Electron-Phonon Interaction in the Tight-Binding Approximation: Validity of the Bloch Formulation*

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(Received 28 April 1971)

We show that the Bloch formulation of the electron-phonon interaction is valid in the tight-binding limit, correctly describes the rigid response of the tightly bound electrons to the ion motion, and introduces corrections of first order in the bandwidth to the "modified-tight-binding" approximation of Frohlich and Mitra and the "Hubbard-Hamiltonian" approximation of Barišić, Labbé, and Friedel. Expressions are derived for the Bloch tight-binding electron-phonon matrix elements.

There is considerable current interest[1-5] in calculating the electron-phonon interaction for transition metals, principally to account for the order of magnitude of observed superconducting transition temperatures. In the Bloch formulation of this problem the electron-phonon interaction is taken between eigenfunctions of the periodic potential, and the validity of this formulation has been suspect in the case of the transition-metal d electrons which are tightly bound to the ion cores. As a result, attempts have been made to proceed directly from the Born-Oppenheimer or adiabatic formulation of the problem, in which the interaction is taken between the adiabatic electron states which follow the ion motion.

The difficulty with the latter approach is that the adiabatic electron states are not eigenfunctions of a translationally symmetric potential, and consequently it is as difficult to solve for them as it is to solve for the electronic states in an amorphous material. Frohlich[1,2,6] has suggested approximating the tight-binding one-electron state corresponding to the ions in static displaced positions by a "modified-tight-binding" form

$$\psi_{\vec{k},\alpha}=\frac{1}{\sqrt{N}}\sum_{\mu} e^{i\vec{k}\cdot\vec{R}_\mu}\,\phi_\alpha(\vec{r}-\vec{R}_\mu-\vec{X}_\mu)\ , \tag{1}$$

where $\vec{X}_\mu$ is the displacement of the μth ion from its equilibrium lattice position $\vec{R}_\mu$, ϕ_α is the localized orbital, and N is the total number of ions. An equivalent assumption has been made by Barišić *et al.*[4] in their "Hubbard-Hamiltonian" formulation of the problem.[7] Here we wish to show that the simple Bloch formulation of the interaction is valid in the tight-binding limit, and is equivalent to using Eq. (1) plus corrections of first order in the tight-binding bandwidth.

In the one-electron approximation we can write the total Hamiltonian for the ions and electrons as

$$\mathcal{H}=H_{\text{ions}}(\vec{X}_\mu)+\textstyle\sum_i H_{\text{el}}(\vec{X}_\mu;\vec{r}_i)\ , \tag{2}$$

$$H_{\text{el}}=\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial\vec{r}_i^{\,2}}+V(\vec{X}_\mu;\vec{r}_i)\ . \tag{3}$$

Here $\vec{r}_i$ is the position coordinate for the ith electron (of mass m), and V is the one-electron self-consistent (e.g., Hartree-Fock-Slater) potential, which includes the interaction of the ith electron with the ions in displaced positions $\vec{X}_\mu$, and with the other electrons, where the latter are assumed to have responded to the positions of the displaced ions. The term H_{ions} contains the kinetic and direct potential energy of the ions, minus the electron-electron potential energy which has been counted twice in $\sum_i H_{\text{el}}$. (This formulation implies that we have obtained V by solving self-consistently for the one-electron states for each possible positional configuration of the ions, and can therefore express the electron-electron potential energy as a functional of the ion positions.)

In the Born-Oppenheimer approximation[8] we first solve for the one-electron adiabatic states ψ:

$$H_{\text{el}}\psi=E_{\text{el}}\psi\ . \tag{4}$$

We then obtain the adiabatic ion wave functions χ by summing over the occupied electron states:

$$\left(H_{\text{ions}}+\sum_{\text{occ}} E_{\text{el}}\right)\chi=E_{\text{ad}}\,\chi\ . \tag{5}$$

Defining an adiabatic Hamiltonian H_{ad} whose eigenfunctions are the adiabatic product states, the electron-phonon matrix element can then be defined by

$$J_{\text{ad}}=\langle\chi'\psi'\,|H_{\text{ions}}+H_{\text{el}}-H_{\text{ad}}|\,\psi\chi\rangle\ , \tag{6}$$

which is small because the nonadiabatic corrections are of order m/M.

In the Bloch formulation we write

$$\begin{aligned}&\mathcal{H}=H_{\text{ions}}+\textstyle\sum_i H_{\text{el}}^{(0)}(\vec{r}_i)+\sum_i \delta V(\vec{r}_i)\ ,\\ &H_{\text{el}}^{(0)}\equiv H_{\text{el}}(\vec{X}_\mu=0;\vec{r}_i)\ ,\end{aligned} \tag{7}$$

where, to first order in the ion displacements,

$$\delta V(\vec{r}) = \sum_{\mu} \vec{X}_{\mu} \cdot \left(\frac{\partial V(\vec{X}_{\mu}; \vec{r})}{\partial \vec{X}_{\mu}} \right) \Big|_{\vec{X}_{\mu}=0} \quad . \tag{8}$$

Solving for the Bloch electron states and the "bare" phonon states,

$$H_{el}^{(0)} \psi^{(0)} = E_{el}^{(0)} \psi^{(0)} \quad , \tag{9}$$

$$H_{ions} \chi^{(0)} = E_{ions}^{(0)} \chi^{(0)} \quad , \tag{10}$$

the Bloch electron-phonon matrix element can be defined by

$$J_{B1} = \langle \chi^{(0)\prime} \psi^{(0)\prime} | \delta V | \psi^{(0)} \chi^{(0)} \rangle \quad . \tag{11}$$

Whether or not the Bloch formulation is valid, by which we mean that this matrix element used in second-order perturbation theory will give a good description of the electron-phonon coupling, depends upon whether δV can be correctly treated as a small perturbation, which in turn implies two conditions: (a) that the adiabatic electron equation (4) can be correctly solved as a small perturbation on the Bloch equation (9); and (b) that the adiabatic ion equation (5) can be solved as a small perturbation on the bare ion equation (10). Condition (a) is readily satisfied, since we can write

$$H_{el} = H_{el}^{(0)} + \delta V \quad , \tag{12}$$

and since the ion displacements $\vec{X}_{\mu}$ are small on the scale of electron coordinates, it follows from (8) that δV is small on the scale of electron energies. However, condition (b) implies rewriting (5) as

$$\left(H_{ions} + \sum_{occ} E_{el}^{(0)} + \sum_{occ} (E_{el} - E_{el}^{(0)}) \right) \chi = E_{ad} \chi \quad , \tag{13}$$

and treating

$$\sum_{occ} (E_{el} - E_{el}^{(0)})$$

as a small perturbation. This is a much more stringent condition, demanding that $(E_{el} - E_{el}^{(0)})$ be small on the scale of *phonon* energies. To meet this condition we cannot invoke the smallness of the ion displacements, since, in fact, $\vec{X}_{\mu}$ are the coordinates in this equation. That is, if the adiabatic electron energy E_{el} depends strongly on the ion positions, then χ will be markedly different from $\chi^{(0)}$, *regardless of the smallness of the ion displacements*, and will not be correctly described by low-order perturbation theory. This is one point which does not appear to have been generally recognized in the literature.

There are two obvious cases in which the adiabatic electron energy does have a sufficiently weak dependence on the ion positions, and in which the Bloch approach is therefore justified: One case is that of a nearly-free-electron (NFE) gas perturbed by a weak pseudopotential; in the limit of a vanishing pseudopotential the adiabatic electron energy is just the free-electron energy, independent of the ion positions. The second obvious case is that of tightly bound electrons with wave functions describable by localized orbitals having small overlap with their near-neighbor counterparts. In the limit of vanishing overlap the adiabatic electron energy is just the energy of the localized orbital, again independent of the ion positions. It follows that the Bloch formulation is valid for tightly bound electrons to low order in the overlap. We also note that if δV is small in the above sense then the important result, shown by several authors, [9] is that the adiabatic and Bloch expressions [Eqs. (6) and (11)] become identical to first order in the ion displacements.

Also note that, since we have defined H_{ions} as including the subtraction of the electron-electron interaction, our bare phonons have certain properties of the renormalized phonons, such as the acoustic branch approaching zero frequency rather than the plasma frequency in the long-wavelength limit. However, the smallness of the renormalization of these bare phonons should be verified in practical cases (both for NFE and tight-binding materials) to justify the use of the Bloch electron-phonon operator (8).

There is one further point to be clarified. In the Bloch formulation we are implicitly writing the adiabatic electron wave functions as

$$\psi_{\vec{k},\alpha} = \psi_{\vec{k},\alpha}^{(0)} + \psi_{\vec{k},\alpha}^{(1)} \quad , \tag{14}$$

where

$$\psi_{\vec{k},\alpha}^{(0)} = \frac{1}{\sqrt{N}} \sum_{\mu} e^{i\vec{k}\cdot\vec{R}_{\mu}} \phi_{\alpha}(\vec{r} - \vec{R}_{\mu})$$

is the Bloch tight-binding function, and by first-order perturbation theory

$$\psi_{\vec{k},\alpha}^{(1)} = \sum_{\vec{k}',\alpha'}{}' \frac{\langle \psi_{\vec{k}',\alpha'}^{(0)} | \delta V | \psi_{\vec{k},\alpha}^{(0)} \rangle}{E_{\vec{k},\alpha}^{(0)} - E_{\vec{k}',\alpha'}^{(0)}} | \psi_{\vec{k}',\alpha'} \rangle \quad , \tag{15}$$

where α' runs over all bands. Let us consider the "rigid-potential approximation" for V:

$$V(\vec{X}_{\mu}; \vec{r}) = \sum_{\mu} U(\vec{r} - \vec{R}_{\mu} - \vec{X}_{\mu}) \quad , \tag{16}$$

where $U(r)$ is an atomiclike potential. Then, we wish to ensure that Eqs. (14) and (15) correctly describe the rigid response of the adiabatic electron states to the motion of the ions, in the limit of vanishing overlap. In that limit we have simply a collection of noninteracting free atoms, so the adiabatic electron state associated with the μth ion is simply

$$\phi_{\alpha}(\vec{r} - \vec{X}_{\mu}), \quad E = E_{\alpha} \tag{17}$$

with respect to an origin at $\vec{R}_{\mu}$, where ϕ_{α} is a

free-atom orbital satisfying

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \vec{r}^{\,2}}+U(r)\right)\phi_\alpha(\vec{r})=E_\alpha\,\phi_\alpha(\vec{r})\ . \tag{18}$$

In the Bloch formulation we are expressing this state as

$$\phi_\alpha(\vec{r})+\phi_\alpha^{(1)}\ , \tag{19}$$

$$\phi_\alpha^{(1)}=\sum_{\alpha'}{}'\ \frac{\langle\phi_{\alpha'}|-\vec{X}_\mu\cdot\partial U/\partial\vec{r}|\phi_\alpha\rangle}{E_\alpha-E_{\alpha'}}\ |\phi_{\alpha'}\rangle\ . \tag{20}$$

Taking the gradient of (18), substituting in (20), and using the closure relation on the complete set of states α', we readily obtain

$$\phi_\alpha^{(1)}=-\vec{X}_\mu\cdot\frac{\partial\phi_\alpha}{\partial\vec{r}}\ ,$$

so (19) becomes

$$\phi_\alpha(\vec{r})-\vec{X}_\mu\cdot\frac{\partial\phi_\alpha}{\partial\vec{r}}=\phi_\alpha(\vec{r}-\vec{X}_\mu) \tag{21}$$

to first order in the ion displacements, in agreement with (17). (It is also readily verified that the perturbation corrections to the energy vanish to any order in $\vec{X}_\mu$ for this rigid-shift problem.) It follows from the above (and can easily be explicitly verified) that if we retain only *one-center* contributions in (15) then (14) becomes

$$\psi_{\vec{k},\alpha}=\frac{1}{\sqrt{N}}\sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu}\phi_\alpha(\vec{r}-\vec{R}_\mu-\vec{X}_\mu)$$

to first order in $\vec{X}_\mu$, which is just the modified-tight-binding assumption [Eq. (1)]. However, there are also multicenter contributions to (15), containing terms of first order in the overlap, or bandwidth, and these terms are implicitly contained in the Bloch matrix element (11), but absent in the modified-tight-binding formulation; these additional terms account for the difference between the Bloch and modified-tight-binding results for the matrix element, being neglected in the assumption of Eq. (1), although they contribute to the matrix element to the same order in the bandwidth as the terms retained. To see whether these differences are quantitatively significant would require a detailed calculation.

Finally, explicit expressions for the Bloch tight-binding matrix-element contributions in the rigid-potential approximation can be obtained by using the familiar expansion of the lattice displacements in terms of the bare phonon annihilation operator b_q^ν:

$$\vec{X}_\mu=\sum_{\vec{q},\nu}\left(\frac{\hbar}{2MN_c\omega_q^\nu}\right)^{1/2}\vec{\epsilon}_q^{\,\nu}\,(b_q^\nu e^{i\vec{q}\cdot\vec{R}_\mu}+b_q^{\nu\dagger}e^{-i\vec{q}\cdot\vec{R}_\mu}),$$

where the symbols have their usual meaning. Writing (11) as

$$J=\langle(N\pm1)_q^\nu\,\psi^{(0)}_{\vec{k}',\alpha'}\,|\,\delta V\,|\,\psi^{(0)}_{\vec{k},\alpha}\,N_q^\nu\rangle\ , \tag{22}$$

where we have introduced phonon states for the ion wave functions, we obtain one-center contributions to (22) given by

$$J_1=-(E_\alpha-E_{\alpha'})\left(\frac{\hbar}{2MN_c\omega_q^\nu}\right)^{1/2}\times\delta(\vec{k}'-\vec{k}\pm\vec{q})\,\vec{\epsilon}_q^{\,\nu}\cdot\langle\phi_{\alpha'}|\,\partial\phi_\alpha/\partial\vec{r}\rangle \tag{23}$$

[where we have again used the gradient of (18)], two-center contributions given by

$$J_2=-\left(\frac{\hbar}{2MN_c\omega_q^\nu}\right)^{1/2}\delta(\vec{k}'-\vec{k}\pm\vec{q})\times\vec{\epsilon}_q^{\,\nu}\cdot\sum_\mu\Big(e^{i\vec{k}'\cdot\vec{R}_\mu}\langle\phi_{\alpha'}(\vec{r}+\vec{R}_\mu)|\,\frac{\partial U}{\partial\vec{r}}(\vec{r})\,|\phi_\alpha(\vec{r})\rangle + e^{-i\vec{k}\cdot\vec{R}_\mu}\langle\phi_{\alpha'}(\vec{r})|\,\frac{\partial U}{\partial\vec{r}}(\vec{r})\,|\phi_\alpha(\vec{r}+\vec{R}_\mu)\rangle\Big)\ , \tag{24}$$

and degenerate three-center contributions given by

$$J_3=\left(\frac{\hbar}{2MN_c\omega_q^\nu}\right)^{1/2}\delta(\vec{k}'-\vec{k}\pm\vec{q})\,\vec{\epsilon}_q^{\,\nu}\cdot\sum_\mu e^{\mp i\vec{q}\cdot\vec{R}_\mu}\frac{\partial}{\partial\vec{R}_\mu}\times\langle\phi_{\alpha'}(\vec{r})|\,U(\vec{r}-\vec{R}_\mu)\,|\phi_\alpha(\vec{r})\rangle\ , \tag{25}$$

as well as three-center contributions which can be similarly derived. The two-center and degenerate three-center expressions were previously derived by Mitra[2] for the case $\alpha'=\alpha$.

Note that the one-center terms vanish by parity unless the band states arise from localized orbitals α and α' of different parity; this is the basis of Hopfield's hypothesis that $p\rightarrow d$ transitions dominate transition-metal superconductivity. Alternatively, Garland and Bennemann[5] postulate that the degenerate three-center contribution (25) is dominant, while Barišić *et al.*[4] hold that the principal contribution arises from two-center terms, although, as discussed above, their expression for these terms differs from (24) due to the modified-tight-binding assumption.

The author wishes to thank Professor John Bardeen for arousing his interest in this area, and to acknowledge helpful conversations with Professor Bardeen, Professor James Garland, and Dr. Volker Heine.

*Supported in part by the U. S. Army Research Office (Durham) under contract No. DA-HC04-69-C-0007.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 3 1 FEBRUARY 1972

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Ising Model with Four-Spin Interactions, F. Y. Wu [Phys. Rev. B 4, 2312 (1971)]. The author's name should read F. Y. Wu instead of F. W. Wu.