

General expressions for reducing the Slater-Koster linear combination of atomic orbitals integrals to the two-center approximation

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This paper contains a derivation of general expressions for reducing Slater-Koster integrals $E_{ij}(l, m, n)$ to the two-center approximation for orbitals i (and j) having arbitrary angular momentum quantum numbers; l, m, n describe the location of one center relative to the other. This has allowed the author to check the entries in Table I of the Slater-Koster paper and provides a means for extending these entries to include states of higher angular momenta. The derived general expressions are especially useful for machine calculations when a large number of particular expressions are required to be evaluated. As a collateral result the missing factors in the energy matrix elements along the Δ line for the face-centered cubic structure given by Slater and Koster and reviewed by Reitz have been noted.

I. INTRODUCTION

The linear combination of atomic orbitals (LCAO) method, or the tight-binding approach, has been thoroughly discussed by Slater and Koster¹ in application to cubic crystals. It is well known that the tight-binding approach is a simplified version and offers intuitive interpretation of the electronic energy bands of solids. This method has been systematically used in recent years to study a wide variety of problems connected with crystalline solids,¹⁻¹⁰ surfaces,^{11,12} amorphous structures,¹³⁻¹⁷ and highly concentrated alloys¹⁸ as a semiempirical interpretation scheme both alone as well as in combination with plane waves in mixed-basis methods. It has been found useful in studying the magnetic properties, metal-insulator transitions, correlation effects, elastic constants, electron-phonon couplings, lattice defects, latent heat of phase changes, etc. For recent developments in LCAO technique as applied to various systems one may refer to the articles by Friedel¹⁹ and Callaway.²⁰

The LCAO method, consistent with the original idea of Slater and Koster,¹ yields energy bands throughout the Brillouin zone by matching energy values at some symmetry points in conjunction with more accurate calculations obtained from other methods (such as APW, OPW, cellular methods, etc.) or fitting with available experimental data. Usually, the two-center integrals involving the atomic orbitals are used as fitting parameters. The energy matrix components are therefore put in terms of such integrals.¹⁻¹⁷ To the end, one adopts Table I of Slater and Koster¹ which expresses the matrix components between the s , p , and d symmetry orbitals as a linear combination of two-center integrals with coefficients in the expansion referred to here as Slater-Koster co-

efficients.

The intent of this paper is to report the general expressions in the two-center approximation for the Slater-Koster energy integrals (or the associated coefficients) which supplement Table I of Slater and Koster and are valid for all values of the angular-momentum quantum numbers. To demonstrate the convenience and use of the general expressions we have presented the derivation of some new energy integrals which involve orbitals with particularly high angular momenta. The derived expressions not only obviate the necessity of handling the energy components separately and thereby reduce the complicity and hardship of their individual derivations but also avoids concomitance of possible errors. Further, our general expressions have been used to check all the particular expressions listed in Table I of Slater and Koster. In the process of checking, as a collateral result we have discovered corrections in some of the expressions for the energy matrix elements along Δ line for the face-centered cubic structure as given by Slater and Koster¹ and reviewed by Reitz.²¹

In Sec. II we present details for the derivation of the general expressions. The deduction of the new results from the general expressions for large angular-momentum quantum numbers and comparison with the Slater-Koster results are presented in Sec. III. Discussion and conclusion are given in Sec. IV.

II. DERIVATION OF THE GENERAL EXPRESSIONS

We consider the most general case of a three-dimensional lattice with unit cells containing a number of basis atoms or ions. If H is the Hamiltonian operator of the system, the energy-matrix components between the Bloch states desig-

nated by μ and ν can be expressed as¹

$$(\mu/\nu)_{\omega',\omega} = \exp[i\vec{k} \cdot (\vec{\tau}_{\omega'} - \vec{\tau}_{\omega})] \\ \times \sum_i \exp(i\vec{k} \cdot \vec{R}_i) \\ \times \int \phi_{\mu}^*(\vec{r} - \vec{\tau}_{\omega'}) H \phi_{\nu}(\vec{r} - \vec{R}_i - \vec{\tau}_{\omega}) d^3r, \quad (1)$$

where \vec{R}_i are the translation vectors; $\vec{\tau}_{\omega}$ (or $\vec{\tau}_{\omega'}$) are the basis vectors; $\phi_{\nu}(\vec{r} - \vec{R}_i - \vec{\tau}_{\omega})$ are the atomic orbitals (or equivalent orbitals such as Lowdin's orthogonalized orbitals²²) localized at the site $\vec{\tau}_{\omega}$ inside the cell located at \vec{R}_i ; $\phi_{\mu}(\vec{r} - \vec{\tau}_{\omega'})$ are the atomic orbitals localized at $\vec{\tau}_{\omega'}$ in the unit cell at the origin.

In LCAO method one is required to evaluate the energy-matrix elements of Eq. (1) to diagonalize the associated secular equation for obtaining the energy bands of the system under consideration. In terms of the usual notations one defines

$$E_{\mu,\nu}(\vec{\tau}_{\omega'}, \vec{R}_i + \vec{\tau}_{\omega}) = \int \phi_{\mu}^*(\vec{r} - \vec{\tau}_{\omega'}) H \phi_{\nu}(\vec{r} - \vec{R}_i - \vec{\tau}_{\omega}) d^3r, \quad (2)$$

which are known as the energy integrals (or E integrals). These integrals can be approximated in terms of the radial two-center integrals as demonstrated by Slater and Koster with coefficients which will be referred to as Slater-Koster coefficients. The process of expressing the E integrals in terms of the two-center integrals consists of rotating the axis systems and transforming the spherical harmonics in one set of axes into spherical harmonics corresponding to another set. The expressions for s , p , and d orbitals have been constructed in Ref. 1 by repeating the process for every pair of orbitals. This is a time-consuming process particularly when the angular momenta of the orbitals involved are large.

In the following we develop general expressions for the E integrals which are valid for all angular momenta concerned with the aim of eliminating the repetitional process for every set of new orbitals.

Since various authors employ real as well as complex orbitals depending on the convenience and the physical problem involved it is necessary to present expressions which are useful for both types of orbitals.

For this purpose we define

$$W_{j_1 m_1, j_2 m_2}(\vec{\tau}_{\omega'}, \vec{R}_i + \vec{\tau}_{\omega}) = \langle j_1 m_1 | H | j_2 m_2 \rangle, \quad (3)$$

in which

$$|j_1 m_1\rangle = u(r) Y_{j_1}^{m_1}(\theta, \phi), \quad (4a)$$

and

$$|j_2 m_2\rangle = v(R) Y_{j_2}^{m_2}(\Theta, \Phi). \quad (4b)$$

Equation (3) differs from Eq. (2) in the sense that Eq. (3) contains complex orbitals, whereas Eq. (2), as it is defined in Ref. 1, contains real orbitals. The orbitals $|j_1 m_1\rangle$ are supposed to be localized at $\vec{\tau}_{\omega'}$ and $|j_2 m_2\rangle$ at $\vec{R}_i + \vec{\tau}_{\omega}$. Other quantum numbers of the orbitals have been suppressed for convenience. $u(r)$ and $v(R)$ are the appropriate radial parts of the orbitals $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ which are measured with respect to the axes systems xyz with origins at $\vec{\tau}_{\omega'}$ and $\vec{R}_i + \vec{\tau}_{\omega}$, respectively. The orientation of the xyz system has been assumed to be the same at the two locations (see Fig. 1). r, θ, ϕ are the coordinates of an electron in the xyz axes system with origin at $\vec{\tau}_{\omega'}$, whereas R, Θ, Φ are the coordinates in the xyz system with origin at $\vec{R}_i + \vec{\tau}_{\omega}$.

Making use of the rotation groups²³

$$|j_1 m_1'\rangle = \sum_{m_1} D_{m_1', m_1}^{(j_1)}(\alpha\beta\gamma) |j_1 m_1\rangle, \quad (5)$$

with $D_{m', m}^{(j)}(\alpha\beta\gamma)$ as the rotation-group elements with $\alpha\beta\gamma$ as the Eulers angles for the rotation of the old axes system (xyz) into a new axes system ($x'y'z'$) where the z' axis is the direction pointing from the origin A at $\vec{\tau}_{\omega'}$ to the origin B at $\vec{R}_i + \vec{\tau}_{\omega}$. (See Fig. 1.) In Eq. (5) $|j_1 m_1'\rangle$ represents the orbitals with respect to the new frame of reference $x'-y'-z'$ with origin at $\vec{\tau}_{\omega'}$.

Analogously,

$$|j_2 m_2'\rangle = \sum_{m_2} D_{m_2', m_2}^{(j_2)}(\alpha\beta\gamma) |j_2 m_2\rangle, \quad (6)$$

where the symbols carry similar meanings. In Eq. (6) $|j_2 m_2'\rangle$ are the orbitals with respect to the new frame of reference $x'-y'-z'$ with origin at $\vec{R}_i + \vec{\tau}_{\omega}$. Substitutions of the expressions of Eqs. (5) and (6) for $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ in Eq. (3) yields

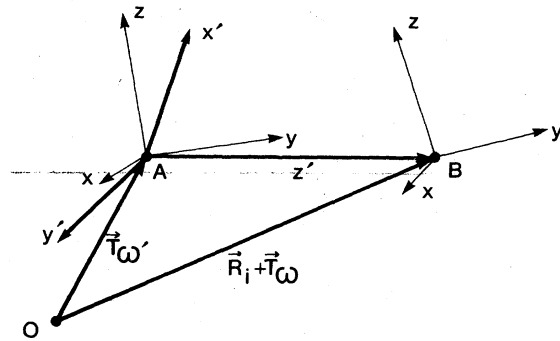


FIG. 1. Depicts the axes systems x, y, z and x', y', z' . The axes systems x', y', z' at A and B (where the atoms are located) are oriented parallel. $\vec{\tau}_{\omega}$ and $\vec{\tau}_{\omega'}$ are the basis vectors and \vec{R}_i is a translation vector.

$$W_{j_1 m_1, j_2 m_2}(\vec{r}_\omega, \vec{R}_i + \vec{r}_\omega) = \sum_{m'_1, m'_2} D_{m'_1, m'_2}^{(j_1)*}(\alpha\beta\gamma) \times D_{m'_2, m'_2}^{(j_2)}(\alpha\beta\gamma) \langle j'_1 m'_1 | H | j_2 m'_2 \rangle'. \quad (7)$$

In the two-center approximation as suggested by Slater and Koster¹ one employs

$$\langle j_1 m'_1 | H | j_2 m'_2 \rangle' = \langle j_1 m'_1 | H | j_2 m'_1 \rangle' \delta_{m'_1, m'_2}. \quad (8)$$

Strictly speaking the above approximation is valid only in the tight-binding approach. Since the LCAO method is usually adopted (as described in Sec. I) as a semiempirical or parametrization scheme, the approximation (8) is not bad as discussed by Slater and Koster—and therefore has been used widely in many problems which indeed simplifies the calculations enormously.

Rewriting Eq. (7) in the two-center approxima-

tion,

$$W_{j_1 m_1, j_2 m_2} = \sum_{m'_1} J(j_1 m_1, j_2 m_2, m'_1) \langle j_1 m'_1 | H | j_2 m'_1 \rangle'. \quad (9)$$

The symbols $J(j_1 m_1, j_2 m_2, m'_1)$ are the Slater-Koster coefficients. Explicitly

$$J(j_1 m_1, j_2 m_2, m'_1) = D_{m'_1, m'_1}^{(j_1)*}(\alpha\beta\gamma) D_{m'_1, m'_2}^{(j_2)}(\alpha\beta\gamma). \quad (10)$$

In Eq. (9) $\langle j_1 m'_1 | H | j_2 m'_1 \rangle'$ are the two-center integrals such as $(ss\sigma)$, $(s p\sigma)$, $(p p\pi)$, etc. frequently referred to in the literature. As, for example,

$$\langle 00 | H | 10 \rangle' = (s p\sigma). \quad (11)$$

Accordingly, we use

$$\langle j_1 m'_1 | H | j_2 m'_1 \rangle' = (j_1 j_2 m'_1). \quad (12)$$

Utilizing the identities²³

$$D_{m', m}^{(j)*}(\alpha\beta\gamma) = (-1)^{m'-m} D_{-m', -m}^{(j)}(\alpha\beta\gamma), \quad (13)$$

$$D_{m'_1, m'_1}^{(j_1)}(\alpha\beta\gamma) D_{m'_2, m'_2}^{(j_2)}(\alpha\beta\gamma) = \sum_{j, m} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m'_1 & m'_2 & m \end{pmatrix} D_{m', m}^{(j)*}(\alpha\beta\gamma) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}, \quad (14)$$

in Eq. (10) we obtain

$$J(j_1 m_1, j_2 m_2, m'_1) = (-1)^{m'_1 - m_1} \sum_j (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m_1 - m_2 \end{pmatrix} D_{0, m'_1 - m_2}^{(j)*}(\alpha\beta\gamma) \begin{pmatrix} j_1 & j_2 & j \\ -m'_1 & m'_1 & 0 \end{pmatrix}, \quad (15)$$

where

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$$

are the usual $3j$ symbols. Next we make use of the relation^{23,24}

$$D_{0, m'_1 - m_2}^{(j)}(\alpha\beta\gamma) = [4\pi/(2j+1)]^{1/2} Y_{j, m'_1 - m_2}^{m'_1 - m_2}(\beta, \alpha), \quad (16)$$

to express Eq. (15) into a simplified form. Thus

$$J(j_1 m_1, j_2 m_2, m'_1) = (-1)^{m'_1 - m_2} \sum_j (4\pi)^{1/2} (2j+1)^{1/2} \begin{pmatrix} j_1 & j_2 & j \\ -m'_1 & m_1 & 0 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m_1 - m_2 \end{pmatrix} Y_{j, m'_1 - m_2}^{m'_1 - m_2}(\beta, \alpha). \quad (17)$$

Explicitly, the spherical harmonics are

$$Y_l^m(\beta\gamma) = (-1)^m \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{1/2} \times P_l^m(\cos\beta) e^{im\alpha}, \quad (18)$$

where P_l^m are the associated Legendre functions given by

$$P_l^m(Z) = (-1)^{(|m|-m)/2} \frac{(1-Z^2)^{|m|/2}}{2^l l!} \frac{d^{l+|m|}}{dZ^{l+|m|}} (Z^2-1)^l \\ = (-1)^{(|m|-m)/2} \frac{(1-Z^2)^{|m|/2}}{2^l l!} \times \sum_{k=[(l+|m|)/2]} \binom{l}{k} (-1)^{l-k} \frac{(2k)! Z^{2k-l-|m|}}{(2k-l-|m|)!}, \quad (19)$$

with $\binom{j}{k}$ as the binomial coefficients; the symbol $[x]$, as usual, represents the integral part of x .

If l, m, n are the direction cosines of the vector $\vec{R}_i + \vec{\tau}_\omega - \vec{\tau}_{\omega'}$ (i.e., the vector joining origin A at $\vec{\tau}_\omega$ to the origin B at $\vec{R}_i + \vec{\tau}_{\omega'}$ in the x - y - z axes system), one can show that

$$\begin{aligned} l &= \sin\beta \cos\alpha, \\ m &= \sin\beta \sin\alpha, \\ n &= \cos\beta. \end{aligned} \quad (20)$$

In view of Eqs. (18)–(20), the expression (17) becomes

$$\begin{aligned} J(j_1 m_1 j_2 m_2 m'_1) &= (-1)^{m_1 - m'_1 + [|m_2 - m_1| - (m_2 - m_1)]/2} \sum_j (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ -m'_1 & m'_1 & 0 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m_1 - m_2 \end{pmatrix} \left[\frac{(j - |m_1 - m_2|)!}{(j + |m_1 - m_2|)!} \right]^{1/2} \\ &\times \frac{(l + im)^{m_2 - m_1}}{2^j j!} \sum_k \binom{j}{k} (-1)^{j-k} \frac{(2k)! n^{2k-j-|m_1-m_2|}}{(2k-j-|m_1-m_2|)!}, \end{aligned} \quad (21)$$

where the factor $(l + im)^{m_2 - m_1}$ can be handled easily for $m_2 \geq m_1$. For $m_2 \leq m_1$ it is convenient to use the identity

$$(l + im)^{m_2 - m_1} = (l - im)^{m_1 - m_2}. \quad (22)$$

Equation (9) involves positive as well as negative values of m'_1 . Perusal of Eq. (21) reveals that, since

$$\begin{pmatrix} j_1 & j_2 & j \\ -m'_1 & m'_1 & 0 \end{pmatrix} = (-1)^{j_1 + j_2 + j} \begin{pmatrix} j_1 & j_2 & j \\ m'_1 - m'_1 & 0 \end{pmatrix},$$

with $j_1 + j_2 + j$ an even integer, Eq. (9) can be modified, in order to reduce the calculational work, to

$$W_{j_1 m_1 j_2 m_2} = \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0}) J(j_1 m_1 j_2 m_2 m'_1) (j_1 j_2 m'_1), \quad (23)$$

which requires only the positive (including zero) values of m'_1 . In Eq. (23) the coefficients $J(j_1 m_1 j_2 m_2 m'_1)$ are exactly the same as given in Eq. (21) and the symbols $(j_1 j_2 m'_1)$ are the two-center matrix elements as defined by Eq. (12).

Recalling the definition of $W_{j_1 m_1 j_2 m_2}$ from Eq. (3) one notes that Eqs. (21) and (23) constitute a general and simple method of expressing the E integrals when the orbitals ϕ_μ and ϕ_ν are the complex ones.

The importance of Eqs. (21) and (23) lies in the fact that they express the E integrals in terms of the basic two-center integrals $(j_1 j_2 m'_1)$ with coefficients which require only the quantum numbers

$j_1 m_1$ and $j_2 m_2$ of the orbitals and the direction cosines l, m, n of the vector joining the two centers of localization of the orbitals.

If the orbitals ϕ_μ and ϕ_ν in Eq. (2) are real, their angular parts can be of the types $(-1)^m (Y_j^m + Y_j^{m*})/\sqrt{2}$, $(-1)^m (Y_j^m - Y_j^{m*})/\sqrt{2}i$, or Y_j^0 which will be termed as functions of x , y , or z types, respectively, in analogy with $(-1)(Y_1^1 + Y_1^{1*}) \sim x$, $(-1)(Y_1^1 - Y_1^{1*}) \sim y$, and $Y_1^0 \sim z$. In the following we shall obtain general expressions for the energy integrals involving these types of functions.

In case the orbitals ϕ_μ and ϕ_ν in Eq. (2) are of the x type, one first expresses the energy matrix elements in terms of the W integrals as

$$\begin{aligned} E_{j_1 m_1 j_2 m_2}^{x,x} &= (-1)^{m_1 + m_2} \text{Re} W_{j_1 m_1 j_2 m_2} \\ &+ (-1)^{m_2} \text{Re} W_{j_1 (-m_1) j_2 (m_2)}, \end{aligned} \quad (24)$$

where we have used the superscripts x, x , on the energy matrix element E appropriately so as to designate the x -type orbitals. As, for example, in Slater-Koster notations,

$$\begin{aligned} E_{1,1,1,1}^{x,x} &= E_{xx}, \\ E_{2,1,2,1}^{x,x} &= E_{zx, zx}, \\ E_{2,2,2,2}^{x,x} &= E_{x^2-y^2, x^2-y^2}. \end{aligned}$$

To further clarify the notations, it should be mentioned that x in the superscript has been used to indicate the angular function which describes the real part of $Y_{j_1}^{m_1}$ (or $Y_{j_2}^{m_2}$) contained in the atomic orbital. Equation (24) yields after simplification

$$\begin{aligned} E_{j_1 m_1 j_2 m_2}^{x,x} &= (-1)^{m_1 + m_2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0}) (j_1 j_2 m'_1) \sum_{k'=0}^{k'_{\max}} n^{k'} \\ &\times \sum_{t=0,2,4}^{t_{\max}} m^t (-1)^{t/2} l^{|m_1 - m_2| - t} h(j_1 m_1 j_2 m_2 m'_1 k' t) \\ &+ (-1)^{m_1} l^{|m_1 + m_2| - t} h(j_1 (-m_1) j_2 m_2 m'_1 k' t), \end{aligned} \quad (25)$$

where

$$k'_{\max} = \max(j_1 + j_2 - |m_1 - m_2|, j_1 + j_2 - |m_1 + m_2|), \quad (26)$$

$$t_{\max} = \max(|m_1 - m_2|, |m_1 + m_2|), \quad (27)$$

and

$$\begin{aligned} h(j_1 m_1 j_2 m_2 m'_1 k' t) = & (-1)^{m'_1 - m_1 + [|m_2 - m_1| - (m_2 - m_1)]/2} \begin{pmatrix} |m_1 - m_2| \\ |m_1 - m_2| - t \end{pmatrix} \\ & \times [\epsilon(m_2 - m_1)]^t \sum_{j=|j_1 - j_2|}^{j_1 + j_2} \frac{(2j+1)}{2^j j!} \left[\frac{(j - |m_1 - m_2|)!}{(j + |m_1 - m_2|)!} \right]^{1/2} \\ & \times \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m_1 - m_2 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -m'_1 & m'_1 & 0 \end{pmatrix} C_{j, |m_1 - m_2|, k'} \end{aligned} \quad (28)$$

The double primes in the t summation in Eq. (25) and the j summation in Eq. (28) indicate that j and t assume values with intervals of 2. The symbol $\epsilon(m)$, in general, is merely a phase factor which gives the sign of m . Mathematically, $\epsilon(m) = \text{sgn}(m)$.

The coefficients $C_{j, m, k}$ (in general) in Eq. (28) are defined by

$$C_{j, m, k} = \begin{cases} (-1)^{(j-m-k)/2} \begin{pmatrix} j \\ k+j+m \end{pmatrix} \frac{(k+j+m)!}{k!}, & \text{for } (j+m) - 2 \left[\frac{j+m}{2} \right] \leq k \leq (j-m) \\ 0 & \text{otherwise or if } k+j+m = \text{odd integer.} \end{cases} \quad (29)$$

It should be noted that $h(j_1 m_1 j_2 m_2 m'_1 k' t)$ is non-zero only when $0 \leq t \leq |m_1 - m_2|$; $0 \leq k' \leq j - |m_1 - m_2|$, and $0 \leq m'_1 \leq \min(j_1, j_2)$.

$$E_{j_1 m_1 j_2 m_2}^{y, y} = (-1)^{m_1 + m_2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0}) (j_1 j_2 m'_1) \sum_{k'=0}^{k'_{\max}} n^{k'}$$

$$\begin{aligned} & \times \sum_{t=0, 2, 4}^{t_{\max}} m^t (-1)^{t/2} [l^{|m_1 - m_2| - t} h(j_1 m_1 j_2 m_2 m'_1 k' t) \\ & - (-1)^{m_1} l^{|m_1 + m_2| - t} h(j_1 (-m_1) j_2 m_2 m'_1 k' t)], \end{aligned} \quad (31)$$

with k'_{\max} , t_{\max} and $h(j_1 m_1 j_2 m_2 m'_1 k' t)$ as defined by Eqs. (26)–(29).

It should be remarked that expression (31) differs from Eq. (25) only in the sign of the second

If both the orbitals ϕ_u and ϕ_v are of the y type, the E integrals become,

$$\begin{aligned} E_{j_1 m_1 j_2 m_2}^{y, y} = & (-1)^{m_1 + m_2} \text{Re} W_{j_1 m_1 j_2 m_2} \\ & - (-1)^{m_2} \text{Re} W_{j_1 (-m_1) j_2 m_2}. \end{aligned} \quad (30)$$

In the above we have used the superscript y, y on E appropriately to designate the types of orbitals involved in E . As for instance, in terms of the Slater-Koster symbols,

$$\begin{aligned} E_{1,1,1,1}^{y, y} &= E_{y, y}, \\ E_{2,1,2,2}^{y, y} &= E_{zy, xy}, \\ E_{2,2,2,1}^{y, y} &= E_{xy, zy}, \end{aligned}$$

where y in the superscript indicates that the angular function which is the imaginary part of $Y_{j_1}^{m_1}$ (or $Y_{j_2}^{m_2}$) has been used in the energy-matrix element.

Simplification of Eq. (30) yields

term in the square bracket.

In case the orbital ϕ_u is of the x type and ϕ_v of the y type the expression for the E integrals becomes

$$E_{j_1 m_1 j_2 m_2}^{x,y} = (-1)^{m_1+m_2} \text{Im} E_{j_1 m_1 j_2 m_2} + (-1)^{m_2} \text{Im} E_{j_1 (-m_1) j_2 m_2}, \quad (32)$$

where the superscripts x, y define the type of orbitals involved; as, for example, in the Slater-Koster notations

$$E_{11,11}^{x,y} = E_{x,y},$$

$$E_{21,22}^{x,y} = E_{zx,xy},$$

$$E_{2,2,2,1}^{x,y} = E_{x^2-y^2,zy},$$

where x and y in the superscript designate that the real and imaginary parts, respectively, of the spherical harmonics have been used in the energy-matrix elements.

Equation (32) takes the simplified form

$$E_{j_1 m_1 j_2 m_2}^{x,y} = (-1)^{m_1+m_2} \sum_{m_1'=0}^{\min(j_1, j_2)} (2 - \delta_{m_1',0}) (j_1 j_2 m_1') \sum_{k'=0}^{k'_{\max}} n^{k'} \times \sum_{t=1,3,5}^{t_{\max}} m^t (-1)^{(t-1)/2} [l^{|m_1-m_2|-t} h(j_1 m_1 j_2 m_2 m_1' k' t) + (-1)^{m_1} l^{|m_1+m_2|-t} \times h(j_1 (-m_1) j_2 m_2 m_1' k' t)], \quad (33)$$

where all symbols carry the same meaning as before. If the orbital ϕ_μ is of the y type and ϕ_ν of the x type,

$$E_{j_1 m_1 j_2 m_2}^{y,x} = -(-1)^{m_1+m_2} \text{Im} E_{j_1 m_1 j_2 m_2} + (-1)^{m_2} \text{Im} E_{j_1 (-m_1) j_2 m_2}, \quad (34)$$

which simplifies to

$$E_{j_1 m_1 j_2 m_2}^{y,x} = (-1)^{m_1+m_2} \sum_{m_1'=0}^{\min(j_1, j_2)} (2 - \delta_{m_1',0}) (j_1 j_2 m_1') \sum_{k'=0}^{k'_{\max}} n^{k'} \times \sum_{t=1,3,5}^{t_{\max}} (-1)^{(t-1)/2} m^t [-l^{|m_1-m_2|-t} h(j_1 m_1 j_2 m_2 m_1' k' t) + (-1)^{m_1} l^{|m_1+m_2|-t} \times h(j_1 (-m_1) j_2 m_2 m_1' k' t)], \quad (35)$$

where the various symbols have already been defined.

There exists a relation between $E_{j_1 m_1 j_2 m_2}^{x,y}$ and $E_{j_2 m_2 j_1 m_1}^{x,y}$, that is;

$$E_{j_1 m_1 j_2 m_2}^{x,y} = (-1)^{j_1+j_2} E_{j_2 m_2 j_1 m_1}^{y,x}. \quad (36)$$

Thus, Eq. (35) is not needed really if Eq. (33) is available. However, Eq. (35) is useful for checking purposes, particularly for checking the results one obtains from Eqs. (33) and (36).

For the case when one or both of the orbitals ϕ_μ and ϕ_ν are of the z type, the associated E expressions can be appropriately obtained from Eqs. (25), (33), and (35). Explicitly, in order to obtain $E_{j_1 0 j_2 m_2}^{z,x}$ one merely substitutes $m_1=0$ in Eq. (25) throughout and divides the result by $\sqrt{2}$. For obtaining $E_{j_1 0 j_2 m_2}^{z,y}$ one substitutes $m_1=0$ in Eq. (33) and divides it by $\sqrt{2}$. Similarly the

integral $E_{j_1 0 j_2 0}^{z,z}$ can be obtained by substituting $m_1=0$ and $m_2=0$ in Eq. (25) and dividing the result by 2. For checking purposes it is important to note that

$$E_{j_1 0 j_2 m_2}^{z,y} = (-1)^{j_1+j_2} E_{j_2 m_2 j_1 0}^{y,z},$$

$$E_{j_1 0 j_2 m_2}^{z,x} = (-1)^{j_1+j_2} E_{j_2 m_2 j_1 0}^{x,z},$$

and

$$E_{j_1 0 j_2 0}^{z,z} = (-1)^{j_1-j_2} E_{j_2 0 j_1 0}^{z,z},$$

where we have employed the superscript z when the angular part of the orbital corresponds to that of the spherical harmonics with magnetic quantum number equal to zero.

Though the expressions deduced above are sufficient for obtaining the results for various possible real orbitals it is useful also to give the simplified expressions

$$E_{j_1 m_1 j_2 0}^{x,z} = \sqrt{2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0})(j_1 j_2 m'_1) \sum_{k'=0}^{j_1 + j_2 - |m_1|} n^{k'} \sum_{t=0,2,4,\dots}^{|m_1|} m^t l^{|m_1| - t} (-1)^{t/2} h(j_1 m_1 j_2 0 k' t), \quad (37)$$

$$E_{j_1 m_1 j_2 0}^{y,z} = -\sqrt{2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0})(j_1 j_2 m'_1) \sum_{k'=0}^{j_1 + j_2 - |m_1|} n^{k'} \sum_{t=1,3,5,\dots}^{|m_1|} m^t l^{|m_1| - t} (-1)^{(t-1)/2} h(j_1 m_1 j_2 0, k' t), \quad (38)$$

$$E_{j_1 0 j_2 m_2}^{z,x} = \sqrt{2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0})(j_1 j_2 m'_1) \sum_{k'=0}^{j_1 + j_2 - |m_1|} n^{k'} \sum_{t=0,2,4,\dots}^{|m_2|} m^t l^{|m_2| - t} (-1)^{t/2} h(j_1 0 j_2 m_2 k' t), \quad (39)$$

$$E_{j_1 0 j_2 m_2}^{z,y} = \sqrt{2} \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0})(j_1 j_2 m'_1) \sum_{k'=0}^{j_1 + j_2 - |m_2|} n^{k'} \sum_{t=1,3,5,\dots}^{|m_2|} m^t l^{|m_2| - t} (-1)^{(t-1)/2} h(j_1 0 j_2 m_2 k' t), \quad (40)$$

$$E_{j_1 0 j_2 0}^{z,z} = \sum_{m'_1=0}^{\min(j_1, j_2)} (2 - \delta_{m'_1, 0})(j_1 j_2 m'_1) \sum_{k'=0}^{j_1 + j_2} n^{k'} h(j_1 0 j_2 0 k' 0). \quad (41)$$

Equations (37)–(41) may be derived in a manner analogous to the one adopted for obtaining Eq. (25).

III. NEW EXPRESSIONS AND COMPARISON WITH THE SLATER-KOSTER RESULTS

In Sec. II we have derived general expressions for the energy integrals which are valid for all the quantum numbers concerned. The expressions are given in terms of the direction cosines l, m, n of the line joining the two centers of location of the orbitals and in terms of the relevant two-center integrals. We have applied these expressions [Eqs. (25), (31), and (33)] to check the particular expressions derived in Ref. 1 for s , p , and d orbitals. One finds that the Slater-Koster coefficients in all the expressions listed in Table I of Ref. 1 are indeed correct.

As for the new expressions we have selected large values of the quantum numbers $j_1 m_1 j_2 m_2$ corresponding to f and g orbitals. One is required to evaluate for the given quantum numbers the coefficients $h(j_1 m_1 j_2 m_2 m'_1 k' t)$ as defined in Eq. (28). Straightforward evaluation of the expressions (25), (31), or (33) then yields results which are listed in Table I. These results are particularly useful for the calculations of the electronic structure of rare-earth metals or salts containing rare-earth atoms or ions.

In our process of checking we have discovered corrections in the expressions given in Ref. 1 for the energy-matrix components for the face-centered-cubic structure. The corrected expressions are written as follows:

$$\begin{aligned} (xz/xz) = (yz/yz) &= E_{xy,xy}(000) + 4E_{xy,xy}(011) \\ &+ 4E_{xy,xy}(110) \cos \zeta \\ &+ 4E_{xy,xy}(011) \cos \zeta, \end{aligned} \quad (42)$$

$$\begin{aligned} ((x^2 - y^2)/(x^2 - y^2)) &= E_{3z^2-r^2, 3z^2-r^2}(000) \\ &+ 4E_{x^2-y^2, x^2-y^2}(110) \\ &+ 6E_{3z^2-r^2, 3z^2-r^2}(110) \cos \zeta \\ &+ 2E_{x^2-y^2, x^2-y^2}(110) \cos \zeta, \end{aligned} \quad (43)$$

$$\begin{aligned} ((3z^2 - r^2)/(3z^2 - r^2)) &= E_{3z^2-r^2, 3z^2-r^2}(000) \\ &+ 4E_{3z^2-r^2, 3z^2-r^2}(110) \\ &+ 6E_{x^2-y^2, x^2-y^2}(110) \cos \zeta \\ &+ 2E_{3z^2-r^2, 3z^2-r^2}(110) \cos \zeta, \end{aligned} \quad (44)$$

where the notations are the same as in Ref. 1. It is obvious that the expressions derived by Slater and Koster do not contain the factors $\cos \zeta$ in the third terms on the right-hand side of the above expressions. Even though the above corrections are not directly related to the subject matter of the paper we are obligated to indicate this correction since the Slater-Koster paper is a classical one and because otherwise such mistakes usually creep in elsewhere as in a review article by Reitz.

TABLE I. List of some of the energy integrals involving f and g orbitals for crystals in terms of two-center integrals.

$E_{s,(2z^2-3x^2-3y^2)z}$	$\frac{1}{2}n(5n^3-3)(sf\sigma)$
$E_{s,35z^4-30r^2z^2+3r^4}$	$\frac{1}{8}(3-30n^2+35n^4)(sg\sigma)$
$E_{s,zx(4z^2-3x^2-3y^2)}$	$\frac{3\sqrt{5}}{2\sqrt{2}}nl(-1+\frac{7}{3}n^2)(sg\sigma)$
$E_{s,xy(6z^2-x^2-y^2)}$	$\frac{1}{2}\sqrt{5}ml(-1+7n^2)(sg\sigma)$
$E_{s,z(x^3-3xy^2)}$	$\frac{\sqrt{35}}{2\sqrt{2}}nl(l^2-3m^2)(sg\sigma)$
$E_{s,x^4-6x^2y^2+y^4}$	$\frac{1}{8}\sqrt{35}(l^4+m^4-6m^2l^2)(sg\sigma)$
E_{s,yx^3-xy^3}	$\frac{1}{2}\sqrt{35}ml(l^2-m^2)(sg\sigma)$
$E_{s,x(4z^2-x^2-y^2)}$	$\frac{\sqrt{3}}{\sqrt{8}}l(5n^2-1)(sf\sigma)$
$E_{s,z(x^2-y^2)}$	$\frac{1}{2}\sqrt{15}n(l^2-m^2)(sf\sigma)$
$E_{s,xyz}$	$\sqrt{15}nlm(sf\sigma)$
E_{s,x^3-3y^2x}	$\frac{\sqrt{5}}{2\sqrt{2}}l(l^2-3m^2)(sf\sigma)$
$E_{z,(2z^2-3x^2-3y^2)z}$	$\frac{1}{2}n^2(5n^2-3)(pf\sigma)$
	$+\frac{\sqrt{3}}{2\sqrt{2}}(-1+6n^2-5n^4)(pf\pi)$
$E_{z,(4z^2-x^2-y^2)x}$	$\frac{\sqrt{3}}{2\sqrt{2}}nl(5n^2-1)(pf\sigma)$
	$+\frac{11}{4}nl(1-\frac{15}{11}n^2)(pf\pi)$
E_{z,y^3-3x^2y}	$\frac{\sqrt{5}}{2\sqrt{2}}nm(3l^2-m^2)(pf\sigma)$
	$-\frac{1}{4}\sqrt{15}nm(3l^2-m^2)(pf\pi)$
$E_{x,(4z^2-x^2-y^2)y}$	$\frac{\sqrt{3}}{2\sqrt{2}}ml(5n^2-1)(pf\sigma)+\frac{1}{4}ml(1-15n^2)(pf\pi)$
$E_{x,z(x^2-y^2)}$	$\frac{1}{4}\sqrt{15}nl(1+l^2-3m^2-n^2)(pf\sigma)$
	$+\frac{\sqrt{5}}{4\sqrt{2}}nl(1-3l^2+9m^2+3n^2)(pf\pi)$
$E_{x,xyz}$	$\frac{1}{4}\sqrt{15}nm(1+3l^2-m^2-n^2)(pf\sigma)$
	$+\frac{\sqrt{5}}{4\sqrt{2}}nm(1-9l^2+3m^2+3n^2)(pf\pi)$
E_{x,x^3-3y^2x}	$\frac{\sqrt{5}}{4\sqrt{2}}[l^2(1+l^2)-m^2(1+6l^2)+m^4+n^2(m^2-l^2)](pf\sigma)$
	$+\frac{1}{8}\sqrt{15}[l^2(1-l^2)+m^2(-1+6l^2)-m^4+n^2(l^2-m^2)](pf\pi)$
E_{x,y^3-3x^2y}	$\frac{\sqrt{5}}{2\sqrt{2}}ml(1+2l^2-2m^2-n^2)(pf\sigma)$
	$+\frac{1}{4}\sqrt{15}ml(1-2l^2+2m^2+n^2)(pf\pi)$
$E_{y,(4z^2-x^2-y^2)y}$	$\frac{\sqrt{3}}{4\sqrt{2}}[-1+l^2-m^2+6n^2-5n^2(l^2-m^2+n^2)](pf\sigma)$
	$+\frac{1}{8}[-1-l^2+m^2-6n^2+15n^2(l^2-m^2+n^2)](pf\pi)$
$E_{3z^2-r^2,z(2z^2-3x^2-3y^2)}$	$\frac{3}{4}n(1-\frac{14}{3}n^2+5n^4)(df\sigma)+(3n/2\sqrt{2})(-1+6n^2-5n^4)(df\pi)$
	$+\frac{1}{4}\sqrt{45}n(1-2n^2+n^4)(df\delta)$
$E_{x^2-y^2,z(x^2-y^2)}$	$\frac{3}{4}\sqrt{5}n(l^2-m^2)^2(df\sigma)$
	$+\frac{\sqrt{5}}{2\sqrt{2}}n[-3(l^2-m^2)^2+2(l^2+m^2)](df\pi)$

TABLE I. (Continued)

	$+\frac{1}{8}n[8+6(l^2-m^2)^2-16(l^2+m^2)](df\delta)$
$E_{3z^2-r^2,y(4z^2-x^2-y^2)}$	$-\frac{\sqrt{3}}{4\sqrt{2}}m(1-8n^2+15n^4)(df\sigma)$
	$+\frac{1}{4}\sqrt{3}mn^2(11-15n^2)(df\pi)$
	$+\frac{\sqrt{15}}{4\sqrt{2}}m(1-4n^2+3n^4)(df\delta)$
$E_{zy,x(4z^2-x^2-y^2)}$	$-\frac{3}{2\sqrt{2}}nml(-1+5n^2)(df\sigma)$
	$+3nml(1-\frac{5}{2}n^2)(df\pi)$
	$+\frac{3\sqrt{5}}{2\sqrt{2}}nlm(-1+n^2)(df\delta)$
$E_{x^2-y^2,x^3-3y^2x}$	$-\frac{1}{16}\sqrt{30}l(1+l^4-10m^2l^2+5m^4-2n^2+n^4)(df\sigma)$
	$+\frac{1}{8}\sqrt{15}l(1-l^4+10l^2m^2-5m^4-n^4)(df\pi)$
	$+\frac{\sqrt{3}}{8\sqrt{2}}l(1+l^4-10m^2l^2+5m^4+6n^2+n^4)(df\delta)$
$E_{zx,xyz}$	$-\frac{3}{4}\sqrt{5}mn^2(1+3l^2-m^2-n^2)(df\sigma)$
	$+\frac{1}{8}\sqrt{10}m(1+3l^2-m^2-3n^2-18n^2l^2+6n^2m^2+6n^4)(df\pi)$
	$+\frac{1}{2}m(1-3l^2+m^2-\frac{3}{2}n^2+\frac{3}{2}n^2l^2-\frac{3}{2}n^2m^2-\frac{3}{2}n^4)(df\delta)$
$E_{x^2-y^2,y^3-3x^2y}$	$-\frac{1}{16}\sqrt{30}m(1+5l^4-10m^2l^2+m^4-2n^2+n^4)(df\sigma)$
	$+\frac{1}{8}\sqrt{15}m(1-5l^4+10m^2l^2-m^4-n^2)(df\pi)$
	$+\frac{\sqrt{3}}{8\sqrt{2}}m(1+5l^4-10m^2l^2+m^4+6n^2+n^4)(df\delta)$
E_{xy,x^3-3y^2x}	$-\frac{1}{16}\sqrt{30}m(-1+5l^4-10m^2l^2+m^4+2n^2-n^4)(df\sigma)$
	$+\frac{1}{8}\sqrt{15}m(-1-5l^4+10m^2l^2-m^4+n^4)(df\pi)$
	$+\frac{\sqrt{3}}{8\sqrt{2}}m(-1+5l^4-10m^2l^2+m^4-6n^2-n^4)(df\delta)$
E_{xy,y^3-3x^2y}	$-\frac{1}{16}\sqrt{30}l(1-l^4+30m^2l^2-5m^4-2n^2+n^4)(df\sigma)$
	$+\frac{1}{8}\sqrt{15}l(1+l^4-10m^2l^2+5m^4-n^4)(df\pi)$
	$+\frac{\sqrt{3}}{8\sqrt{2}}l(1-l^4+10m^2l^2-5m^4+6n^2+n^4)(df\delta)$
$E_{(2z^2-3x^2-3y^2)z,(2z^2-3x^2-3y^2)z}$	$-\frac{1}{4}n^2(5n^2-3)^2(ff\sigma)$
	$+\frac{3}{8}(1-n^2)(1-5n^2)^2(ff\pi)$
	$+\frac{15}{4}n^2(1-n^2)^2(ff\delta)$
	$+\frac{5}{8}(1-n^2)^3(ff\phi)$
$E_{x^3-3y^2x,x^3-3y^2x}$	$-\frac{5}{16}(1+l^6-15m^2l^4+15m^4l^2-m^6-3n^2+3n^4-n^6)(ff\sigma)$
	$+\frac{15}{32}(1-l^6+15m^2l^4-15m^4l^2+m^6-n^2-n^4+n^6)(ff\pi)$
	$+\frac{3}{16}(1+l^6-15m^2l^4+15m^4l^2-m^6+5n^2-5n^4-n^6)(ff\delta)$
	$+\frac{1}{32}(1-l^6+15m^2l^4-15m^4l^2+m^6+15n^2+15n^4+n^6)(ff\phi)$
$E_{xyz,xyz}$	$-\frac{15}{8}n^2(1-l^4+6m^2l^2-m^4-2n^2+n^4)(ff\sigma)$
	$+\frac{15}{16}(1-l^4+6m^2l^2-m^4-3n^2+9n^2l^4-54n^2l^2m^2+9n^2m^4$
	$+11n^4-9n^6)(ff\pi)$
	$+\frac{1}{2}(1+l^4-6m^2l^2+m^4-\frac{15}{4}n^2-\frac{3}{4}n^2l^4+\frac{27}{2}n^2l^2m^2$
	$-\frac{3}{4}n^2m^4+\frac{5}{2}n^4+\frac{3}{4}n^6)(ff\delta)$
	$+\frac{3}{16}(1-l^4+6m^2l^2-m^4+5n^2+n^2l^4-6n^2m^2l^2+n^2m^4$
	$-5n^4-n^6)(ff\phi)$

IV. DISCUSSION AND CONCLUSION

In Sec. I the usefulness of the energy-matrix elements (as emphasized by Slater and Koster) for the band-structure calculations using LCAO method as a parametrization, semiempirical, or interpolation scheme has been mentioned. The energy-matrix elements contain the energy integrals [the E integrals in Eq. (2)] which are usually expressed in terms of the two-center integrals [Eqs. (9) and (11) with coefficients Eq. (10)] termed as Slater-Koster coefficients.

In Sec. II general expressions for the E integrals (or Slater-Koster coefficients) have been developed [see Eqs. (25), (31), (33), (35), and (37)–(41)] which are valid for all angular-momentum quantum numbers. The Slater-Koster coefficients depend only on the angular quantum numbers of the orbitals, namely, $j_1 m_1 j_2 m_2$, and the direction cosines l, m, n of the vector joining the two centers where the orbitals are localized. The general expressions developed are appropriate to both real and complex orbitals.

In Sec. III the E integrals from Sec. II have been employed to prove the correctness of the two-center expressions of Slater and Koster for all combinations of s, p , and d orbitals. New expressions for integrals involving f and g orbitals have also been obtained in Sec. III (see Table I) by making use of the general expressions derived in Sec. II, which are otherwise cumbersome to obtain because of their high values of the angular-momentum quantum numbers.

As a side track it was pointed out in Sec. III that some of the expressions for the energy-matrix components given in Ref. 1 and also in Ref. 21 for the face-centered-cubic crystal missed $\cos\xi$ factors. The corrected expressions [Eqs. (42)–(44)] have been listed in Sec. III.

To emphasize the importance of our general expressions it is worth mentioning that these are

not limited to the simple atomic orbitals as one may conclude from their derivations in Sec. II but are useful (from group-theoretical arguments) also for the equivalent orbitals such as Löwdins orthogonalized orbitals or in general, two functions localized at different centers if the angular-momentum quantum numbers are appropriately taken into account. This idea has been made clear (especially for Löwdins orthogonalized orbitals) by Slater and Koster and has recently been evoked by Wolfram and co-workers¹² for explaining the bulk and surface properties of perovskites.

Further importance of the developed expressions is evident if one notes that it is now possible to tabulate the energy-matrix elements for the f and higher orbitals for different lattices analogous to the ones obtained by Slater and Koster for s, p , and d orbitals in cubic structures and extended by Miasek² and Egorov *et al.*⁶ to hexagonal structures.

The derived expressions are useful for calculations of the properties not only of solids and surfaces but also of defects on surfaces,²⁵ clusters, and complexes²⁶ embedded in solids particularly when the f or higher orbitals are involved. At present we are engaged in interpreting the optical properties²⁷ of TiO_2 by making a general "machine program" useful for any set of values of j_1, m_1, j_2, m_2 and n, l, m for calculating the expressions derived here and by using a recent expansion²⁸ of a Slater orbital from one center onto the other for evaluation of two-center integrals. A preliminary report of the derived expressions has been presented by the author previously.²⁹

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$$D_{m_1 0}^{(l)}(\alpha, \beta, \gamma) = (-1)^m \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_l^m(\beta, \gamma),$$

$$D_{0, m}^{(l)}(\alpha \beta \gamma) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_l^m(\beta, \alpha).$$

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