\kappa R_{ij})$ represents the two-center bond integral between orbitals on sites i and j that have already been renormalized [16] or contracted [17] by the presence of their surrounding neighbors so that κ is not a constant but is dependent on the local atomic density or effective coordination about the bond. The screening function S^{ij} represents the fact that the bonding between a given pair of atoms i and j is weakened by the presence of a third atom k in their vicinity. It accounts for the large discontinuity that is observed in the fitted $ss\sigma$ bond integral curve between first and second nearest neighbors in elemental bcc molybdenum [11]. By a careful fitting of parameters, the Ames group were able to reproduce the electronic structure and binding energy curves of C and Si over a wide range of coordinations [10,12]. However, although this TB parametrization has been highly successful in modeling elemental systems such as self-diffusion on silicon surfaces [12] or laser ablation of diamond surfaces [13], it has not been extended to multicomponent systems due to the rapid increase in the number of *ad hoc* fitting parameters.

We will, therefore, derive the analytic form of the screening function by starting from the *nonorthogonal* two-center TB representation. Its secular equation takes the form

$$(H - \epsilon_n S)c_n = 0, \qquad (3)$$

where S is the nonorthogonality matrix with components $S_{iL,jL'}^{\mu\nu} = \langle i\mu lm \mid j\nu l'm' \rangle$. μ and ν label the chemical species at sites i and j, respectively, and lm, $l'm'$ denote real cubic harmonics. We can think of the orbitals $\mid i\mu l\rangle$ and $\mid j\nu l'\rangle$ as already having been renormalized by their local environment [9,16,17] but we will not consider this

effect explicitly in this Letter. Within the two-center approximation the elements of the Hamiltonian matrix H can be written in terms of the fundamental two-center bond integrals and the usual Slater-Koster angular functions [2]. The bond integrals take the physically transparent form $\beta_{ll'\tau}^{\mu\nu} = \langle i\mu l\tau|\frac{1}{2}(V_i^\mu + V_j^\nu)|j\nu l'\tau\rangle$ provided that the zero of energy is chosen as the average on-site energy $\frac{1}{2}(H_{il,il}^{\mu\mu} + H_{jl',jl'}^{\nu\nu})$ [3,18], where V_i^μ and V_j^ν are the atomic potentials at sites i and j, respectively.

The *orthogonal* two-center TB secular equation, therefore, can be written in the form

$$(S^{-1}H - \epsilon_n I)c_n = 0, \qquad (4)$$

where I is the unit matrix. In general, $S^{-1}H$ is not Hermitian [19] but for real matrix elements it can be expressed as the sum of symmetric and antisymmetric contributions

$$S^{-1}H = \frac{1}{2}(S^{-1}H + HS^{-1}) + \frac{1}{2}(S^{-1}H - HS^{-1}). \qquad (5)$$

For s valent systems, if we make the common Wolfsberg-Helmholtz approximation that $\beta_{ss\sigma} = -AS_{ss\sigma}$ [18] and assume that all sites have the same on-site energy, then $SH = HS$ and the antisymmetric contribution vanishes. We will assume that this is true in general, so that our orthogonal two-center TB secular equation is given by

$$(\tilde{H} - \epsilon_n I)c_n = 0, \qquad (6)$$

where our screened Hamiltonian matrix $\tilde{H} = \frac{1}{2}(S^{-1}H + HS^{-1})$ is symmetric [20].

In this Letter, we are interested in the environmental dependence of the *intersite* bond integrals. Within the tight-binding bond model [21] the on-site energies are adjusted self-consistently for local charge neutrality (as is appropriate for metallic systems such as the molybdenum silicides), and the on-site nonorthogonality shifts are incorporated into the repulsive term to the binding energy [9,17]. These will be discussed elsewhere [22]. By writing $S = I + O$ where O is the overlap matrix, the intersite screened Hamiltonian matrix elements can be written as

$$\tilde{H}_{i,j} = H_{i,j}[(I + O)_{i,i}^{-1} + (I + O)_{j,j}^{-1}]/2$$
$$+ \sum_k'[H_{i,k}(I + O)_{k,j}^{-1} + (I + O)_{i,k}^{-1}H_{k,j}]/2, \qquad (7)$$

where, for compactness, L, L', and L'' have been absorbed into i, j, and k and the chemical species labels μ and ν have been omitted. The prime in the summation denotes summing over all atomic sites $k \neq i \neq j$. We have neglected terms involving differences in the on-site energies E_l^μ. However, these are expected to be small for the molybdenum silicides since for $MoSi_2$, $E_p^{Si} - E_d^{Mo} = 1.7$ eV compared to a pd bandwidth of 18 eV.

The elements of the inverse matrix $(I + O)^{-1}$ may be obtained directly from our recently developed BOP theory

[14]. This expresses the elements of the Green's function matrix $G(E) = (EI - H)^{-1}$ in a rapidly convergent real-space manner by imposing the physical constraint that at any level of approximation the poles of the intersite Green's function G_{ij} are the same as those of the average on-site Green's function $(1/2)(G_{ii} + G_{jj})$. Putting [23] $E = 1$ and $H = -O$ within this constrained BOP formalism to three-levels of Lanczos recursion [14], we find that the inverse matrix elements can be written as

$$[(I + O)_{i,i}^{-1} + (I + O)_{j,j}^{-1}]/2 = 1 + (\overline{\mu}_2 - \overline{\mu}_3)$$
$$/\det(I + O)_{\mathcal{L}3} \qquad (8)$$

and

$$(I + O)_{i,j}^{-1} = (-O_{i,j} + \sum_k' O_{i,k}O_{k,j})/\det(I + O)_{\mathcal{L}3}. \qquad (9)$$

The average pth moment, $\overline{\mu}_p = (1/2)(\mu_p^i + \mu_P^j)$, can be expressed in terms of all of the self-returning paths of length p that start and end on atom i and atom j, respectively, since $\mu_p^k = \langle k|\hat{O}^p|k\rangle$, where $\hat{O}$ is the overlap operator. As might be expected for the inverse of a matrix, the denominator in Eqs. (8) and (9) is just the determinant of the nonorthogonality matrix with respect to the appropriate Lanczos basis [14]. It takes the form

$$\det(I + O)_{\mathcal{L}3} = 1 + O_{i,j}^2 - 2\overline{\mu}_2 + \overline{\mu}_3, \qquad (10)$$

where the label $\mathcal{L}3$ reminds us that we have evaluated the determinant to *three* levels within the constrained BOP formalism [24]. We will see later in Fig. 1 that working to three levels is sufficient for an accurate representation of the screened bond integrals. We must stress, however, that the above approximation is *exact* for the inversion of 3×3 matrices such as would arise for the *three-atom s*-valent trimer, for example. The corresponding Löwdin expansion [4], on the other hand, would have replaced the determinant in the denominator of Eqs. (8) and (9) by unity which, for most materials, is a poor approximation as the overlap integrals are not small.

The screening function in Eq. (1) may now be obtained explicitly by substituting Eqs. (8) and (9) into Eq. (7) and by using the rotation matrices for the s, p, and d orbitals. We find

$$S_{ll'\tau}^{ij} = \frac{(c_1^{ij})_{ll'\tau} - (\overline{\mu}_2)_{ll'\tau} + (\overline{\mu}_3)_{ll'\tau}}{1 + O_{ll'\tau}^2(R_{ij}) - 2(\overline{\mu}_2)_{ll'\tau} + (\overline{\mu}_3)_{ll'\tau}}, \qquad (11)$$

where the ith atom second-moment contribution is

$$(\mu_2^i)_{ll'\tau} = O_{ll'\tau}^2(R_{ij}) + \sum_{k\neq i,j}[(1 + \delta_{\tau0})/2]O_{ls\sigma}^2(R_{ik})g_{l\tau}^2(\theta_{jik})$$

and the ith atom third-moment contribution is

$$(\mu_3^i)_{ll'\tau} = \sum_{k\neq i,j}(1 + \delta_{\tau0})O_{ikji}^3 g_{l\tau}(\theta_{jik})g_{l'\tau}(-\theta_{ijk}),$$

with $O^3_{ikji} = O_{ls\sigma}(R_{ik})O_{sl'\sigma}(R_{kj})O_{l'l\sigma}(R_{ji})$. θ_{jik} is the angle between bond ij and ik. The angular functions are defined by $g_{0\sigma}(\theta) = 1$; $g_{1\sigma}(\theta) = \cos\theta$, $g_{1\pi}(\theta) = \sin\theta$;

$g_{2\sigma}(\theta) = (1/4)(1 + 3\cos2\theta)$, $g_{2\pi}(\theta) = (\sqrt{3}/2)\sin2\theta$, $g_{2\delta}(\theta) = (\sqrt{3}/4)(1 - \cos2\theta)$. c^{ij}_1 is the interference contribution linking orbitals $|i\mu l\tau\rangle$ and $|j\nu l'\tau\rangle$, namely,

$$(c^{ij}_1)_{ll'\tau} = \sum_{k \neq i,j} [(1 + \delta_{\tau 0})/4]\{[\beta_{ls\sigma}(R_{ik})O_{sl'\sigma}(R_{kj}) + O_{ls\sigma}(R_{ik})\beta_{sl'\sigma}(R_{kj})]g_{l\tau}(\theta_{jik})g_{l'\tau}(-\theta_{ijk})$$
$$- [\beta_{ls\sigma}(R_{ik})O_{sl\sigma}(R_{ki})O_{ll'\tau}(R_{ij})g^2_{l\tau}(\theta_{jik})$$
$$+ O_{ll'\tau}(R_{ij})O_{l'l\sigma}(R_{jk})\beta_{sl'\sigma}(R_{kj})g^2_{l'\tau}(\theta_{ijk})]\}/\beta_{ll'\tau}(R_{ij}).$$

We see that for the $ss\sigma$ bond c^{ij}_1 is not too dissimilar in form to that suggested by the Ames group in Eq. (2). Our expression for the screening function has been evaluated by assuming that the screening of the ij bonds is carried out via the valence s orbitals on the neighboring sites k. This has been shown to be a good approximation within screened (LMTO) theory, where the valence p and d contributions to the screening are found to be much weaker than the s [4]. We have also neglected all four-body contributions to Eq. (11). In addition, we have assumed that the determinants entering the off-diagonal ik and kj elements in Eq. (7) are the same as that of the ij bond in

whose screening we are interested in. The determinants in the denominator of the elements of the inverse matrix would, of course, be identical if all of the nonvanishing terms within the Lanczos-type BOP expansion had been retained [14].

Equation (11) is the key result of this Letter. It is exact for the s valent dimer and trimer. For the dimer there are no three-membered ring contributions so that $S = -b^2_1/(1 - b^2_1)$ where $b^2_1 = O^2$. Therefore $\tilde{\beta}_{ss\sigma}/\beta_{ss\sigma} = 1/(1 - O^2) > 1$; i.e., within the orthogonal TB representation we find *antiscreening* of the original bond integral. For the equilateral trimer, it follows from Eqs. (1) and (11) that $\tilde{\beta}_{ss\sigma}/\beta_{ss\sigma} = 1/(1 + O - 2O^2)$ so that the effective bond integral is *screened* provided $O < 1/2$.

The power of this novel analytic screening function will be demonstrated by considering the environmental dependence of the bond integrals in elemental bcc Mo, model bcc Si, and the binary bcc-related $C11_b$ MoSi$_2$. In particular, we are interested in the behavior of the bond integrals between the valence p orbitals on Si and the d orbitals on Mo because the TB pd bond model has been shown to provide an excellent description of the structural trends within the transitional metal-sp valent binary compounds [25], the defect energetics of the titanium aluminides [6], and the key bonding behavior in the molybdenum silicides [26,27]. The points in Fig. 1 show the *numerical* values for the appropriate σ and π bond integrals. They were computed by solving Dyson's equation in real space for the screened LMTO structure constants within the short-range (α_s, α_p, α_d) representation [4] that leads to vanishing bond integrals at third nearest neighbors and beyond. The points corresponding to the first and second nearest neighbors were obtained at $(0.9, 1.0, 1.1)\Omega_0$, where Ω_0 is the equilibrium volume. These numerical points illustrate two important features of the environmental dependence of the bond integrals. First, we see that there is a large discontinuity between the first and second nearest neighbors for the $pp\sigma$, $pp\pi$, and $dd\pi$ bond integrals, but that this discontinuity is absent for $dd\sigma$. Second, we see that there is a noticeable environmental dependence in the behavior of the first nearest neighbor $pp\pi$ bond integral in going from elemental bcc Si to binary $C11_b$ MoSi$_2$.

Both of these features are contained within our *analytic* screening function. For simplicity [28] we have taken $\beta^{\mu\nu}_{ll'\tau}(R_{ij}) = A^{\mu\nu}_{ll'\tau} \exp(-\lambda^{\mu\nu}_{ll'\tau}R_{ij})$ and $O^{\mu\nu}_{ll'\tau} = -\beta^{\mu\nu}_{ll'\tau}/|A^{\mu\nu}_{ll'\tau}|$ and assumed that they cut off before the third neighbors. The values of A and λ were obtained
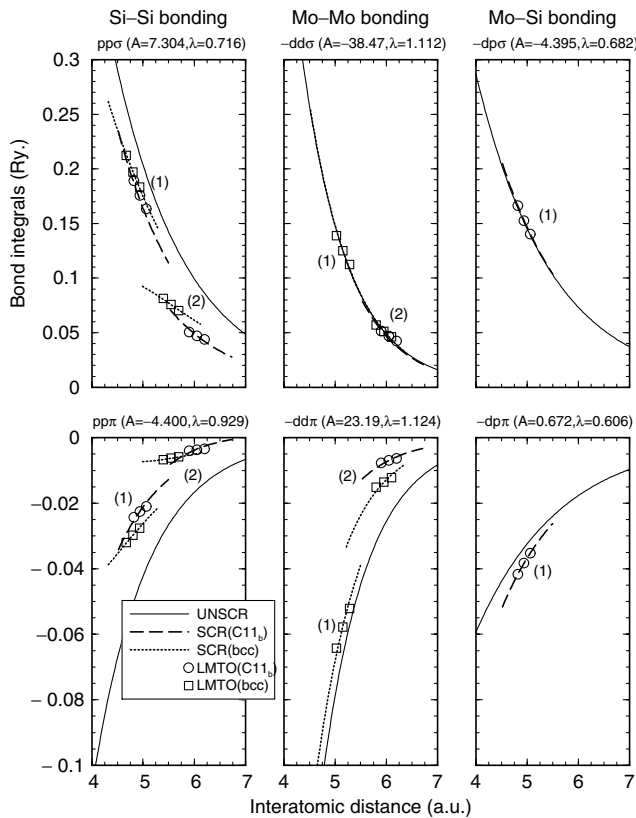

FIG. 1. The σ and π bond integrals within elemental bcc Mo and bcc Si and within binary $C11_b$ MoSi$_2$. The analytic unscreened (solid curves) and screened results for the $C11_b$ structure (dashed curves) and bcc structure (dotted curves) are plotted. The numerical screened LMTO values are presented by the circles and squares for the $C11_b$ and bcc structures, respectively. (1) and (2) label the first and second nearest neighbor curves, respectively.

by fitting the first and second nearest neighbor screened LMTO points. The resultant *unscreened* bond integrals β are shown by the solid curves in Fig. 1 with appropriate values of A and λ recorded above each panel. The corresponding *s*-valent screening overlap integrals have exponents $\lambda_{sd\sigma}^{MoMo} = 0.602$, $\lambda_{sp\sigma}^{SiSi} = 0.626$, $\lambda_{ds\sigma}^{MoSi} = 0.690$, $\lambda_{ps\sigma}^{SiMo} = 0.395$. As expected, the *dd* bond integrals have approximately the same exponents with the ratio $A_\sigma : A_\pi : A_\delta = -6.0 : 3.6 : -0.8$ being close to that of the canonical ratio $A_\sigma : A_\pi : A_\delta = -6 : 4 : -1$ [4].

The *screened* analytic curves in Fig. 1 reproduce the numerical screened LMTO values very well. In particular, they display the large discontinuity between the first and second nearest neighbors in $pp\sigma$, $pp\pi$, and $dd\pi$, whereas they display no discontinuity in $dd\sigma$. This behavior can be traced directly to the angular dependence of the screening function which is absent in the empirical form of Eq. (2). The bcc lattice (and the closely related $C11_b$ lattice) have nearest neighbor bond angles of $\cos^{-1}(1/\sqrt{3})$ so that $g_{2\sigma} = (1/4)(1 + 3\cos 2\theta)$ vanishes identically, causing the surrounding neighbors to leave the $dd\sigma$ bond unscreened. On the other hand, the second nearest neighbor $dd\pi$ bond is heavily screened, both its magnitude and slope being reduced by a factor of 3. This is critical for the behavior of the second nearest neighbor force constants and removes the problem of the unstable $T2$ phonon mode at the N point that is found in most two-center TB fits. For the case of bcc Mo, by using unscreened bonding integrals we find that $\omega_N(T2) = 1.0$ THz, $\omega_N(T1) = 6.3$ THz, $\omega_N(L) = 5.2$ THz [29], whereas within the present formalism the corresponding values of 3.6, 5.9, and 8.3 THz are consistent with the experimental values of 4.5, 5.8, and 8.1 THz, respectively [22].

In conclusion, we have derived an explicit expression for the screening function that reflects the environmental dependence of the two-center σ, π, and δ bond integrals within an orthogonal TB representation. This provides the first reliable method for predicting the analytic behavior of transferable TB bond integrals and will help extend the accuracy and applicability of the TB model to technologically important multicomponent systems.

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