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Binding energy of an impurity in an ionic crystal

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An analysis is made of the binding energy of an impurity in an ionic crystal in terms of the frequency shifts in the LO branch, arising out of the coupling of the polar modes through the polarization of the impurity. Estimates are obtained for the energy shifts of both tightly-bound and loosely-bound impurities. The connection of this approach with the bound-polaron problem is discussed.

I. INTRODUCTION

In an earlier paper[1] a simple model of a polar crystal-impurity system had been used to obtain the local optical modes generated by the impurity, and it had been pointed out that there will be a change in the binding energy of the impurity due to the generation of the local modes. If the impurity is analyzed in terms of the hydrogen-atom model,[2] in an ionic crystal the perturbed impurity levels would be those of a bound polaron which has received attention lately.[3-6] The main object of this paper is to evaluate the shift in the energy of the impurity by a microscopic and semiclassical approach of the sort indicated in Ref. 1. The basic feature of this approach is the evaluation of the additional coupling between the dipolar oscillations in the unit cells through the induced polarization of the impurity. This additional coupling leads to frequency shifts in the LO branch (assumed to be undispersed), and the resulting change in the zero-point energy of LO oscillations gives the change in the binding energy of the impurity. The additional coupling depends on the polarizability of the impurity and hence, depends on the particular quantum state it is in. We shall see that this approach gives the energy shifts for both a tightly bound and a loosely bound impurity, and in the limit of the electron associated with the impurity being free, gives the usual value of this energy obtained from polaron theory. Also, in the appropriate limits the results can be compared with those of the earlier workers[3,4] who have used a macroscopic continuum model for the bound polaron.

II. LATTICE AND IMPURITY MODELS

For simplicity we consider, as in Ref. 1, an ionic crystal with an undispersed LO branch with frequency ω_0, which is the frequency of the dipolar oscillations in each of the N unit cells. We will also assume that the conduction band has an isotropic nondegenerate minimum, so that the donor electron has an effective mass m. The dipolar oscillations in the $\vec{1}$th lattice cell are of an effective dipolar moment $\vec{\mu}_{\vec{1}}$ which has associated with it an effective charge e^* and an effective mass M. In the presence of the impurity its equation of motion can be written in the time-independent form

$$M(\omega_0^2-\omega^2)\vec{\mu}_{\vec{1}}(\omega)=(e^*)^2(4\pi)^2 \times\sum_{\vec{1}'}\overleftrightarrow{\mathrm{F}}(\vec{1},\vec{1}';\omega)\vec{\mu}_{\vec{1}'}(\omega)\ . \quad (2.1)$$

The force-constant tensor $(4\pi)^2\overleftrightarrow{\mathrm{F}}(\vec{1},\vec{1}';\omega)$ gives the force on the $\vec{1}$th dipole due to the $\vec{1}'$th one through the incuded polarization of the impurity, and it vanishes in the absence of the impurity giving ω_0 as the unperturbed LO branch frequency.

It will be shown in the Appendix that the explicit form of $\overleftrightarrow{\mathrm{F}}(\vec{1},\vec{1}';\omega)$ is

$$\overleftrightarrow{\mathrm{F}}(\vec{1},\vec{1}';\omega)=\int[\nabla_{\vec{1}}\nabla_{\vec{1}}G(\vec{\mathrm{R}}_{\vec{1}}-\vec{\mathrm{r}}')]\overleftrightarrow{\alpha}(\vec{\mathrm{R}}-\vec{\mathrm{r}}') \times[\nabla_{\vec{1}'}\nabla_{\vec{1}'}G(\vec{\mathrm{r}}'-\vec{\mathrm{R}}_{\vec{1}'})]\,d^3r'\ , \quad (2.2)$$

where $(\nabla\nabla)$ is the diadic formed out of the gradient operator, $G(\vec{\mathrm{r}}-\vec{\mathrm{r}}')$ is the electrostatic potential Green's function given by

$$G(\vec{\mathrm{r}}-\vec{\mathrm{r}}')=-\frac{1}{(2\pi)^3}\int\frac{d^3k\exp[i\vec{\mathrm{k}}\circ(\vec{\mathrm{r}}-\vec{\mathrm{r}}')]}{k^2}\ , \quad (2.3)$$

$\vec{\mathrm{R}}$ is the location of the center of the impurity, and $\overleftrightarrow{\alpha}(\vec{\mathrm{r}}-\vec{\mathrm{R}})$ is a polarizability density which can be evaluated in terms of the quantum states of the impurity. $\overleftrightarrow{\alpha}(\vec{\mathrm{r}})$ can be written

$$\overleftrightarrow{\alpha}(\vec{\mathrm{r}},\omega)=\int d^3k\,\overleftrightarrow{\alpha}(\vec{\mathrm{k}},\omega)\exp[i(\vec{\mathrm{k}}\circ\vec{\mathrm{r}})]\ , \quad (2.4)$$

where, as shown in the Appendix, for an impurity which can be approximated by a hydrogenic system in a state $|n\rangle$,

$$\alpha_n(\vec{\mathrm{k}},\omega)=-\frac{e^2}{\hbar}\sum_m\Bigg(\frac{\langle n|\vec{\mathrm{r}}_e|m\rangle\langle m|\exp[i(\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_e)]|n\rangle}{\omega_{nm}+\omega}$$

$$+\frac{\langle m|\vec{r}_e|n\rangle\langle n|\exp[i(\vec{k}\cdot\vec{r}_e)]|m\rangle}{\omega_{nm}-\omega}\Bigg)\frac{i\vec{k}}{k^2}\,. \tag{2.5}$$

Here $\vec{r}_e$ is the coordinate of the electron.

When $|n\rangle$ is a totally symmetric state, such as $|1s\rangle$,

$$\overleftrightarrow{\alpha}_n(\vec{k},\omega)\equiv\alpha_n(\vec{k},\omega)\overleftrightarrow{I}\,, \tag{2.6}$$

i.e., it is an isotropic tensor. For $k\to 0$,

$$\alpha_n(\omega)=\frac{2e^2}{\hbar}\sum_m \omega_{nm}\frac{\langle n|z_e|m\rangle\langle m|z_e|n\rangle}{\omega_{nm}^2-\omega^2}\,. \tag{2.7}$$

In $\vec{k}$ space, the secular equation (2.1) can be written

$$\vec{\mu}_{\vec{l}}(\omega)=\frac{A(\omega)}{(2\pi)^3}\sum_{\vec{l}'}\int d^3k\,d^3k'\left(\frac{\vec{k}\vec{k}}{k^2}\right)\overleftrightarrow{\alpha}(\vec{k}-\vec{k}')\times\left(\frac{\vec{k}'\vec{k}'}{k'^2}\right)\exp[i(\vec{k}\cdot\vec{R}_{\vec{l}}-\vec{k}'\cdot\vec{R}_{\vec{l}'})]\times\exp[-i(\vec{k}-\vec{k}')\cdot\vec{R}]\,\vec{\mu}_{\vec{l}'}(\omega)\,. \tag{2.8}$$

Here

$$A(\omega)=(4\pi)^2(e^*)^2/M(\omega_0^2-\omega^2)\,. \tag{2.9}$$

Introducing the definition

$$\vec{\nu}(\vec{k})=\sum_{\vec{l}}\vec{\mu}_{\vec{l}}\exp[-i(\vec{k}\cdot\vec{R}_{\vec{l}})]\,, \tag{2.10}$$

multiplying both sides of Eq. (2.8) by $\exp[-i(\vec{k}\cdot\vec{R}_{\vec{l}})]$, and summing over $\vec{l}$ we get,

$$\vec{\nu}(\vec{k})=\frac{A(\omega)}{(2\pi)^3}\int d^3k'\,d^3k''\left(\frac{\vec{k}'\vec{k}'}{k'^2}\right)\times\overleftrightarrow{\alpha}(\vec{k}'-\vec{k}'')\left(\frac{\vec{k}''\vec{k}''}{k''^2}\right)\exp[-i(\vec{k}'-\vec{k}'')\cdot\vec{R}]\times\left(\sum_{\vec{l}}\exp[-i(\vec{k}'-\vec{k}'')\cdot\vec{R}_{\vec{l}}]\right)\vec{\nu}(\vec{k}'')\,. \tag{2.11}$$

Noting that

$$\sum_{\vec{l}}\exp[-i(\vec{k}'-\vec{k})\cdot\vec{R}_{\vec{l}}]=N\sum_{\vec{g}}\delta_{\vec{k}',\vec{k}+\vec{g}}\,, \tag{2.12}$$

where $\vec{g}$ is a reciprocal-lattice vector, and from Eq. (2.10),

$$\vec{\nu}(\vec{k}+\vec{g})\equiv\vec{\nu}(\vec{k})\,, \tag{2.13}$$

and the fact that

$$\sum_{\vec{k}}\equiv\frac{V}{(2\pi)^3}\int d^3k=\frac{NV_0}{(2\pi)^3}\int d^3k\,, \tag{2.14}$$

where V_0 is the volume of each unit cell, we can write Eq. (2.11) in the form

$$\vec{\nu}(\vec{k})=A(\omega)\,\rho\sum_{\vec{g}}\exp[-i(\vec{k}+\vec{g})\cdot\vec{R}]\times\frac{(\vec{k}+\vec{g})(\vec{k}+\vec{g})}{(\vec{k}+\vec{g})^2}\int d^3k'\,\overleftrightarrow{\alpha}(\vec{k}-\vec{k}'+\vec{g})\left(\frac{\vec{k}'\vec{k}'}{k'^2}\right)\times\exp[i(\vec{k}'\cdot\vec{R})]\,\vec{\nu}(\vec{k}')\,. \tag{2.15}$$

Here $\rho=N/V=1/V_0$, the density of the crystal. Using the formula

$$\int_{\text{All } k' \text{ space}} d^3k'\,F(\vec{k}')=\sum_{\vec{g}}\int_{V^*}d^3k'\,F(\vec{k}'+\vec{g})\,, \tag{2.16}$$

where $V^*=(2\pi)^3/V_0$ is the volume of the first Brillouin zone, and

$$\sum_{\vec{k}\in V^*}=\frac{N}{V^*}\int_{V^*}d^3k\,, \tag{2.17}$$

we can write Eq. (2.15) as

$$\vec{\nu}(\vec{k})=A(\omega)\,\rho\sum_{\vec{g},\vec{g}'}\frac{(\vec{k}+\vec{g})(\vec{k}+\vec{g})}{(\vec{k}+\vec{g})^2}\times\exp[-i(\vec{k}+\vec{g})\cdot\vec{R}]\left(\frac{V^*}{N}\right)\sum_{\vec{k}'\in V^*}\overleftrightarrow{\alpha}(\vec{k}-\vec{k}'+\vec{g}-\vec{g}')\times\frac{(\vec{k}'+\vec{g}')(\vec{k}'+\vec{g}')}{(\vec{k}'+\vec{g}')^2}\exp[i(\vec{k}'+\vec{g}')\cdot\vec{R}]\,\vec{\nu}(\vec{k}')\,. \tag{2.18}$$

We thus have a $3N\times 3N$ secular determinant

$$|\hat{I}-\hat{S}|=0\,, \tag{2.19}$$

whose roots give the perturbed LO frequencies. The explicit form of the 3×3 submatrices of $\hat{S}$ is

$$S_{(\vec{k},\vec{k}')\in V^*}=A(\omega)\,\rho\left(\frac{V^*}{N}\right)\times\sum_{\vec{g},\vec{g}'}\exp[-i(\vec{k}-\vec{k}'+\vec{g}-\vec{g}')\cdot\vec{R}]\,\frac{(\vec{k}+\vec{g})(\vec{k}+\vec{g})}{(\vec{k}+\vec{g})^2}\times\overleftrightarrow{\alpha}(\vec{k}-\vec{k}'+\vec{g}-\vec{g}')\,\frac{(\vec{k}'+\vec{g}')(\vec{k}'+\vec{g}')}{(\vec{k}'+\vec{g}')^2}\,. \tag{2.20}$$

Equations (2.18)–(2.20) form the basis of the present treatment.

III. EVALUATION OF THE ENERGY SHIFTS

The problem of evaluation of the change in the zero-point energy of the LO modes from the secular determinant of Eq. (2.19) is exactly analogous to that of evaluation of the phonon self-energy of an impurity.[7] The change in the zero-point energy is

$$\Delta E=\frac{1}{2\pi i}\oint\left(\frac{\hbar\omega}{2}\right)d\omega\left(\frac{d}{d\omega}\ln|\hat{I}-\hat{S}|\right)=\frac{-\hbar}{4\pi i}\oint\ln|\hat{I}-\hat{S}|\,d\omega=\frac{\hbar}{4\pi i}\oint\sum_{j=1}^{\infty}\frac{[\mathrm{Tr}(\hat{S}^j)]}{j}\,. \tag{3.1}$$

In this the contour encloses the positive real axis, but for our purpose we need to take only the dominant contribution from the pole at ω_0 occurring in $A(\omega)$. We shall now apply the formalism to a few cases.

A. Very tightly bound impurity

If the electron orbital of the impurity has an extension small compared with the lattice constant, $\overleftrightarrow{\alpha}(\vec{\mathrm{k}},\omega)\equiv\alpha(\omega)\overleftrightarrow{\mathrm{I}}$, where $\alpha(\omega)$ for the ground state is k independent and is given by an expression of the form of Eq. (2.7). For instance, if in a hydrogenic system we consider only the transition to $|2p\rangle$ from $|1s\rangle$,

$$\alpha(\omega)=\left(\frac{32\times 8}{243}\right)^2\left(\frac{E_{1s}-E_{2p}}{(E_{1s}-E_{2p})^2-\hbar^2\omega^2}\right)e^2a_0^2\ , \quad (3.2)$$

where a_0 is the Bohr radius in the medium.

When $\alpha(\omega)$ is k independent, $S_{\vec{\mathrm{k}},\vec{\mathrm{k}}'}$ of Eq. (2.20) becomes separable

$$S_{(k,k')\in V^*}=A(\omega)\,\rho\left(\frac{V^*}{N}\right)\alpha(\omega)\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})\overleftrightarrow{\mathrm{P}}^*(\vec{\mathrm{k}}')\ , \quad (3.3)$$

where

$$\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})=\sum_{\vec{\mathrm{g}}}\frac{(\vec{\mathrm{k}}+\vec{\mathrm{g}})(\vec{\mathrm{k}}+\vec{\mathrm{g}})}{(\vec{\mathrm{k}}+\vec{\mathrm{g}})^2}\exp[-i(\vec{\mathrm{k}}+\vec{\mathrm{g}})\cdot\vec{\mathrm{R}}]\ . \quad (3.4)$$

The secular equation then becomes,

$$\left|\overleftrightarrow{\mathrm{I}}-\alpha(\omega)A(\omega)\,\rho\left(\frac{V^*}{N}\right)\sum_{\vec{\mathrm{k}}\in V^*}\overleftrightarrow{\mathrm{P}}^*(\vec{\mathrm{k}})\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})\right|=0\ . \quad (3.5)$$

It may be noted that

$$\begin{aligned}\frac{V^*}{N}\sum_{\vec{\mathrm{k}}\in V^*}\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})\exp(i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_l)&=(2\pi)^3\\ &\times\frac{1}{(2\pi)^3}\int_{\mathrm{All}\ k\ \mathrm{space}}d^3k\left(\frac{\vec{\mathrm{k}}\vec{\mathrm{k}}}{k^2}\right)\exp[i\vec{\mathrm{k}}\circ(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})]\\ &=(2\pi)^3(\nabla_{\vec{l}}\nabla_{\vec{l}})G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})\ . \quad (3.6)\end{aligned}$$

Hence,

$$\begin{aligned}\frac{V^*}{N}\sum_{\vec{\mathrm{k}}\in V^*}\overleftrightarrow{\mathrm{P}}^*(\vec{\mathrm{k}})\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})&=\frac{V^*}{N}\sum_{(\vec{\mathrm{k}},\vec{\mathrm{k}}')\in V^*}\overleftrightarrow{\mathrm{P}}^*(\vec{\mathrm{k}})\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}}')\left(\frac{1}{N}\sum_{\vec{l}}\exp[i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\circ\vec{\mathrm{R}}_{\vec{l}}]\right)\\ &=\frac{1}{V^*}\sum_{\vec{l}}\left[\left(\frac{V^*}{N}\sum_{\vec{\mathrm{k}}'\in V^*}\overleftrightarrow{\mathrm{P}}^*(\vec{\mathrm{k}}')\exp[-i\vec{\mathrm{k}}'\circ\vec{\mathrm{R}}_{\vec{l}}]\right)\left(\frac{V^*}{N}\sum_{\vec{\mathrm{k}}\in V^*}\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{k}})\exp(i\vec{\mathrm{k}}\circ\vec{\mathrm{R}}_{\vec{l}})\right)\right]\\ &=\frac{(2\pi)^6}{V^*}\sum_{\vec{l}}[\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})]^2\ . \quad (3.7)\end{aligned}$$

Since $V^*=(2\pi)^3\rho$, we can write Eq. (3.5) as

$$\left|\overleftrightarrow{\mathrm{I}}-\alpha(\omega)A(\omega)(2\pi)^3\sum_{\vec{l}}[\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})]^2\right|=0. \quad (3.8)$$

The explicit forms of $\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})$ and its square are

$$\begin{aligned}\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})&=\frac{1}{4\pi|\vec{\mathrm{R}}_1-\vec{\mathrm{R}}|^5}\\ &\times[3(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})-\overleftrightarrow{\mathrm{I}}(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})^2]\ . \quad (3.9\mathrm{a})\end{aligned}$$

$$\begin{aligned}[\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})]^2&=\frac{1}{(4\pi)^2|\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}}|^8}\\ &{}_{\mathrm{F}}\times[3(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})+\overleftrightarrow{\mathrm{I}}(\vec{\mathrm{R}}_{\vec{l}}-\vec{\mathrm{R}})^2]\ . \quad (3.9\mathrm{b})\end{aligned}$$

For a substitutional impurity in a cubic lattice the summation over $\vec{l}$ will render the diadic in Eq. (3.8) diagonal, and it reduces to a triply degenerate set of secular equations

$$\left(\frac{2(2\pi)^3\alpha(\omega)}{d^6}\right)\left(\frac{e^{*2}}{M(\omega_0^2-\omega^2)}\right)\left({\sum_{\vec{l}}}'\frac{1}{|\vec{l}|^6}\right)=1\ , \quad (3.10)$$

where d is the lattice constant and in the sum over $\vec{l}$ the divergent term $\vec{l}=\vec{0}$ is excluded.

An approximate solution of this equation is

$$\omega\approx\omega_0-\frac{(2\pi)^3\alpha(\omega_0)}{d^6}\left(\frac{e^{*2}}{M\omega_0}\right){\sum_{\vec{l}}}'\frac{1}{|\vec{l}|^6}\ , \quad (3.11)$$

and the corresponding change in the zero-point energy is

$$\Delta E\approx-\frac{3\hbar V^*\alpha(\omega_0)}{V_0}\left(\frac{e^{*2}}{M\omega_0}\right){\sum_{\vec{l}}}'\frac{1}{|\vec{l}|^6}\ . \quad (3.12)$$

This expression is reminiscent of the sum of the London interaction energies of the impurity with the dipolar oscillators in each unit cell.

The quantity $e^{*2}/M\omega_0^2V_0$ can be written, using the well-known Born result, in the form

$$\frac{e^{*2}}{M\omega_0^2V_0}=\frac{\epsilon_0-1}{4\pi\epsilon_0}\ , \quad (3.14)$$

where ϵ_0 is the static dielectric constant. If the high-frequency dielectric constant ϵ_∞ is different from unity, then $(\epsilon_0-1)/\epsilon_0$ becomes $1/\epsilon_\infty-1/\epsilon_0$, and is usually written $1/\overline{\epsilon}$. With this notation we get

$$\Delta E\approx-\left(\frac{3\hbar\omega_0}{\overline{\epsilon}}\right)\frac{2\pi^2\alpha(\omega_0)}{d^3}{\sum_{\vec{l}}}'\frac{1}{|\vec{l}|^6}\ . \quad (3.15)$$

For the particular choice of $\alpha(\omega)$ given in Eq. (3.2), the above expression reduces to

$$\begin{aligned}\Delta E&\approx-\frac{3\hbar\omega_0}{\overline{\epsilon}}\left(\frac{E_{1s}-E_{2p}}{(E_{1s}-E_{2p})^2-\hbar^2\omega_0^2}\right)\\ &\times\left(\frac{e^2}{a_0}\right)\left(\frac{a_0}{d}\right)^3\left[2\pi^2\left(\frac{32\times 8}{243}\right)^2{\sum_{\vec{l}}}'\frac{1}{|\vec{l}|^6}\right]\ . \quad (3.16)\end{aligned}$$

The expression (3.16) differs from what would be obtained from the expression for the frequency shifts given by Dean *et al.*[8] in a model based on the Fröhlich Hamiltonian by the factor $(a_0/d)^3$, and has the necessary feature of vanishing from $a_0 \rightarrow 0$ in the real tight-binding limit, whereas their expression goes to a finite value in this limit.

B. Loosely bound impurity

If we take the example of an impurity in which the electron is essentially free, it can be shown from Eq. (2.5) using box-normalized plane wave states that

$$\alpha(\vec{k}, \omega) \cong (e^2/Vm\omega^2)\, \delta(\vec{k})\overleftrightarrow{I} . \qquad (3.17)$$

Then Eq. (2.18) becomes (with $\vec{k} \in V^*$),

$$\vec{\nu}(\vec{k}) = \frac{A(\omega)e^2}{Vm\omega^2}\left(\frac{V^*}{(2\pi)^3}\right)\left(\sum_{\vec{g}} \frac{(\vec{k}+\vec{g})(\vec{k}+\vec{g})}{(\vec{k}+\vec{g})^2}\right)\vec{\nu}(\vec{k}) . \qquad (3.18)$$

As expected in this translationally invariant case, there is no $\vec{R}$ dependence of the secular equation.

The summation over $\vec{g}$ is apparently divergent, the divergence arising out of the fact that the dipolar oscillators are regarded as points. Since they are not really points, but have finite size, there would be a convergence factor with each term in the series which would diminish quite rapidly with $\vec{g}$.[9] We can then take only the term for $\vec{g} = \vec{0}$ as a first estimate, and if we use the formula (3.1) and take only the contribution of the pole at $\omega = \omega_0$ in the first term, we get

$$\Delta E = -\frac{(4\pi)^2 e^{*2}}{2M\omega_0}\, \frac{e^2}{m\omega_0^2}\, \frac{N}{V}\, \frac{V^*}{(2\pi)^3}\, \frac{\hbar}{2}$$

$$= -4\pi^2\left(\frac{e^{*2}}{M\omega_0^2}\right)\left(\frac{\hbar e^2}{m\omega_0}\right)\rho^2 .$$

In terms of the parameter $\overline{\epsilon}$ introduced in Eq. (3.15), the polaron size $l_0 = (\hbar/2m\omega_0)^{1/2}$, and the Fröhlich coupling constant[10] $\alpha = (e^2/2\overline{\epsilon}l_0)/\hbar\omega_0$, the above expression can be written

$$\Delta E = -\alpha\hbar\omega_0(4\pi\rho l_0^3) . \qquad (3.19)$$

This expression for the energy shift differs from that for a free polaron in Fröhlich's theory by the factor of the order of ρl_0^3. In our approach no account has been taken of the effect of the finite size of the polaron as in Fröhlich's theory. This introduces a cutoff in $\vec{k}$ space in taking the trace in Eq. (3.1) at a value of $k \sim 1/l_0$. Replacing the summation over $\vec{k}$ in the trace by an integral over a volume $\sim (1/l_0)^3$ it can be shown that the factor ρl_0^3 cancels out giving Fröhlich's result, apart from an unimportant numerical factor.

If the electron is nearly free, $\alpha(\vec{k}, \omega)$ can be approximated in the form

$$\alpha(\vec{k}, \omega) = (e^2/m\omega^2) f(|\vec{k}|) . \qquad (3.20)$$

This form can be obtained by following the procedure used by Platzman,[3] who expands the energy denominator in Eq. (2.5). Here $f(\vec{k})$ has a peak at $k = 0$, has a width of the order of $1/a_0$, and has the property $f(\vec{k} \rightarrow \vec{0}) = 1/(2\pi)^3$. If we use this in Eq. (2.18) and (3.1), take only the term $\vec{g} = \vec{g}' = 0$ for the reason stated above, and take the contribution only from the pole at $\omega = \omega_0$, we get a series

$$\Delta E = \sum_j \Delta E_j , \qquad (3.21)$$

where

$$\Delta E_1 = -\alpha\hbar\omega_0(4\pi\rho l_0^3) , \qquad (3.22)$$

which is just the free-electron contribution.

The next term becomes

$$\Delta E_2 = \frac{\hbar}{4\pi i}\oint \frac{1}{2}\,\mathrm{Tr}\,\hat{S}^2 = -\frac{\hbar}{4}\left(\frac{5}{4\omega_0^7}\right)\left(\frac{e^{*2}}{M}\right)(4\pi)^4\, \frac{e^4}{m^2}\rho^2\left(\frac{V^*}{N}\right)^2$$

$$\times \sum_{(\vec{k},\vec{k}')\in V^*} \mathrm{Tr}\left(\frac{\vec{k}\vec{k}}{k^2}\right)\frac{\vec{k}'\vec{k}'}{k'^2}\, \frac{\vec{k}'\vec{k}'}{k'^2}\, \frac{\vec{k}\vec{k}}{k^2}$$

$$\times f(|\vec{k}-\vec{k}'|)f(|\vec{k}'-\vec{k}|) .$$

A good approximation for the above sum can be made as follows. Since the width of $f(|\vec{k}|)$, i.e., $1/a_0$ is supposed to be small, we can set $\vec{k} \approx \vec{k}'$, sum over $\vec{k}$ and integrate over $\vec{k}'$ only in the neighborhood of $\vec{k}$. Thus

$$\left(\frac{V^*}{N}\right)^2 \sum_{(\vec{k},\vec{k}')\in V^*} \mathrm{Tr}\left(\frac{\vec{k}\vec{k}}{k^2}\right)\left(\frac{\vec{k}'\vec{k}'}{k'^2}\right) f^2(|\vec{k}-\vec{k}'|)$$

$$\approx V^* \int_{\text{sphere of radius } 1/a_0} d^3k''\, f^2(|k''|)$$

$$\approx \frac{V^*}{(2\pi)^6}\, \frac{4\pi}{3a_0^3} .$$

In summing over $\vec{k}$ the aforesaid correction for the finite size of the polaron is neglected. We then get

$$\Delta E_2 \approx -\frac{40\hbar\pi^2}{3}\left(\frac{e^{*2}}{M\omega_0^2}\right)^2 \frac{e^4}{m^2\omega_0^3}\, \frac{\rho^3}{a_0^3}$$

$$= -\tfrac{40}{3}(\hbar\omega_0)\,\alpha^2(l_0^3\rho)\left(\frac{l_0}{a_0}\right)^3 . \qquad (3.23)$$

If the correction due to polaron size is made we get

$$\Delta E_2 \approx -\tfrac{40}{3}(\hbar\omega_0)\,\alpha^2\left(\frac{l_0}{a_0}\right)^3 , \qquad (3.24)$$

apart from inessential numerical factors.

Since the energy shifts due to the free electron is always there, in this formalism the lowest-order correction to the binding energy of the loosely bound impurity will be given by ΔE_2 of (3.24) and this is inversely proportional to the ratio of the volume of the region of spread of the electron orbital to the volume of the polaron.

IV. CONCLUDING REMARKS

It has lately been demonstrated[11-13] that one can use semiclassical techniques for evaluation of the effect of interaction of radiation with an atom, such as radiative corrections, by considering the coupling between the atom and the field to be due to the polarizability of the atom. The results of this approach are equivalent to what one obtains using perturbation theoretic methods in quantum electrodynamics starting with the basic electron-field interaction ($e\vec{A}\cdot\vec{p}/mc$). The approach in this paper is analogous to the above semiclassical methods. Instead of starting with the Fröhlich Hamiltonian we establish the coupling between the impurity and the polar vibrations of the host crystal through the polarizability of the former using linear response theory, and thus avoid the use of perturbation theory on the Fröhlich Hamiltonian. It would be a simple matter to evaluate quantities such as the phonon Lamb shifts by this formalism. Further extensions of this approach will be reported later.

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APPENDIX

The polarization developed on an atom due to an arbitrary sinusoidally oscillating field

$$\vec{\mathcal{E}}(\vec{r},t)=\vec{\mathcal{E}}(\vec{r},\omega)\,e^{-i\omega t} \tag{A1}$$

can be obtained as follows. The relation between $\vec{\mathcal{E}}(\vec{r},\omega)$ and the corresponding electrostatic potential $\phi(\vec{r},\omega)$ is

$$\vec{\mathcal{E}}(\vec{r},\omega)=-\nabla\phi(\vec{r},\omega)\ . \tag{A2}$$

In terms of Fourier transforms

$$\vec{\mathcal{E}}(\vec{k},\omega)=\int e^{-i\vec{k}\cdot\vec{r}}\,\vec{\mathcal{E}}(\vec{r},\omega)\,d^3r\ , \tag{A3}$$

Eq. (A2) can be written

$$\vec{\mathcal{E}}(\vec{k},\omega)=-i\vec{k}\phi(\vec{k},\omega)$$

or

$$\phi(\vec{k},\omega)=i\,\frac{\vec{k}\cdot\vec{\mathcal{E}}(\vec{k},\omega)}{k^2}\ . \tag{A4}$$

We are considering only the longitudinal electric field here, as transverse field effects (retardation effects) will be negligible here.

The polarizable impurity may be described by a charge $(+e)$ at $\vec{R}$ and $(-e)$ at $(\vec{R}+\vec{r}_e)$. The interaction energy of the field with this system is then

$$\begin{aligned}H_{\text{int}}(t)&=[e\phi(\vec{R},\omega)-e\phi(\vec{R}+\vec{r}_e;\omega)]\,e^{-i\omega t}\\&=\left(\frac{ei}{(2\pi)^3}\int\frac{\vec{k}\cdot\vec{\mathcal{E}}(\vec{k},\omega)}{k^2}\,[1-\exp(i\vec{k}\cdot\vec{r}_e)]\right.\\&\qquad\left.\times\exp(i\vec{k}\cdot\vec{R})\,d^3k\right)e^{-i\omega t}\ .\end{aligned} \tag{A5}$$

If we have a single $\vec{k}$ component in the electric field in the interaction Hamiltonian, so that the integral over $\vec{k}$ does not occur in (A5), from linear-response theory[14] the induced polarization of the atom in state $|n\rangle$ can be written

$$\vec{P}_n(t)=\frac{1}{i\hbar}\int_{-\infty}^{t}\langle n|[\vec{p}(t-t'),H_{\text{int}}(t')]|n\rangle\,dt' \tag{A6}$$

where $\vec{p}=e\vec{r}_e$, the dipole moment operator, and $\vec{p}(t-t')$ is taken in the Heisenberg representation. After some simple manipulations Eq. (A6) can be written

$$\vec{P}_n(t)=\overleftrightarrow{\alpha}_n(\vec{k},\omega)\,\vec{\mathcal{E}}(\vec{k},\omega)\exp[i(\vec{k}\cdot\vec{R}-\omega t)]\ , \tag{A7}$$

where

$$\begin{aligned}\overleftrightarrow{\alpha}_n(\vec{k},\omega)=-\frac{e^2}{\hbar}\sum_m&\left(\frac{\langle n|\vec{r}_e|m\rangle\langle m|\exp(i\vec{k}\cdot\vec{r}_e)|n\rangle}{\omega_{nm}+\omega}\right.\\&\left.+\frac{\langle m|\vec{r}_e|n\rangle\langle n|\exp(i\vec{k}\cdot\vec{r}_e)|m\rangle}{\omega_{nm}-\omega}\right)\frac{i\vec{k}}{k^2}\ .\end{aligned} \tag{A5$'$}$$

This is in diadic notation with the diadic formed out of the vectors $\langle n|\vec{r}_e|m\rangle$ and $i\vec{k}/k^2$.

If we have a superposition of fields with different wave numbers, the generalization of (A7) would be (dropping the time varying factor)

$$\begin{aligned}P_n(\omega)&=\int d^3k\,\overleftrightarrow{\alpha}_n(\vec{k},\omega)\,\vec{\mathcal{E}}(\vec{k},\omega)\exp(i\vec{k}\cdot\vec{R})\\&=\int\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r},\omega)\,\vec{\mathcal{E}}(\vec{r},\omega)\,d^3r\ .\end{aligned} \tag{A8}$$

Since $\overleftrightarrow{\alpha}_n(\vec{k},\omega)$ is a peaked function of $\vec{k}$ with a spread of the order of $1/a_0$, where a_0 is the Bohr radius, we expect $\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r},\omega)$ to be peaked at $\vec{r}=\vec{R}$ with a spread of the order of a_0, or the atomic size. Hence $\vec{r}$ in $\vec{\mathcal{E}}(\vec{r},\omega)$ in (A8) can be set equal to $\vec{R}$ to get a polarization density

$$\vec{p}(\vec{r},\omega)\cong\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r},\omega)\,\vec{\mathcal{E}}(\vec{R},\omega)\ . \tag{A9}$$

For a point dipole $\vec{\mu}(\vec{r}\,')$ at $\vec{r}\,'$, the electric field at $\vec{r}$ is given by

$$\begin{aligned}\vec{\mathcal{E}}(\vec{r})&=-\nabla_r\phi(\vec{r})=-\nabla_r[-\vec{\mu}\cdot\nabla_rG(\vec{r}-\vec{r}\,')]\,4\pi\\&=4\pi[\nabla_r\nabla_rG(\vec{r}-\vec{r}\,')]\,\vec{\mu}\ .\end{aligned} \tag{A10}$$

Here $G(\vec{r}-\vec{r}\,')$ is the electrostatic Green's function defined in Eq. (2.3). If we consider a dipole $\vec{\mu}_{\vec{l}'}$ at $\vec{R}_{\vec{l}}$, use Eqs. (A10) and (A9) to find the polarization density at $\vec{r}$, we get

$$\begin{aligned}\vec{p}(\vec{r},\omega)&=4\pi\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r};\omega)\,[\nabla_r\nabla_rG(\vec{r}-\vec{R}_{\vec{l}'})]\,\vec{\mu}_{\vec{l}'}\\&=4\pi\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r};\omega)\,[\nabla_{\vec{l}'}\nabla_{\vec{l}'}G(\vec{r}-\vec{R}_{\vec{l}'})]\,\vec{\mu}_{\vec{l}'}\ .\end{aligned} \tag{A11}$$

The field due to this polarization distribution at a point $\vec{R}_{\vec{l}}$ will be

$$\vec{\mathcal{E}}(\vec{R}_{\vec{l}})=(4\pi)\int\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{R}_{\vec{l}}-\vec{r})\,\vec{p}(r,\omega)\,d^3r$$

$$=(4\pi)^2\int[\nabla_{\vec{l}}\nabla_{\vec{l}}G(\vec{R}_{\vec{l}}-\vec{r})]\,\overleftrightarrow{\alpha}_n(\vec{R}-\vec{r})$$

$$\times[\nabla_{\vec{l}'}\nabla_{\vec{l}'}G(\vec{r}-\vec{R}_{\vec{l}'})]\,d^3r\,. \tag{A12}$$

This field will produce a force on the oscillating charge in the dipole oscillator at $\vec{R}_{\vec{l}}$, and hence we get Eq. (2.1) with $\overleftrightarrow{F}(\vec{l},\vec{l}';\omega)$ given by Eq. (2.2)

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