Electron-Phonon Matrix Elements*

by

David A. Liberman

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

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We have shown elsewhere[1] that the wave function of an electron in a lattice may be written as a sum of scattered waves, one coming from each cell:

$$\psi(\underset{\sim}{r}) = \sum_i e^{i\underset{\sim}{k}\cdot\underset{\sim}{a}_i}\, \varphi(\underset{\sim}{r} - \underset{\sim}{a}_i) \quad . \tag{1}$$

(For simplicity we consider the case of only one atom per cell located at the position $\underset{\sim}{a}_i$.) The function φ is the solution of the equation[1]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\underset{\sim}{r}) - E\right]\varphi(\underset{\sim}{r}) = -\, v(\underset{\sim}{r}) \sum_i{}' e^{i\underset{\sim}{k}\cdot\underset{\sim}{a}_i}\, \varphi(\underset{\sim}{r} - \underset{\sim}{a}_i) \quad , \tag{2}$$

where the primed sum excludes the term corresponding to the cell at the origin, $\underset{\sim}{a}_o \overset{\text{zero}}{=} \underset{\sim}{0}\cdot v(\underset{\sim}{r})$ is the potential due to the atom at the origin.

It seems reasonable to assume that a good approximation to the wave function of an electron in a slightly distorted lattice will be a similar sum of scattered waves coming now from atoms located at positions $\underset{\sim}{R}_i$ -

$$\psi(\underset{\sim}{r};\underset{\sim}{R}_1,\cdots,\underset{\sim}{R}_N) = \sum_i e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_i}\, \varphi(\underset{\sim}{r} - \underset{\sim}{R}_i) \tag{3}$$

- where the $\underset{\sim}{R}_i$'s differ slightly from their equilibrium values, the $\underset{\sim}{a}_i$'s. We have in fact shown that a much stronger statement can be made[2]: that, for systems as disordered as a liquid, the wave function

of an electron may be written in the form of equation (3). In that case, however, it is necessary to modify equation (2). For a distorted lattice it will be sufficient to find $\varphi(\underset{\sim}{r})$ for a perfect lattice (equation (2)), and then use it in (3).

We can now write down the wave function of the electron and lattice in the adiabatic approximation which is just the product of the electron wave function $\psi(\underset{\sim}{r}; \underset{\sim}{R}_1, \cdots, \underset{\sim}{R}_N)$ and the wave function of the vibrating lattice $\Omega(\underset{\sim}{R}_1, \cdots, \underset{\sim}{R}_N)$, and from this calculate the electron-phonon matrix elements. These are easily shown to be[3]

$$H'_{BA} = -\sum_i \frac{\hbar^2}{2m} \int (\Omega_B \psi_B)^* \left[\Omega_A \nabla_i^2 \psi_A + 2 \nabla_i \Omega_A \cdot \nabla_i \psi_A\right] d^{3N} \underset{\sim}{R}\, d^3 \underset{\sim}{r} \quad . \tag{4}$$

After the differentiations of ψ_A with respect to the atomic coordinates are made, they are to be replaced by their equilibrium values, the lattice vectors $\underset{\sim}{a}_i$. This means we are calculating the matrix elements to the lowest order in the phonon amplitude. It is not possible to do better by this method as the φ calculated from equation (2) is not good enough.

Our method differs from the usual calculation of electron-phonon matrix elements[3] which start with electron wave functions for an undistorted lattice and use as a perturbation the difference between $\Sigma_i v(\underset{\sim}{r} - \underset{\sim}{R}_i)$ and $\Sigma_i v(\underset{\sim}{r} - \underset{\sim}{a}_i)$. If $v(\underset{\sim}{r})$ is weak enough to permit the calculation of $\varphi(\underset{\sim}{r})$ by perturbation theory, it is found that the same result is obtained for the electron-phonon matrix elements as by the conventional methods with free electron wave functions.

In conclusion we wish to remark that this method does not enable us to avoid taking account of the screening of the ion-electron interaction by the plasma electrons. This enters through the correct choice of $v(\underset{\sim}{r})$ and its effect on φ.

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[1] A paper on this work will be submitted to the Physical Review. A somewhat restricted version of the same method was given long ago by J. Korringa, Physica XIII, 392 (1947).

[2] A paper on electron wave functions in liquids will be submitted to the Physical Review.

[3] J. M. Ziman, Electrons and Phonons (Oxford University Press, London, 1960).