Adiabatic Theory of an Electron in a Deformable Continuum*

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A scaling analysis of the adiabatic eigenstates of an electron placed in a deformable continuum with and without the presence of a Coulombic defect is set forth. This procedure enables us to obtain exact information about the system's adiabatic eigenstates for various models of the electron-lattice interaction.

A long-standing fundamental problem in solid-state physics is that of determining the circumstances in which the carrier-induced atomic displacements do or do not *qualitatively* affect eigenstates of an electronic charge carrier in a insulator (produce a substantial polaron effect). Studies of the effect of the electron-lattice interaction on the electronic states have employed both a variety of models and a variety of approaches. In particular, three-dimensional systems as well as systems of lesser dimensionality have been investigated. In addition researchers have addressed rather distinct models of the electron-lattice interaction; among others the long-range interaction of an electron with the electric dipoles associated with longitudinal-optical-mode displacements[1] and the short-range interactions characteristic of both polar and nonpolar materials (analogous to the deformation potential) have received considerable attention.[2-4]

In this work we present an adiabatic treatment of the ground state of a carrier placed in a deformable continuous medium with and without the presence of a static (defect-related) Coulombic potential well. The results provide definitive predictions as to the nature of the adiabatic ground state—in particular the degree of spatial localization—and its dependence on range and strength of the electron-lattice interaction, as well as on the dimensionality of the system. A general summarizing statement: It is found that the degree of localization of the adiabatic ground state may vary *continuously* or *discontinuously* with changes in physical parameters (such as electron-lattice coupling strength), depending on the character of the electron-lattice interaction and on the dimensionality of the system. Furthermore with an alteration of the physical parameters, states other than the ground state can, in some instances, abruptly appear in (or disappear from) the solution.

The adiabatic approach is based on a physical picture in which the motion of an excess electron is sufficiently rapid compared to the motion of the (relatively heavy massed) atoms of the system so that the electron may be assumed to adjust to the instantaneous positions of the atoms. In this (adiabatic) limit (the kinetic energy of the lattice atoms is neglected) the ground-state energy of the coupled electron-atom system is the minimum of the sum of the electron's ground-state energy (itself a function of the dilation of the continuum) and the strain energy of the deformable continuum. In particular, the Hamiltonian of an electron placed in a deformable continuum containing a defect is

$$H_e = \hat{T}_e + V_d(\vec{r}) + \int d\tau' Z(\vec{r},\vec{r}')\Delta(\vec{r}'), \tag{1}$$

where $\hat{T}_e$ is the electron's kinetic energy operator, and the remaining two terms are the contributions to the potential energy of an electron at $\vec{r}$ associated, respectively, with the presence of the defect and with the dilation of the deformable continuum. The final term, the electron-continuum (electron-lattice) interaction, depicts a linear dependence of the potential energy of an electron at $\vec{r}$ on the dilation associated with each point of the continuum, $\Delta(\vec{r}')$; $Z(\vec{r},\vec{r}')$ is a function which characterizes the strength and range of the electron-continuum interaction. The relevant electronic energy, E_{el}, for a given strain field, $\Delta(\vec{r})$, is given by

$$E_{el} = \int d\tau \Psi^*(\vec{r}) H_e \Psi(\vec{r}), \tag{2}$$

where $\Psi(\vec{r})$ is the lowest-energy eigenfunction of H_e. Finally the strain energy of the continuum in

the usual harmonic approximation is simply

$$E_s = \tfrac{1}{2} S \int d\tau' \, \Delta^2(\vec{r}'), \tag{3}$$

where S is a strain constant.

The ground-state energy of the coupled system corresponds to a situation in which the distortion pattern, characterized by $\Delta(\vec{r})$, is such as to yield the lowest total energy, $E_{el}+E_s$. Minimizing the total energy with respect to $\Delta(\vec{r})$, one readily finds that

$$\Delta(\vec{r}) = -S^{-1} \int d\tau' \, |\Psi(\vec{r}')|^2 Z(\vec{r}', \vec{r}). \tag{4}$$

To calculate explicitly the ground-state electronic eigenfunctions one must solve the eigenvalue equation $H_e \Psi = E_{el} \Psi$ with H_e being given by Eq. (1) and $\Delta(\vec{r}')$ being given by Eq. (4). This is generally a formidable task.

For our present purposes it will suffice to employ an alternative procedure. To begin, we utilize Eq. (4) to express the ground-state energy in terms of the ground-state electronic eigenfunctions. Explicitly, we write

$$E = T_e - V_d - V_{int} + E_s, \tag{5}$$

where $E_s = \tfrac{1}{2} V_{int}$ and

$$T_e = (\hbar^2/2m) \int d\tau \, |\nabla \Psi(\vec{r})|^2, \tag{6a}$$

$$V_d = -\int d\tau \, |\Psi(\vec{r})|^2 V_d(\vec{r}), \tag{6b}$$

$$V_{int} = S^{-1} \int d\tau \, |\Psi(\vec{r})|^2 \int d\tau' \, Z(\vec{r}, \vec{r}') \int d\tau'' \, Z(\vec{r}'', \vec{r}') |\Psi(\vec{r}'')|^2. \tag{6c}$$

Since the above energy is (by construction) the minimum energy of the coupled system, any alteration of the wave function $\Psi(r)$ must necessarily increase the total energy, E. In particular, if we change the length scale of the (normalized) eigenfunction, replace $\Psi(\vec{r})$ by $R^{-d/2} \Psi(\vec{r}/R)$ (d is the dimensionality of the system), the energy (now a function of R) of a finite-radius eigenstate must have its minimum at the scale corresponding to the actual eigenstate, at $R = 1$.

To proceed further we must introduce explicit forms for the electron-continuum interaction function $Z(\vec{r}, \vec{r}')$. In the case of the standard long-range interaction of the carrier with the deformation-induced electric polarization of the continuum one has $Z(\vec{r}, \vec{r}') = E_L |\vec{r} - \vec{r}'|^{-2}$. The continuum version of the short-range interaction of the molecular-crystal and deformation-potential models is the local interaction $Z(\vec{r}, \vec{r}') = E_S \delta(\vec{r} - \vec{r}')$. Generalizing, we write the interaction function as the sum of these two contributions. In addition we henceforth take the defect potential to be Coulombic: $V_d(\vec{r}) \propto |\vec{r}|^{-1}$.

Introducing the above described functions into Eqs. (5) and (6), we explicitly calculate $E(R)$. The result is

$$E(R) = T_e/R^2 - \tfrac{1}{2}(V_{int}^{S}/R^d + V_{int}^{S,L}/R^2 + V_{int}^{L}/R^{4-d}) - V_d/R, \tag{7}$$

where T_e and V_d are given by Eqs. (6a) and (6b), and

$$V_{int}^{S} = (E_S^2/S) \int d\tau \, |\Psi(\vec{r})|^4, \tag{8a}$$

$$V_{int}^{S,L} = (2E_S E_L/S) \int d\tau \int d\tau'' \, |\Psi(\vec{r})|^2 |\Psi(\vec{r}'')|^2 / |\vec{r} - \vec{r}''|^2, \tag{8b}$$

$$V_{int}^{L} = (E_L^2/S) \int d\tau \int d\tau' \int d\tau'' \, |\Psi(\vec{r})|^2 |\Psi(\vec{r}'')|^2 / |\vec{r} - \vec{r}'|^2 |\vec{r}' - \vec{r}''|^2, \tag{8c}$$

with $V_{int} = V_{int}^{S} + V_{int}^{S,L} + V_{int}^{L}$.

At this point we can, with relatively little effort, obtain several well-known results of polaron theory. Consider first the standard optical polaron problem characterized by the study of a *three-dimensional* defect-free continuum in which the carrier interacts with the continuum solely via the previously described *long-range* component of the electron-continuum interaction: $d = 3$, $V_d = 0$, and $V_{int}^{S} = V_{int}^{S,L} = 0$. As illustrated by the curve of Fig. 1(a), for this case $E(R)$ $[= T_e R^{-2} - \tfrac{1}{2} V_{int}^{L} R^{-1}]$ possesses a solitary minimum at $R = 4T_e/V_{int}^{L} \equiv 1$. This means that the electron exists in a finite-radius, bound state ($E_{el} = T_e - V_{int}^{L} = -3V_{int}^{L}/4 < 0$) with the polaron (bound electron plus distortion) always being energetically stable ($E = E_{el} + E_s = -\tfrac{1}{4} V_{int}^{L} < 0$). Furthermore, the ratio of the electron's energy ($-3V_{int}^{L}/4$) to the strain energy of the continuum ($\tfrac{1}{2} V_{int}^{L}$) is simply $-3{:}2$. These results were previously obtained by Pekar.[5]

An adiabatic theory of a carrier in a *one-dimensional* system interacting with the defect-free continuum solely via the *short-range* component of the electron-continuum interaction was developed in Ref. 2. Despite the difference between the two models, the above results, with

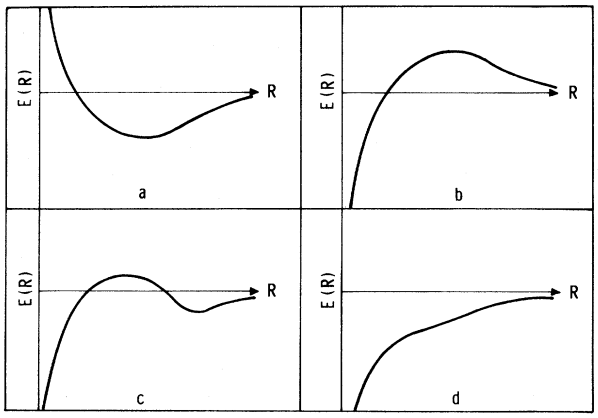

FIG. 1. Representative $E(R)$ curves.

$V_{\rm int}{}^{S}$ simply replacing $V_{\rm int}{}^{L}$, were again obtained. The reason for this agreement is now clear: With $d=1$ and $V_d = V_{\rm int}{}^{L} = V_{\rm int}{}^{S,L} = 0$ one sees from Eq. (7) that $E(R) = T_e R^{-2} - \frac{1}{2} V_{\rm int}{}^{S} R^{-1}$ only differs from the energy function $E(R)$ characteristic of the Pekar problem by the substitution of $V_{\rm int}{}^{S}$ for $V_{\rm int}{}^{L}$.

The situation of a carrier in a three-dimensional defect-free deformable continuum for which the electron-continuum interaction is short ranged may be seen to be qualitatively distinct from the one-dimensional version of the problem. Specifically, with $d=3$ and $V_d = V_{\rm int}{}^{L} = V_{\rm int}{}^{S,L} = 0$, Eq. (7) reduces to $E(R) = T_e R^{-2} - \frac{1}{2} V_{\rm int}{}^{S} R^{-3}$; as illustrated in Fig. 1(b) this function possesses no finite-radius minimum. The only minima which occur are at $R=\infty$, corresponding to an unbound electron in an unstrained continuum, and at $R=0$, corresponding to an electron self-trapped in an infinitely deep and infinitesimally localized deformation-induced potential well. These two situations are, respectively, the continuum analogies of rigid-lattice conduction-band states and small-polaron states (the carrier and its induced lattice deformation being essentially confined to a single unit cell) associated with a carrier in a discrete lattice. The notion that only these two situations, but no intermediate-range polaron, could exist in a three-dimensional system characterized by a short-range electron-lattice interaction has been advanced previously on the basis of an approximate adiabatic argument[4] and variational calculations.[3,4] Our exact adiabatic results are consistent with such an hypothesis.

In proceeding to investigate more complicated systems, we shall henceforth restrict our attention to three-dimensional models. The first situation to be considered is that of an electron in the presence of a Coulombic defect for which the electron-continuum interaction possesses only the previously discussed long-range component. In this case one finds, from Eq. (7) with $V_{\rm int}{}^{S} = V_{\rm int}{}^{S,L} = 0$, that, as in Fig. 1(a), $E(R) = T_e R^{-2} - (V_d + \frac{1}{2} V_{\rm int}{}^{L}) R^{-1}$ possesses a solitary minimum at $R = 2T_e/(V_d + \frac{1}{2} V_{\rm int}{}^{L}) \equiv 1$. This circumstance corresponds to the electron being stably bound in the potential well provided by the defect and the carrier-induced dilation of the continuum with the ground-state energy $E = -\frac{1}{2}(V_d + \frac{1}{2} V_{\rm int}{}^{L})$.

The situation of a carrier in the presence of a Coulombic defect which interacts with the continuum only via the *short-range* component of the electron-continuum interaction is, however, qualitatively different. In this case, $V_{\rm int}{}^{L} = V_{\rm int}{}^{S,L} = 0$, one has that the energy function, $E(R) = T_e R^{-2} - V_d R^{-1} - \frac{1}{2} V_{\rm int}{}^{S} R^{-3}$, always possesses a minimum at $R=0$ and will [Fig. 1(c)] or will not [Fig. 1(d)] possess an additional finite-radius minimum depending, respectively, on whether $T_e{}^2$ is greater than or less than $3V_{\rm int}{}^{S} V_d/2$. Thus with a continuous change of the physical parameters the finite-radius solution will cease to exist (become dynamically unstable with respect to forming the continuum analog of a small polaron) if $3V_{\rm int}{}^{S} V_d/2$ is thereby increased to surpass $T_e{}^2$. The inclusion of the long-range component of the electron-continuum interaction along with the short-range component does not qualitatively alter this conclusion. In fact, this more general situation is formally the same as that in which only the short-range component is considered: $T_e - \frac{1}{2} \times V_{\rm int}{}^{S,L}$ replaces T_e and $V_d + \frac{1}{2} V_{\rm int}{}^{L}$ replaces V_d. Finally it is noted that the problem of a carrier in a defect-free three-dimensional continuum which interacts with the continuum via both the long-range and the short-range components of the electron-continuum interaction is also formally the same as that of a carrier in the Coulombic well interacting with the continuum dilation solely via the short-range interaction. In this case, T_e must be replaced by $T_e - \frac{1}{2} V_{\rm int}{}^{S,L}$ and V_d replaced by $\frac{1}{2} V_{\rm int}{}^{L}$. Thus a purely short-range electron-continuum interaction always yields two distinct states, a small-polaron-like state and a nonpolaronic (unbound dilationless) state, Fig. 1(b). The addition of a long-range component to the electron-continuum interaction can convert the nonpolaronic state to a finite-radius polaronic state, Fig. 1(c). As depicted in Fig. 1(d), with a sufficiently strong long-range component of the interaction, the finite-radius state shrinks in

size until it can no longer exist without collapsing into a small-polaron state.

Finally it is noted that in a discrete (atomic) system both the electron-lattice interaction energy and the strain energy saturate at some maximum value when the electron's radius shrinks smaller than the interatomic separation. One method of incorporating this effect into the continuum model is to disregard the $E(R)$ curve at values of the scaling factor R less than that characteristic of the onset of the saturation effect, R_s. This procedure simply serves to eliminate the small-polaron solution if R_s lies between a maximum and a minimum (at $R=1$) of $E(R)$. If $R_s > 1$ the solitary solution corresponds to small-polaron formation. In systems with a short-range component of the electron-lattice interaction a change in the physical parameters can produce the abrupt appearance (or disappearance) of small-polaron states (at R_s) in the non-ground-state solution. The energies of such small-polaron states are not, however, generally given correctly by this modified continuum model. One does see, in agreement with Refs. 3 and 4 and Shore, Sander, and Kleinman,[6] that although the nature of the ground state may change abruptly with an alteration of the physical parameters, in the adiabatic limit the ground-state energy does not.

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[1]H. Fröhlich, Proc. Roy. Soc. London, Ser. A 160, 230 (1937).

[2]T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959).

[3]D. Emin, Adv. Phys. 22, 57 (1973).

[4]Y. Toyozawa, Prog. Theor. Phys. 26, 29 (1961).

[5]S. I. Pekar, *Untersuchungen Über die Electronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954).

[6]H. B. Shore, L. M. Sander, and L. Kleinman, Nature (London) 245, 44 (1973).

Momentum-Transfer Dependence of the $L_{II,III}$ Edge of Mg†

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We report measurements of the $L_{II,III}$ x-ray threshold in Mg at momentum transfers of $q=0$ and 1.8 Å^{-1}. We found that a straightforward application of the theory of Mahan, Nozières, and De Dominicis failed to describe the data. We conclude that for Mg, and probably for all polyvalent metals, other effects are at least as important as this theory for describing absorption threshold shapes.

The shapes of soft-x-ray thresholds in simple metals depart from the simple step function expected in the one-electron approximation.[1] Some metals show a peaking at threshold; others do not. Mahan, Nozières, and De Dominicis (MND) formulated a theory to explain these observations.[2] This many-electron theory describes the effect on threshold shapes of interactions between the core hole and conduction electrons. Peaking is predicted when transitions occur to s partial waves in the conduction band; when transitions to higher partial waves occur, a more rounded threshold shape is predicted, because the screening charge of the core hole is expected to be dominated by s waves. Consequently, when the core is a p state, peaking is predicted, while s core states should have rounded thresholds. These predictions are in qualitative agreement with soft-x-ray absorption spectra.[1] Inelastic electron scattering can provide a more stringent test of the theory since different conduction-band partial waves can be selected for a given core state by varying the momentum transfer.[3] This type of test was first proposed by Doniach, Platzman, and Yue.[4]

The operator causing the transition in electron scattering is $e^{i\vec{q}\cdot\vec{r}}$ where $\vec{q}$ is the momentum transfer and $\vec{r}$ the position operator of an electron in the sample. Since the core state is well localized the transition matrix element can be expanded as

$$\langle\psi_f|1+i\vec{q}\cdot\vec{r}-\tfrac{1}{2}(\vec{q}\cdot\vec{r})^2+\ldots|\psi_i\rangle, \quad (1)$$

where ψ_f and ψ_i are the exact final and initial