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Electron-phonon interactions in transition metals

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The problem of the electron-phonon interaction in transition metals is approached from the point of view that nonorthogonal tight-binding representations of the d-band electronic structure are very appropriate in such materials. Expressions for the electron-phonon matrix elements using this representation are derived. The quantitative validity of the method is demonstrated by calculating $\langle I^2 \rangle$, the Fermi-surface average of the electron-phonon coupling constant for 4d bcc transition metals and alloys. The variation of $\langle I^2 \rangle$ in these materials is understood physically as arising from the variation of the average Fermi velocity and of the bond order.

I. INTRODUCTION

The electronic properties of most of the transition metals and their compounds (TMC hereafter) are dominated by the d electrons. These d electrons are tightly bound compared to the s-p states of similar energy and form bands with strong-atomic character to their wave functions. It has long been recognized[1] that the TMC are best described with the tight-binding approximation for the d bands, as a starting point, in contrast to the free-electron approximation for, say, the alkali metals.

However, one objection has been that the d states are not true bound states, but only resonances which decay into plane waves outside the atom in question.[2] This is certainly a serious point for isolated transition-metal impurities in nearly free-electron metals. For bulk TMC, where the direct d-d overlap between the resonances on neighbor atoms is large compared to the s-d hybridization energy, this point is not significant. The appropriateness of tight binding for d electrons has continually been emphasized by Friedel,[3] who with his collaborators has shown that many of the properties of transition metals and alloys follows naturally from this point of view.

The use of the tight-binding method for *ab initio* band-structure calculations has been hindered by computational problems in calculating self-consistent *atomic* wave functions and potentials in bulk TMC. The augmented plane wave (APW) and the Korringa-Kohn-Rostoker (KKR) method of calculations[4-6] are extensively used to calculate electronic structure of TMC. Impressive understanding[6] of TMC has been achieved thereby.

Mueller[7] and Hodges, Ehrenreich, and Lang[8] have successfully fitted results of such band-structure calculations for copper by an empirical scheme in which the basis functions are linear combinations of the five tight-binding d functions and a few plane waves to represent the s-p electrons. This led to proofs of the equivalence of the KKR method to such hybrid schemes.[9] It is worth realizing for our purpose that these proofs suggest a considerable arbitrariness in the apportioning of the Hamiltonian to the plane-wave block and the tight-binding block. Also, the angular decomposition defined with respect to a muffin tin does not correspond to that in the usual tight-binding method, which is defined with respect to atomic orbitals. Therefore a direct comparison of the parameters in the two methods is not easily possible.

In recent years there has been considerable interest in calculating parameters determining the superconducting transition temperature T_c of TMC from first principles. A lot of effort in this direction has been devoted to extensions[10,11] of the APW and the KKR methods to calculate the electron-phonon matrix elements. We believe that as with most other properties of TMC, the tight-binding method for calculating parameters of importance in superconductivity provides, besides the ease in computation, a clear physical understanding of the processes involved.

The easiest way to overcome the quantitative difficulty in obtaining the tight-binding parameters is to fit existing band-structure calculations by tight binding. For tight binding to be a physical reality rather than merely an interpolation scheme, one must explicitly consider the nonorthogonality of the orbitals. Without nonorthogonality the tight-binding parameters obtained by fitting the band-structure can often be unphysical. For problems involving electron-phonon interactions, consideration of nonorthogonality is vital, since if one starts with an orthogonal basis set for electrons in the equilibrium lattice configuration, it will not remain orthogonal in a distorted lattice. We shall demonstrate the orthogonality effects quantitatively by comparing our results with some work[12, 13] done with the tight-binding (TB) scheme.

The superconducting transition temperature is determined by some average phonon frequency $\langle \omega \rangle$ and a dimensionless parameter λ.[14] λ is given by[14]

$$\lambda = N(0)\langle I^2 \rangle / m\langle \omega^2 \rangle \,, \tag{1.1}$$

where $N(0)$ is the density of states near the Fermi surface, m is the ion mass, $\langle \omega^2 \rangle$ is a suitably defined average over the phonon spectrum, and $\langle I^2 \rangle$ is an average of the square of the electron-phonon matrix element over the Fermi surface. The quantity $\langle I^2 \rangle$ has been deduced from experimental results for a number of superconducting TMC. It follows a number of interesting physical trends.[14-16] It has been possible to understand these trends qualitatively[15, 16] by analytically solving the properties of a single nonorthogonal tight-binding band (NTB) of electrons. To quantitatively test these ideas and to establish the simplicity and naturalness of the tight-binding approach to TMC, we will present here calculations of $\langle I^2 \rangle$ for a series of $4d$-bcc transition metals and alloys based on their actual electronic structure.

Before we calculate $\langle I^2 \rangle$, we need an expression for the electron-phonon Hamiltonian. In Sec. III, we derive such a Hamiltonian in NTB in full generality. We also clarify in that section the relationship of our electron-phonon Hamiltonian with the more traditional Bloch formulation. In Sec. IV we present our calculational procedure and in Sec. V our results. We compare them with experiment and with various physical features of transition metals. We end in Sec. VI with a general discussion of our results and of previous work on this problem.

II. ELECTRON-PHONON MATRIX

A. Nonorthogonal tight-binding formalism

To establish the notation, we shall briefly summarize the essentials of the nonorthogonal tight-binding (NTB) approximation for electronic-band structure. In its simplest form, one starts with the assumption that the Hamiltonian for the electrons in the solid can be written as

$$H_e = T_e + \sum_i V(r - R_i) \,, \tag{2.1}$$

where T_e is the kinetic-energy operator, and $V(r - R_i)$ is the potential energy associated with the ion at the lattice site i. Here $V(r - R_i)$ is regarded as a self-consistent potential including the effects of screening, and exchange and correlations in some parametrized one-electron fashion. One next assumes that it is possible to find localized orbitals $\phi_{in}(r)$ centered at site i with quantum number n that bear one-to-one correspondence with the wave functions of the isolated atom. [In a more sophisticated version, one can include in the potential energy in (2.1), terms associated with interstitial sites and likewise define self-consistent interstitial orbitals. We do not include such refinements in this paper.] The orbitals at the same site may be taken to be orthogonal, but an orbital at one site is in general not orthogonal to an orbital at a neighboring site:

$$(\phi_{in}, \phi_{jm}) = S_{in,\,jm} \,, \tag{2.2}$$

$$S_{in,\,jm} = \delta_{nm} \quad \text{for } i = j \,. \tag{2.2$'$}$$

The tight-binding Hamiltonian matrix $H_{nm}(k)$ can be constructed in more than one way. The one we have adopted is

$$H_{nm}(\vec{k}) = H^{(1)}_{nm}(\vec{k}) + H^{(2)}_{nm}(\vec{k}) + H^{(3)}_{nm}(\vec{k}) \,, \tag{2.3}$$

where for a monatomic solid,

$$H^{(1)}_{nm} \equiv H^{(1)}_{in,\,im} \,, \tag{2.4}$$

where

$$H^{(1)}_{in,\,im} = \int d^3r\, \phi^*_{in}(r)[T_e + V(\vec{r} - \vec{R}_i)]\, \phi_{im}(\vec{r}) \,,$$

$$+ \sum_j \int d^3r\, \phi^*_{in}(\vec{r}) V(\vec{r} - \vec{R}_j)\, \phi_{im}(\vec{r}) \tag{2.4$'$}$$

[the first term in (2.4′) is often referred to as the one-center terms, and the second is referred to as the crystal-field term];

$$H^{(2)}_{m,n}(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{R_{ij}} H^{(2)}_{im,\,jn} \exp(i\vec{k} \cdot \vec{R}_{ij}) \,, \tag{2.5}$$

$$H^{(2)}_{im,\,jn} = \int d^3r\, \phi^*_{im}(\vec{r})[T_e + V(\vec{r} - \vec{R}_i) + V(\vec{r} - \vec{R}_j)]\phi_{jn}(\vec{r}) \tag{2.5$'$}$$

(the crystal-field term and $H^{(2)}_{m,n}$ are often referred to as the two-center terms), and the three-center terms are defined by

$$H^{(3)}_{mn}(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{R_{ij}} H^{(3)}_{im,\,jn} \exp(i\vec{k} \circ \vec{R}_{ij}) \,, \tag{2.6}$$

$$H^{(3)}_{im,\,jn} = \sum_{l \neq i,j} \int d^3r\, \phi^*_{im}(r) \times [T_e + V(\vec{r} - \vec{R}_l)]\, \phi^*_{jn}(\vec{r}) \,. \tag{2.6$'$}$$

The eigenvalues $E_{k\mu}$ are given by

$$| H_{nm}(\vec{k}) - S_{nm}(\vec{k})E_{k\mu}| = 0 . \tag{2.7}$$

The stationary states (Bloch waves) are given by

$$\psi_{k\mu}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{i} \exp(i\vec{k}\cdot\vec{R}_i)A_{\mu n}(\vec{k})\phi_{in}(\vec{r}) , \tag{2.8}$$

where A is the eigenvector matrix given by

$$HA = SAE, \tag{2.9}$$

$$A^{\dagger}SA = I, \tag{2.10}$$

where I is the identity matrix. A thus defined is not unitary. Sometimes Eq. (2.9) is written as

$$S^{-1/2}HS^{-1/2}A_u = A_u E, \tag{2.11}$$

where A_u are unitary matrices. The relation between A and A_u is

$$A = S^{-1/2}A_u \tag{2.12}$$

$$A^{\dagger} = A_u^{\dagger} S^{-1/2} . \tag{2.12$'$}$$

B. Scattering-matrix element

We wish to calculate the matrix element $g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}$ for scattering from an electronic state $\vec{k}'\mu'$ to a state $\vec{k}\mu$, when the ions are displaced from their equilibrium position in the αth Cartesian direction. We will now derive $g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}$ by the method of time-perturbation theory.

A general time-dependent state $\Phi(t)$ in the presence of the perturbation can be written as

$$\Phi(t) = \sum_{k\mu} C_{\vec{k}\mu}(t)\psi_{\vec{k}\mu}(t) . \tag{2.13}$$

In the absence of the perturbation, $\psi_{\vec{k}\mu}(t)$ has the time dependence $\exp(-iE_{\vec{k}\mu}t)$. We choose a representation in which in the presence of the perturbation $\psi_{\vec{k}\mu}(t)$ is given by

$$\psi_{\vec{k}\mu}(t) = \frac{1}{\sqrt{N}} \sum_{in} \phi_{in}(\vec{r},t)\exp(i\vec{k}\cdot\vec{R}_i) \times A_{n\mu}(\vec{k})\exp(-iE_{\vec{k}\mu}t) , \tag{2.14}$$

where $\phi_{in}(\vec{r}t)$ varies with time on the scale of the perturbation, i.e., at the phonon frequency. We can also write $\Phi(t)$ in terms of the $\phi_{im}(\vec{r},t)$,

$$\Phi(t) = \sum_{i,m} \phi_{im}(\vec{r},t)C_{im}(t) . \tag{2.15}$$

$C_{im}(t)$ are related to $C_{\vec{k}\mu}(t)$ by

$$C_{im}(t) = \sum_{k\mu} \exp(i\vec{k}\cdot\vec{R}_i)A_{m\mu}(k) \times \exp(-iE_{\vec{k}\mu}t)C_{\vec{k}\mu}(t) . \tag{2.16}$$

The equation of motion for $\Phi(t)$ is

$$i\dot{\Phi} = H'\Phi, \tag{2.17}$$

for any Hamiltonian H'. Due to the motion of the ions, the tight-binding Hamiltonian and overlap parameters will in general alter, and we write that

$$H'_{im,jn} = H_{im,jn} + \delta H_{im,jn'} , \tag{2.18}$$

$$S'_{im,jn} = S_{im,jn} + \delta S_{im,jn'} , \tag{2.19}$$

where δH and δS are the changes due to the perturbation. On substituting Eq. (2.15) for $\Phi(t)$ in Eq. (2.17), multiplying both sides by $\phi^{*}_{jn}(\vec{r},t)$, and integrating over $\vec{r}$, we get

$$i \sum_{i,m} S'_{im,jn}\dot{C}_{jn} \cong \sum_{im,jn} H'_{im,jn}C_{jn} . \tag{2.20}$$

In obtaining (2.20) we have neglected a term $\dot{\phi}_{im}(\vec{r},t)$ in comparison with $\dot{C}_{im}$. As mentioned earlier, the time dependence of $\phi(\vec{r},t)$ are on the scale of the phonon frequencies and is negligible compared to the time scales of C_{im}, which are of the order of electronic frequencies.

From Eq. (2.16) we get

$$\dot{C}_{im} = \sum_{k\mu} A_{m\mu}(\vec{k})\exp(i\vec{k}\cdot\vec{R}_i) \times \exp(-iE_{\vec{k}\mu}t)(\dot{C}_{\vec{k}\mu} - iE_{\vec{k}\mu}C_{\vec{k}\mu}) . \tag{2.21}$$

Substituting (2.21) in (2.20), using the eigenvalue equation (2.9), multiplying on the left by $A^{\dagger}$ and using the normalization (2.12), we get the desired equation of motion for $C_{\vec{k}\mu}$:

$$i\dot{C}_{\vec{k}\mu} \simeq \sum_{m,n} A^{\dagger}_{\mu m}(\vec{k})[\delta H_{mn}(\vec{k})A_{n\mu'}(\vec{k}') - \delta S_{mn}(\vec{k})A_{n\mu'}(\vec{k}')E_{\vec{k}\mu}]C_{\vec{k}'\mu'} . \tag{2.22}$$

In deriving (2.22) we have dropped a second-order term proportional to $\delta S\dot{C}$ compared to the rest, which are all first order in the perturbation.

The preceding development has been quite general and provides the scattering matrix for electronic states for any perturbation which alters the Hamiltonian and overlap matrices. Now we specialize to the case of phonon perturbations.

C. Electron-phonon matrix element

To do this we must consider the variation of the elements of H and S with the deviation u_i of particle i from the lattice site R_i. The one-center term in (2.4′) is not altered as the distance between the atoms is varied. For the crystal-field terms we can write

$$\delta H^{(1),\alpha}_{im,in}=\sum_j \nabla_{i-j,\alpha}H^{(1)}_{im,in}\cdot(\vec{u}_i-\vec{u}_j)\ ,\qquad \nabla_{i-j,\alpha}\equiv\frac{\partial}{\partial R^{\alpha}_{ij}}\ , \tag{2.23}$$

where we have noted that the crystal-field term depends implicitly on the lattice site j as given by (2.4′); for the terms in $H^{(2)}$,

$$\delta H^{(2),\alpha}_{im,jn}=\nabla_{i-j,\alpha}H^{(2)}_{im,jn}\cdot(\vec{u}_i-\vec{u}_j)\ , \tag{2.24}$$

and for the three-center integrals

$$\delta H^{(3),\alpha}_{im,jn}=\sum_l\,[\nabla_{i-j,\alpha}H^{(3)}_{im,jn}\cdot(\vec{u}_i-\vec{u}_j)+\nabla_{j-l,\alpha}H^{(3)}_{im,jn}\circ(\vec{u}_j-\vec{u}_l)+\nabla_{l-i,\alpha}H^{(3)}_{im,jn}\cdot(\vec{u}_l-\vec{u}_i)] \tag{2.25}$$

where we have again noted that $H^{(3)}_{im,jn}$ given by (2.6′) depends implicitly on another set of sites labeled l.

For the variation of the overlap integral we only have a two-center like term. Therefore

$$\delta S^{\alpha}_{im,jn}=\nabla_{i-j,\alpha}S_{im,jn}\cdot(\vec{u}_i-\vec{u}_j)\ . \tag{2.26}$$

The ∇ operator in Eqs. (2.23)–(2.26) is to be understood as a functional derivative, since we desire the total renormalized change in the Hamiltonian and overlap matrix elements to linear order in the atomic displacements. In general due to the atomic displacements, the self-consistent atomic potential and atomic wave functions are altered by screening, correlations, and exchange variations. These effects are assumed to be included in the definitions (2.23)–(2.26).

The one-center, two-center, and three-center contributions in general yields expressions for the electron-phonon matrix element that are of different functional form from each other. Since the calculations reported in this paper neglect the crystal field and the three-center contributions (as being small), we give here the results for the contributions $H^{(2)}$ alone.

We write the atomic displacements in terms of (dimensionless) normal coordinates $u_{q\lambda}$

$$u_{i\alpha}=\sum_{\vec{q},\lambda}\vec{\epsilon}^{\,\alpha}_{q\lambda}e^{i\vec{q}\cdot\vec{R}_i}u_{q\lambda}\ , \tag{2.27}$$

where $u_{\vec{q}\lambda}$ is the displacement for a wave vector $\vec{q}$ and polarization λ and $\epsilon^{\alpha}_{\vec{q}\lambda}$ is the matrix element in the α Cartesian direction q the corresponding polarization vector. Using (2.27) in (2.24), (2.26), and performing the indicated summations in (2.22), we get

$$i\dot{C}_{\vec{k}\mu}\simeq\sum\epsilon^{\alpha}_{\vec{k}-\vec{k}',\lambda}\,g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}\,C_{\vec{k}'\mu'}(u_{\vec{k}-\vec{k}',\lambda})\ , \tag{2.28}$$

where $g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}$ is the desired electron-phonon matrix element

$$g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}=\sum A^{\dagger}_{\mu m}(\vec{k})[\gamma^{\alpha}_{mn}(\vec{k})-\gamma^{\alpha}_{mn}(\vec{k}')]A_{n\mu'}(\vec{k}')\ , \tag{2.29}$$

and $\gamma^{\alpha}_{mn}(\vec{k})$ and $\gamma^{\alpha}_{mn}(\vec{k}')$ are the Fourier transforms of

$$(\nabla_{\alpha}H_{im,jn}-E_k\nabla_{\alpha}S_{im,jn});$$

$$\gamma^{\alpha}_{mn}(\vec{k}')=\sum_{R_{ij}}(\nabla_{\alpha}H_{im,jn}-E_{\vec{k}}\nabla_{\alpha}S_{im,jn})\times\exp(i\vec{k}'\cdot\vec{R}_{ij})\ . \tag{2.30}$$

This asymmetry in the definition of $\gamma(\vec{k})$ and $\gamma(\vec{k}')$ is due to our nonunitary A matrices. For calculations of $\langle I^2\rangle$, where both states $\vec{k}$ and $\vec{k}'$ are at the Fermi energy, $E_{\vec{k}}$ in (2.30) is replaced by E_F, and we need not concern ourselves here with this peculiarity. Note that for nonoverlapping s state orbitals, (2.29) reduces to the result of Baristic, Labbe, and Friedel.[16]

D. Bloch formulation

Most of the work on electron-phonon interactions in simple metals is based on Bloch's expression for the electron-phonon matrix elements. It is of some interest to compare the results derived above with this expression expressed in tight-binding form. Bloch's expression can be derived by time-dependent perturbation theory, much as was done above but with a different basis set. The difference lies in keeping the localized functions $\phi_{in}(r)$ *time-independent* even in the presence of the perturbation. One then obtains instead of Eq. (2.22)

$$i\dot{C}_{\vec{k}\mu}\cong\sum_{mn}A^{+}_{\mu m}(\vec{k})\,\delta\mathcal{H}_{mn}(\vec{k},\vec{k}')A_{n\mu'}(\vec{k}')C_{\vec{k}'\mu'}\ , \tag{2.31}$$

where

$$\delta\mathcal{H}_{mn}(\vec{k},\vec{k}')=\sum_{R_{ij}}(\phi_{mi}\,|\,\delta H|\,\phi_{nj})\exp[i(\vec{k}-\vec{k}')\cdot\vec{R}_{ij}]\ , \tag{2.32}$$

where δH is the change in the total Hamiltonian due to the perturbation.

The difference between the two expressions (2.22) and (2.31) is that the shift of the orbitals due to the perturbation is being explicitly considered in (2.22), while it is not in (2.31). Since the two expressions are derived merely with different basis sets, they must be equivalent. The change in the electronic wave function for a given perturbation must be the same, but only if the scattering to all possible final states is summed over. Using (2.31) will in general require summing over a larger number of higher states to build up the change in the wave function with the perturbation than (2.22). If however, we are concerned with energy conserving transitions, i.e., $\epsilon_{\vec{k}\mu}=\epsilon_{\vec{k}'\mu'}$ as in transport theory or in the calculation of $\langle I^2\rangle$, the two expressions are identical. This may be proved as follows. Taking the difference between (2.22) and (2.31), we get

$$\sum_{\substack{im\\jn}} A^{+}_{\mu m}(\vec{k})e^{-i\vec{k}\cdot\vec{R}_i}[(\delta\phi_{im},H\phi_{jn})+(\phi_{im}H,\delta\phi_{jn})-\{(\delta\phi_{im},\phi_{jn})+(\phi_{im},\delta\phi_{jn})\}E_{k\mu}]A_{n\mu'}(k')e^{i\vec{k}'\cdot\vec{R}_j}$$

$$=(E_{\vec{k}\mu}-E_{\vec{k}'\mu'})\sum_{\substack{im\\jn}} A^{+}_{\mu m}(\vec{k})e^{-i\vec{k}\cdot\vec{R}_i}(\delta\phi_{im'}\phi_{jn})e^{i\vec{k}'\cdot\vec{R}_j}A_{\mu'n}(\vec{k}') \ . \tag{2.33}$$

From the discussion above, we conclude that arguments[13] against the applicability of Bloch formulation to TMC are incorrect. It is however true that Bloch formulation is not as *convenient* for *d* electrons as it is for nearly free electrons. An improvement on our work would be to treat the electronic structure in a hybrid scheme—plane waves for *s* and *p* electrons and tight binding for the *d* electrons. A hybrid scheme for the electron-phonon interactions can then be developed using the Bloch formulation for interaction of *s*, and *p* electrons with phonons and the method presented in Sec. II C above for the *d* electrons. We have found however that *s* and *p* electrons contribute so little to $\langle I^2\rangle$, and even to the phonon spectrum, in transition metals compared to the *d* electrons, that the admittedly crude treatment of *s* and *p* electrons by tight-binding introduces little error in the final results. This, however, may not be true for transition metal compounds like NbC, Nb_3Sn, etc., where the contribution of the *s*-*p* orbitals of carbon, tin, etc., may be significant.

E. Approximate electron-phonon matrix

For a tight-binding *s* band, the electron-phonon matrix elements can be expressed in terms of the electronic velocities.[15,16] For multiple *d* bands, it is also possible to do so with some seemingly drastic approximations. The derivation is given in the Appendix. We have found in our calculations, that the results using the approximate derived in the Appendix are valid far beyond the range its derivation would suggest, due possibly to a cancellation of errors in physical quantities like $\langle I^2\rangle$ which involve averages in *k* space. The result of the Appendix is

$$g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'} \simeq q^2\{v^{\alpha}_{\vec{k}}[A^{+}(\vec{k})S(\vec{k})A(\vec{k}')]_{\mu\mu'} -[A^{+}(\vec{k})S(\vec{k}')A(\vec{k}')]_{\mu\mu'}v^{\alpha}_{\vec{k}'\mu'}\}, \tag{2.34}$$

where $v^{\alpha}_{\vec{k}\mu}$ is the αth component of the electronic velocity in the state $\vec{k}\mu$ and q^{-2} is the product of the lattice constant and the logarithmic derivation of the typical tight binding matrix element with distance. Equation (2.34) leads to simple analytic results for $\langle I^2\rangle$ which have the right qualitative behavior. We have also found that (2.34) is a very good recipe for locating phonon anomalies[17] in TMC merely from a knowledge of the band structure.

III. EXPRESSION FOR $\langle I^2\rangle$

The quantity $\langle I^2\rangle$ is defined as

$$\langle I^2\rangle = N(0)^{-2}\sum_{\mu\mu'}\int\frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|}\int\frac{d\sigma_{\vec{k}'}}{|v_{\vec{k}'\mu'}|} \times\sum_{\alpha}|g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'}|^2 \ . \tag{3.1}$$

With maximal use of symmetry, it is possible to express (3.1) in terms of single Fermi-surface integrals provided we use the expression (2.29) for $g^{\alpha}_{k\mu,k'\mu'}$, i.e., neglect the crystal field and three-center contributions to electron-phonon scattering. The crystal-field terms themselves are smaller than the two-center terms by over a factor of five and we expect their derivatives also to be smaller. The three-center integrals are usually over an order of magnitude smaller than the two center integrals.

With (2.29), we obtain

$$\langle I^2\rangle = 2\left(\sum_l d_l a_l D_l - \sum_{m,n,\alpha} C^{\alpha}_{mn} C^{\alpha}_{nm}\right), \qquad (3.2)$$

where

$$a_l = [N(0)d_l]^{-1} \sum_{\mu,m} \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} |A_{m\mu}(\vec{k})|^2 , \qquad (3.3)$$

$$D_l = [N(0)d_l]^{-1} \sum_{\mu,\alpha,m} \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} \left| \sum_n A_{n\mu} \gamma^{\alpha}_{nm}(\vec{k})\right|^2 \qquad (3.4)$$

$$\dot{C}^{\alpha}_{mn} = [N(0)]^{-1} \sum_{\mu' m'} \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} A^*_{m\mu} A_{m'\mu} \gamma^{\alpha}_{m'n} . \qquad (3.5)$$

Here l refers to the irreducible representation of the cubic group with dimensionality d_l. Thus $d_s = 1$, $d_p = 3$, $d_t = 3$, $d_e = 2$. In (3.2)–(3.5) m and m' are summed over orbitals belonging to a given l. The second term in (3.2) is smaller than the first by the Schwarz inequality and turns out in our numerical calculations to be, in fact, about two orders of magnitude smaller. The first term has a simple physical meaning: a_l measures the fractional occupation of the lth orbital at the Fermi surface and D_l the total normalized scattering out of the lth orbital.

The first term in (3.2) follows simply from noting that the Fermi-surface integral,

$$\sum \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} A^*_{m\mu} A_{m'\mu} \sim \delta_{mm'} ,$$

etc. To derive the second term, we have used that

$$C^{\alpha}_{m'n} = \sum_{m\mu} \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} A^*_{m\mu} A_{m'\mu} \gamma^{\alpha}_{mn}(\vec{k})$$

$$= -\sum_{m\mu} \int \frac{d\sigma_{\vec{k}}}{|v_{\vec{k}\mu}|} A^*_{m\mu} A_{m'\mu} \gamma^{\alpha *}_{nm}(\vec{k}) ,$$

and that $C^{\alpha}_{m'n}$ is real.

The advantage of the form (3.2) is that all the integrals need only be done in $\frac{1}{48}$ of the Brillouin zone for a cubic lattice.

The above results differ from those in orthogonal tight binding (OTB) because the term $E\nabla S$ is missing in OTB and because in NTB $A^+A \neq 1$, $\sum_l d_l a_l \neq 1$. In NTB for bonding states one finds $a \equiv \sum d_l a_l < 1$, for antibonding states $a > 1$.

For a qualitative discussion, we may use the approximation (2.34) for $\gamma(\vec{k})$ in terms of the electronic velocities. If the occupations of the various orbitals at the Fermi surface are very similar, one finds approximately

$$\langle I^2\rangle \sim \langle v_F^2\rangle \equiv \sum_\mu \int d\sigma_{\vec{k}}/v_{\vec{k}\mu} \Big/ \int d\sigma_{\vec{k}} v^{-1}_{\vec{k}\mu} ,$$

the average squared Fermi velocity. If the occupation of one orbital is dominant one finds approximately $\langle I^2\rangle \sim \langle v_F^2\rangle a$, where a defined above is a measure of bond order, being greater than 1 for antibonding states and less than 1 for bonding states. Note that $\langle v_F^2\rangle$ also reflects the bonding or antibonding character of the orbitals at the Fermi surface, being larger for the latter.

IV. PROCEDURE OF CALCULATIONS

The calculations proceed in the following stages.

A. Fitting the band structure to obtain nonorthogonal tight-binding parameters

We determine NTB parameters by fitting to the self-consistent calculations[18] of band structure for Nb. We have used a set of nine basis orbitals s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, and $d_{3z^2-r^2}$. Coupling parameters to the nearest and next-nearest neighbor were used. In general this leads to 44 parameters; 4 orbital energies, and 10 coupling parameters, each for the nearest and next-nearest neighbors and for H and S. In practice, we have limited the number of parameters by imposing certain relations between the parameters, as is often done by theoretical chemists. For all the d-d parameters we impose that the overlap parameters be proportional to the bonding parameters.

$$S(dd\eta) = K_d H(dd\eta) , \quad \eta = \sigma, \pi, \delta .$$

with the same constant K_d which is treated as a fitting parameter. Similarly, $S(pp\eta) = K_p H(pp\eta)$, for $\eta = \sigma, \pi$. Further for the s-p, s-d, and p-d parameters we require that

$$(sp\sigma) = (ss\sigma \times sp\sigma)^{1/2}$$

$$(pd\sigma) = (pp\sigma \times dd\sigma)^{1/2} , \quad \text{etc.}$$

We have determined all the nine disposable d-d parameters from a least-square fit to the purely d-like eigenstates at $\Gamma(\Gamma_{12}, \Gamma_{25'})$, $H(H_{12}, H_{25'})$, $N(N_2, N_3)$ and along the directions $\Delta(\Delta_2, \Delta_{2'})$, $G(G_2)$, and $\Sigma(\Sigma_2)$, which can be expressed analytically. The remaining eight disposable s and p parameters are then determined by a least-square fit to the energies of 10 $\vec{k}$ points along the symmetry directions. All the parameters are given in Tables I(a)–I(c). Our band structure agrees well with that of Ref. 18; the rms error is 0.15 eV. Both the band structures are exhibited in Ref. 17, Fig. 1.

Our determination of the parameters involving the s and p orbitals is not to be taken too seriously; tight binding is certainly not valid for them. However, they are not important for the average electron-phonon matrix element in the Fermi surface for materials in which the d density dominates

TABLE I. (a). Atomic orbital energies for (in Ry) our NTBS fit. For comparison, the OTB values of Ref. 26 are shown, referring to the same zero energy as our values. Note that the crystal field splitting $E_{dt} - E_{de}$ is only half in NTBS than in OTBS. (b). First-nearest-neighbor bond energy and overlap parameters for our NTBS calculation. For comparison we give the corresponding values calculated from Herman-Skillman atomic orbitals and potentials. Also shown are the values of Ref. 26. Since in Ref. 26 the two-center approximation was not used, we have calculated the two-center terms from those given there by a least-squares fit. (c). Second-neighbor bond energy and overlap parameters for our NTBS calculation. Also shown are the Herman-Skillman atomic values and those from Ref. 26.

(a)	NTBS	OTBS (Ref. 26)
E_s	0.13	0.198
E_α	0.412	0.535
E_d	−0.222	−0.137
E_{de}	−0.262	−0.212

(b)	NTBS		Herman-Skillman		OTBS (Ref. 26)
	H (Ry)	*S*	*H* (Ry)	*S*	*H* (Ry)
ss	−0.108	0.0	−0.216	0.501	−0.75
spσ	0.112	−0.010	⋯	⋯	0.107
sdσ	−0.104	0.010	−0.072	0.087	−0.098
ppσ	0.115	−0.065	⋯	⋯	0.147
ppπ	−0.022	0.012	⋯	⋯	0.012
pdπ	−0.017	0.068	⋯	⋯	−0.120
pdπ	0.041	−0.026	⋯	⋯	0.028
ddσ	−0.100	0.071	−0.117	0.082	−0.095
ddπ	0.078	−0.055	0.104	−0.106	0.040
ddδ	−0.014	0.010	−0.027	0.038	0.010

(c)	NTBS		Herman-Skillman		
2*nn*	*BE* (RY)	*OV*	*BE* (RY)	*OV*	OTBS (Ref. 26)
ss	−0.043	0.068	−0.177	0.42	−0.047
sp	0.074	0.095	⋯	⋯	0.092
sd	−0.056	0.059	−0.064	0.089	−0.049
pp	0.129	0.132	⋯	⋯	0.159
pp	−0.029	0.030	⋯	⋯	0.0
pd	−0.096	0.082	⋯	⋯	−0.075
0*d*	0.026	0.022	⋯	⋯	0.0
dd	−0.072	0.051	0.070	0.064	−0.056
dd	0.024	−0.017	0.057	0.070	0.0
dd	⋯	⋯	−0.013	0.021	0.0

near the Fermi surface. This is true for all the materials we consider, except those for which the Fermi level lies near the bottom of the big dip in the density of states; this occurs around $Nb_{0.3}Mo_{0.7}$.

B. Determination of the Fermi surface

The rigid band model is assumed valid for the 4*d* metals and alloys of the bcc structure. The Fermi energy is determined from the density of states by electron counting and the wave vectors at the Fermi surface for a given number of electrons/atom is determined. To determine the Fermi surface, we work in $\frac{1}{48}$ of the Brillouin zone, which is divided into 512 tetrahedra. The tetrahedral method of Rath and Freeman[19] is adopted. The centers of the tetrahedra at the Fermi surface are determined; the rms velocity $|v_{\vec{k}\mu}|$ for each band, the eigenvectors $A_{m\mu}(\vec{k})$ and the surface area associated with each such point is also calculated. The Fermi-surface parameters are given in Table II.

C. Calculation of $\gamma^{\alpha}_{m,n}(\vec{k})$

We express the transfer and overlap integrals, $H_{im,jn}$ and $S_{im,jn}$, in terms of the bond parameters of Table I by the tables given by Slater and Koster.[20] We analytically take the derivatives of the expressions in terms of the three cartesian co-

TABLE II. Lattice constants and Fermi-surface parameters for the 4*d* bcc transition metals and alloys.

Electron/atom	Lattice constant (a-u)	E_F(Ry)	$N(0)$ (Ry^{-1})	$\langle v^2 \rangle$ $\times 10^8$ (cm/sec)^2	a
4.75	6.30	−0.333	33.75	0.213	0.853
5.00 (Nb)	6.225	−0.323	22.94	0.259	0.864
5.20	6.165	−0.313	20.56	0.328	0.874
5.40	6.110	−0.300	15.015	0.348	0.888
5.60	6.050	−0.282	6.7	0.626	0.873
5.80	5.990	−0.250	5.9	0.606	0.911
6.00 (Mo)	5.935	−0.218	6.7	0.568	0.964
6.25	5.860	−0.193	11.61	0.387	1.033

ordinates. This leaves only the radial derivative to be numerically determined. The physics of the radial derivatives is rather interesting and we discuss it in some detail.

The radial derivatives. Ideally, the radial derivative should be evaluated by calculating the variation of the Hamiltonian and overlap integral between a given pair of atoms as the distances between them is varied keeping all the other atoms at their equilibrium lattice sites. Such a calculation would be extremely hard. An alternative method is to calculate the self-consistent band structures for a few different periodic lattice configurations, and to fit the results with tight binding. One can then examine how the radial derivative varies with the configuration, and thereby estimate the many-body effects on the radial derivative and thus on the electron-phonon matrix element.

However, band structure calculations with different lattice structures are not available for the transition metals. The best thing at hand is the self-consistent band structure of bcc Nb[18] at the equilibrium lattice constant and at 5% smaller lattice constant. We have evaluated the radial derivative of the Hamiltonian and overlap integrals by fitting these band structure results and assuming the integrals vary exponentially. This procedure determines the exponents to an accuracy of only about 10%.

We have also evaluated the radial derivatives by calculating them from Herman-Skillman wave functions and potentials. These results are within 20% of those calculated from the fitted band structure. This indicates that renormalizations, etc., are corrections only of this order.

The one shortcoming of the above reasoning is that in both methods of calculation, the configurations examined leave the atoms concerned locally neutral. We may, however, argue that we would not expect the wave-vector dependence of the electron-phonon matrix element to be affected significantly by renormalization effects (through their effect on the radial derivatives) if the susceptibility

$$\chi_q = \sum_k \frac{(f_{\vec{k}+\vec{q}} - f_{\vec{k}})}{(\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})} ,$$

is not significantly q dependent. This quantity has been evaluated for the bcc transition metals[21] and in fact satisfies this criteria well.

To go back to the procedure of our calculation, with the radial derivatives at hand either from the fitted band structure or from Herman-Skillman atomic calculations, we can Fourier transform to derive $\gamma^{\alpha}_{m,n}(\vec{k})$ given by (2.30).

D. Calculation of $\langle I^2 \rangle$

With the Fermi surface information and the derived $\gamma^{\alpha}_{m,n}(\vec{k})$, we have complete information of the integrands in (3.2). The integrals can all be done over $\frac{1}{48}$ of the Fermi surface and the results multiplied by 48. The Fermi surface program developed by Rath and Freeman[19] is used.

V. RESULTS AND DISCUSSION

We have calculated $\langle I^2 \rangle$ for the 4*d* bcc system ranging from an electron/atom (e/a) ratio of 4.5 to 6.5. The results and the experimentally deduced values are shown in Fig. 1 and Table III. Considering the 10%–20% uncertainty in both sets of values, the agreement may be regarded as very good. In the results shown in Fig. 1, the value of the radial derivative is calculated from Nb Herman-Skillman wave functions and potentials and the alloy lattice constants. Actually the values of the derivatives derived from Mo Herman-Skillman wave functions and potentials at Mo lattice constants are about 15% larger than those from Nb Herman-Skillman wave functions and potentials at Nb lattice constant. This means that the decreased lattice constant of Mo overcompensates the reduced atomic size of Mo. Had we calculated the results with the derivatives derived from bandstructure for Nb the agreement for Nb would

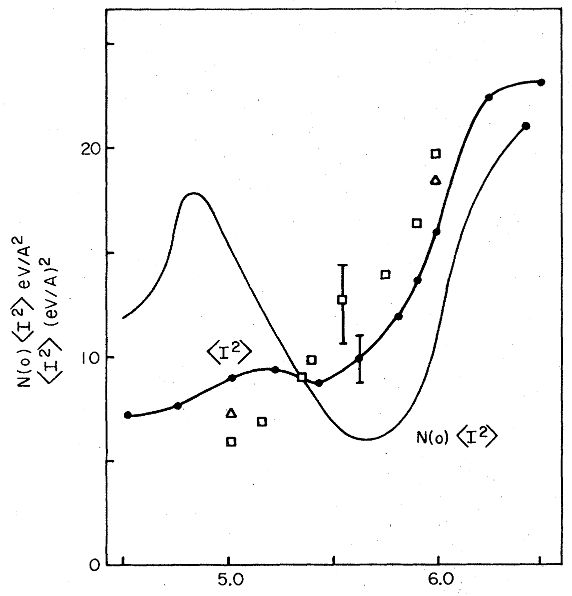

FIG. 1. Calculated values of $\langle I^2\rangle$ for various electron/atom ratios in the $4d$ bcc transition metals and alloys compared with the empirical values: □. Δ denotes the best values calculated to data by the rigid muffin-tin method, Ref. 24. Also plotted is the calculated $N(0)\langle I^2\rangle$.

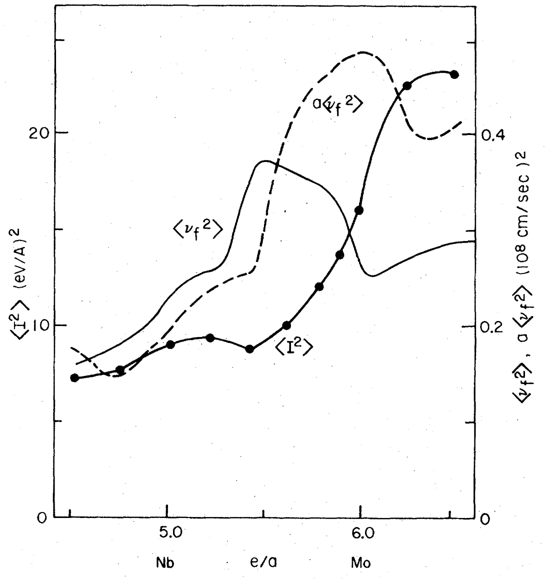

FIG. 2. $\langle v_F^2\rangle$ and $a\langle v_F^2\rangle$ for various electron/atom ratios in the $4d$ bcc transition metals and alloys compared with the calculated $\langle I^2\rangle$. Note that the variation in $\langle I^2\rangle$ is generally proportional to that of the product of bond order a and the average-squared Fermi velocity.

have been even better. If we scale these derivatives with changing e/a ratio with the same factor as the derivatives from atomic wave functions and potentials, the overall agreement improves over that shown in Fig. 1. This however would be stretching the point a bit.

We have also plotted, in Fig. 2, the variation of $\langle v_F^2\rangle$ and $a_d\langle v_F^2\rangle$ with e/a to test the validity of the approximation discussed at the end of Sec. III. Here a_d is the bond order of the d bond; $a_d = 3a_t + 2a_e$. The general trend of $a_d\langle v_F^2\rangle$ is similar to that of $\langle I^2\rangle$. This proportionality is very interesting and has a simple physical interpretation. The electron-phonon matrix elements are large when small lattice displacements cause relatively large changes in electronic energy. This requires that the relevant electronic states have rapid variation in their energy with wave vector, i.e., a large velocity. The dependence of $\langle I^2\rangle$ on the bond order a_d reflects the fact that the antibonding states have rapid variation in the wave functions in the interstitial regions and are therefore more sensitive to lattice displacements than the bonding states. (A part of this effect is of course already

TABLE III. Average electron-phonon matrix element calculated here and compared with the empirical values calculated by other methods. (a) From Ref. 27, (b) Ref. 24, (c) Ref. 25, (d) Ref. 24, (e) $\langle I^2\rangle$ calculated with OTB parameters of Ref. 12, (f) this work; OTB values were obtained by putting $\nabla S = 0$ and $A = 1$.

Electron/atom	$\langle I^2\rangle$ empirical	$\langle I^2\rangle$ calculated here	$\langle I^2\rangle$ (OTB)	$\langle I^2\rangle$ (muffin-tin)
4.75		7.8		
5.00 (Nb)	6.0^a	9.1	21.6^e	8.7^c
	7.3^b		16.5^f	9.3^d
5.20		9.5		
5.40		8.8		
5.60		10.1		
5.80		12.0		
6.00 (Mo)	18.6^a			
	20.0^b	16.0	21.0^f	15.5^d
6.25		22.8		

contained in the electronic velocities.)

We have also decomposed the contributions to $\langle I^2\rangle$ in order to study the importance of each orbital. We find that by far the strongest contribution in the range between Nb and Mo comes from t_{2g} orbitals. The main reason for this is that this orbital is dominant by a factor of 3 over e_g and, in general, by even more over p and s. Only in the region $e/a > 6$, the e_g orbital admixture becomes approximately equal to the t_{eg}. The terms D_t and D_e are of the same order of magnitude, i.e. the d-electron-phonon coupling is of the same strength, irrespective of the orbital character. The s and p electrons contribute little to $\langle I^2\rangle$ because there is only a small admixture of s-p orbitals near the Fermi surface in most of the e/a range between Nb and Mo, and because both the radial and the angular parts of ∇H and ∇S are smaller than for d orbitals. Similarly, the s-d and p-d hybridization effects are unimportant for $\langle I^2\rangle$. All this is best seen by the results of a calculation where all ∇H_{mn} and ∇S_{mn} are set equal to zero unless both m, n refer to d orbitals. We then get $\langle I^2\rangle_d \simeq 0.8 I^2$. We conclude that the principal mechanism for the strong electron-phonon coupling is the strong coupling to lattice displacements of the d electrons.

A further point of interest is how our results differ from those obtained by OTB. There are two differences in the NTB electron-phonon matrix element compared to OTB. First, the term $E_F \nabla S$ is about 30% of ∇H and tends to cancel it. Second, the orbital coefficients A_μ^m are not normalized to 1 as in OTB, but vary from $|A|^2 \simeq 0.8$ in bonding states near $e/a = 3$ to $|A|^2 \sim 1$ near $e/a = 7$. The results for $\langle I^2\rangle$ with OTB are given in Table III using parameters of Peter *et al.*[12] These are about twice as large as the experimental results. There has been some other work based on tight-binding methods by Birnboim and Gutfreund.[13] These calculations are, however, done with a model band structure rather than a realistic band structure, and therefore cannot be usefully compared with the present results.

A lot of effort[7,18,19] has been directed toward calculating electron-phonon interactions in TMC, starting from electronic states that are decomposed in an angular momentum representation around each atom, as is done in the APW and the KKR schemes. This general approach was initiated by Hopfield,[22] who started with the conception that superconductivity is an *atomic* property; therefore a basis set with an angular momentum decomposition around an atom should be a good starting point. He showed that λ is proportional to the p- (and f-) wave contribution to the density of states. Later more precise work[23-25] has shown that Hopfield erred in the interpretation of his derived expressions, and what is relevant for λ in this formalism is the p- and f-wave electronic density at one atom when looked at from a neighbor! This proof would seem to us to have damaged the basic premise of the work which sought to understand superconductivity on an atomic basis. Besides, it is not very helpful to learn that $\langle I^2\rangle$ is proportional to the f-wave electronic density at one atom when looked at from the other; this latter quantity has no clear physical meaning, nor does one know how it varies from element to element or structure to structure.

A very attractive looking expression[23] has been derived to calculate λ from the above approach, which expresses $\langle I^2\rangle$ in terms of phase shifts of various angular momentum components. In practice to calculate[23-25] with these expressions, the assumption of the "rigidly moving muffin tin" is used to evaluate the electron-phonon matrix element. Questions have been raised about the importance of the interstitial region,[28,29] neglected in this approximation, and of ways to properly screen[28] the "rigidly moving muffin tin." The most careful of the calculations[24] using this approach, however, agrees as well with the experimental results as our calculations.

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We are very grateful to Dr. J. Rath for providing us with programs for the tetrahedral method of Fermi surface integration. We would also like to thank Dr. D. A. Papaconstantopoulos for sending us detailed APW results for the Nb band structure at different lattice constants.

APPENDIX: APPROXIMATE ELECTRON-PHONON MATRIX

An approximate expression for the electron-phonon matrix element can be derived which, we have found, is useful far beyond the range its derivation would suggest.

We first start by noting that

$$\nabla_{k\alpha} H_{mn}(\vec{\mathrm{k}}) = \frac{1}{\sqrt{N}} \sum_{R_{ij}} R_{ij}^{\alpha} H_{mn}(\vec{\mathrm{R}}_{ij}) \exp(i\vec{\mathrm{k}} \cdot \vec{\mathrm{R}}_{ij}) , \tag{A1}$$

and compare it with the Fourier transform of the derivative of the Hamiltonian matrix entering in (2.30), i.e., with

$$\sum_{R_{ij}} \nabla_{R_{ij},\alpha} H_{mn}(\vec{\mathrm{R}}_{ij}) \exp(i\vec{\mathrm{k}} \cdot \vec{\mathrm{R}}_{ij}) . \tag{A2}$$

Now $\nabla_{R_{ij},\alpha} H_{mn}(R_{ij})$ can in general be written as a sum of the radial and of the angular derivatives,

$$\nabla_{R_{ij},\alpha} H_{mn}(R_{ij}) = (\nabla_{\mathrm{rad},\alpha} + \nabla_{\mathrm{ang},\alpha}) H_{mn}(R_{ij}) . \tag{A3}$$

The radial derivative of $H_{mn}(R_{ij})$ for localized orbitals can be written

$$\nabla_{\mathrm{rad},\,\alpha} H_{mn}(R_{ij}) = (R^{\alpha}_{ij}/r_{mn}) H_{mn}(R_{ij}) \,, \tag{A4}$$

where r_{mn} is the characteristic fall-off distance of $H_{mn}(R_{ij})$ with R_{ij}. If we ignore the angular derivative for the moment and insert (A.4) in (A.2), we note that the k dependence of (A.1) and (A.2) is identical. If we further make the assumption that r_{mn} is dependent of m and n, which is not a bad assumption if we confine our attention to the d orbitals alone, we conclude that the two expressions (A.1) and (A.2) are proportional to each other.

Now consider the angular derivatives. The length parameter introduced in taking the derivative is now $|R_{ij}|^{-1}$ rather than r^{-1}_{mn}, the $\vec{k}$ dependence of (A.3) from the angular derivative is the same as that of (A.1), but the magnitude of the derivative is not proportional to $H_{mn}(\vec{R}_{ij})$. This is shown by an example. Consider, for instance $H_{xy,yz}$ and its derivative with respect to x.

$$(R_x/|R|) H_{xy,yz} = [l^2 n(dd\pi - dd\delta) + l^2 m^2 n(3dd\sigma - 4dd\pi + dd\delta)] \,, \tag{A.4a}$$

where $dd\sigma$, $dd\pi$, and $dd\delta$ are the bond-parameters for a given pair of atoms at a distance $|R|$ and l, m, and n are the direction cosines of one with respect to the other. The result of taking the angular derivative is

$$|R| \left.\frac{d}{dR_x}\right|_{\mathrm{ang}} H_{xy,yz} = (1 - 2l^2) n(dd\pi - dd\delta) + m^2 n(1 - 4l^2)(3dd\delta - 4dd\pi + dd\delta) \,. \tag{A.5}$$

Let us now use (A.4a) and (A.5) in (A.1) and (A.2), respectively. On performing the sums over nearest neighbors, the k dependence in both expressions will be the same since it comes from the n index common to (A.4a) and (A.5) for the nearest neighbors, (A.4a) yields

$$(8/\sqrt{3})[\tfrac{1}{3}(dd\pi - dd\delta) + \tfrac{1}{9}(3dd\sigma - 4dd\pi + dd\delta)] \times \cos k_x a \cos k_y a \sin k_z a \,, \tag{A.6}$$

while (A.5) yields

$$(8/\sqrt{3})[\tfrac{1}{3}(dd\pi - dd\delta) - \tfrac{1}{9}(3dd\sigma - 4dd\pi + dd\delta)] \times \cos k_x a \cos k_y a \sin k_z a \,. \tag{A.7}$$

The angular derivatives are however smaller by a factor $r_{mn}/|R|$ which is typically about 0.3. Further the difference of typical terms like (A.6) and (A.7) is generally small compared to the radial terms. We may therefore roughly approximate (A.2) by $q^2\nabla_{\vec{k}\alpha} H_{mn}(\vec{k})$, where q is of the order of the geometrical mean of the lattice constant and typical exponential fall off of the d-d Hamiltonian-matrix element. We can similarly approximate (A.2) with S instead of H by $q^2\nabla_{\vec{k}\alpha} S_{mn}(\vec{k})$. The electron phonon matrix element is then (2.29) with $\gamma^{\alpha}_{mn}(\vec{k})$ approximated as

$$\gamma^{\alpha}_{mn}(\vec{k}) \simeq q^2[\nabla_{k\alpha} H_{mn}(\vec{k}) - E_k \nabla_{k\alpha} S_{mn}(\vec{k})] \,. \tag{A.8}$$

Now consider

$$\sum_{mn} A^{+}_{\mu m}(\vec{k}) \gamma^{\alpha}_{mn}(\vec{k}) A_{n\mu'}(\vec{k}') \,. \tag{A.9}$$

Using (A.8), (A.9) is equal to

$$\begin{aligned} q^2(&\vec{v}_{\vec{k}\mu}[A^{+}(\vec{k})S(\vec{k})A(\vec{k}')]_{\mu\mu'} \\ &+ \{E_{\vec{k}\mu'}[A^{+}(\vec{k})\nabla S(\vec{k})A(\vec{k}')]_{\mu\mu'}\} \\ &+ E_{\vec{k}\mu}[\nabla A^{+}(\vec{k})S(\vec{k})A(\vec{k}')]_{\mu\mu'} \\ &- [\nabla A^{+}(\vec{k})H(\vec{k})A(\vec{k}')]_{\mu\mu'}) \,. \end{aligned} \tag{A.10}$$

We expect the first term to be generally much larger than the rest. The rest are important only in regions of strong hybridization. If we restrict our attention to scattering at the Fermi energy, the second term is zero. If we keep only the first term in (A.10) and make a similar approximation for the term involving $\vec{\gamma}_{mn}(\vec{k}')$ in $g_{\vec{k}\mu,\vec{k}'\mu'}$, we have

$$\begin{aligned} g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'} \cong q^2\{ & v^{\alpha}_{\vec{k}\mu}[A^{+}(\vec{k})S_{\vec{k}}A(\vec{k}')]_{\mu\mu'} \\ & - [A^{+}(k)S(\vec{k}')A(\vec{k}')]_{\mu\mu'} v_{\vec{k}'\mu'}\} \,. \end{aligned} \tag{A.11}$$

If nonorthogonality effects are neglected, one gets the even simpler result:

$$\begin{aligned} g^{\alpha}_{\vec{k}\mu,\vec{k}'\mu'} \simeq q^2\{ & v^{\alpha}_{\vec{k}\mu}[A^{+}(\vec{k})A(\vec{k}')]_{\mu\mu'} \\ & - [A^{+}(\vec{k})A(\vec{k}')]_{\mu\mu'} v^{\alpha}_{\vec{k}'\mu'}\} \,. \end{aligned} \tag{A.12}$$

With this approximation, we can go a long way towards evaluating $\langle I^2 \rangle$ analytically. The results are discussed in Sec. III. We have also found that (A.11)–(A.12) are a very good recipes for locating phonon anomalies in transition metals merely from a knowledge of the band structure.

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