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Dispersion self-energy of an impurity in a dielectric

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The effect of an impurity on the spectral properties of a dielectric medium is analyzed, using the dispersion self-energy formalism. Estimates are made of the energy shifts of the impurity. The case of the free electron in a dielectric medium is discussed as the limit of a loosely bound impurity, and a generalization of the stationary polaron picture is derived. The effect of the finiteness of the dielectric medium on the energy shift is analyzed within this formalism, taking the example of an electron in a thin dielectric film.

I. INTRODUCTION

In an earlier paper[1] (hereafter referred to as I), the binding energy of an impurity in an ionic crystal had been evaluated through the frequency shift of the LO mode of the crystal. This approach is not directly applicable to an impurity in a general dielectric medium. However, many of the properties of an impurity in a dielectric medium, such as its binding energy and the features of its spectrum can be related to the dielectric response of the medium. In general, there will be many contributions to the dielectric response, and a theory of the properties of an impurity must take all of them into consideration. Our object in this paper is to present an analysis of the properties of an impurity in a dielectric medium, based on the dispersion self-energy formalism.

II. GENERAL THEORY

The theory of dispersion energy can be adapted to this problem in the following manner. We consider an impurity at $\vec{R}$, whose dynamic polarizability density in its nth quantum state can be represented by $\alpha_n(\vec{r}-\vec{R};\omega)$. The electric field at any point $\vec{r}$ in the medium is connected to that at $\vec{r}'$ through the relation

$$\vec{E}(\vec{r};\omega)=\int \overleftrightarrow{G}(\vec{r},\vec{r}';\omega) \times\alpha_n(\vec{r}'-\vec{R};\omega)\cdot\vec{E}(\vec{r}';\omega)\,d^3r' . \tag{1}$$

Here $\overleftrightarrow{G}(\vec{r},\vec{r}';\omega)$ is the dyadic Green's function connecting the field at $\vec{r}$ with a dipole source at $\vec{r}'$.

If the size of the impurity is small, i.e., if $\alpha(\vec{r}-\vec{R};\omega)$ is highly peaked near $\vec{r}\approx\vec{R}$, Eq. (1) can be written in an approximate form

$$\vec{E}(\vec{r};\omega)\approx\overleftrightarrow{G}_n(\vec{r},\vec{R};\omega)\cdot\vec{E}(\vec{R};\omega), \tag{2}$$

where

$$\overleftrightarrow{G}_n(\vec{r},\vec{r}',\omega)\equiv\int \overleftrightarrow{G}(\vec{r},\vec{r}'';\omega)\alpha_n(\vec{r}''-\vec{r}';\omega)\,d^3r'' . \tag{3}$$

Equation (2) leads to the secular equation

$$|\overleftrightarrow{I}-\overleftrightarrow{G}_n(\vec{R},\vec{R};\omega)|=0, \tag{4}$$

whose roots give the perturbed frequencies of the field, and hence the change in its zero-point energy, which is the dispersion self-energy of the impurity.

The above theory for a small impurity has been used in earlier work.[2-4] A more general theory must obtain the secular equation from Eq. (1) for all sizes of the impurity. This is readily done taking the Fourier transform of this equation,

$$\vec{E}(\vec{k})=\int \overleftrightarrow{G}(\vec{k},\vec{k}'+\vec{k}'')\alpha_n(\vec{k}')\cdot\vec{E}(\vec{k}'') \times e^{-i\vec{k}\cdot\vec{R}}\,d^3k'\,d^3k'' , \tag{5}$$

where

$$\alpha_n(\vec{k})=\frac{1}{(2\pi)^3}\int e^{-i\vec{k}\cdot\vec{r}}\alpha_n(\vec{r})\,d^3r , \tag{6}$$

and a similar equation is satisfied by $\vec{E}(\vec{k})$, and

$$\overleftrightarrow{G}(\vec{k},\vec{k}')=\frac{1}{(2\pi)^3}\int \overleftrightarrow{G}(\vec{r},\vec{r}')e^{-i\vec{k}\cdot\vec{r}} \times e^{i\vec{k}'\cdot\vec{r}'}\,d^3r\,d^3r' . \tag{7}$$

The procedure for evaluating $\alpha_n(k,\omega)$ from the electronic wave functions of the impurity has been outlined in I. Its explicit form (as a dyadic) is

$$\overleftrightarrow{\alpha}_n(\vec{k},\omega)=-\frac{e^2}{(2\pi)^3\hbar}\sum_m\left(\frac{\langle n|\vec{r}_e|m\rangle\langle m|e^{i(\vec{k}\cdot\vec{r}_e)}|n\rangle}{\omega_{nm}+\omega}+\frac{\langle m|\vec{r}_e|n\rangle\langle n|e^{i(\vec{k}\cdot\vec{r}_e)}|m\rangle}{\omega_{nm}-\omega}\,\frac{i\vec{k}}{k^2}\right). \tag{8}$$

It will be an isotropic tensor when $|n\rangle$ is a symmetric state, and we shall be concerned with only this situation. Replacing the integration over k'' in Eq. (5) by a summation, it can be written

$$\vec{E}(\vec{k})=\sum_{\vec{k}''}\overleftrightarrow{G}_n(\vec{k},\vec{k}'')\cdot\vec{E}(\vec{k}''), \tag{9}$$

where

$$\overleftrightarrow{G}_n(\vec{k},\vec{k}'')=\frac{(2\pi)^3}{V}\int\overleftrightarrow{G}(\vec{k},\vec{k}'+\vec{k}'')\alpha_n(\vec{k}')\times e^{-\vec{k}\cdot\vec{R}}d^3k'\,. \tag{10}$$

V is the volume of the solid, assumed to be large. Equation (9) leads to the more exact secular equation

$$D_n(\omega)\equiv|\hat{I}-\hat{G}_n(\omega)|=0\,. \tag{11}$$

Here, both $\hat{I}$ and $\hat{G}_n$ are infinite dimensional matrices, and the (3×3) submatrices of $\hat{G}_n(\omega)$ are the $\hat{G}_n(\vec{k},\vec{k}'')$ defined in Eq. (10).

The expression for the dispersion self-energy, as indicated in earlier work[2-4] becomes

$$E_s^{(n)}=\frac{\hbar}{4\pi i}\oint d\omega\,\mathrm{Tr}\sum_l\left([\hat{G}_n(\omega)]^l/l\right). \tag{12}$$

To the first two leading orders, this can be written

$$E_s^{(n)}=\frac{\hbar}{4\pi i}\oint d\omega\,\mathrm{Tr}\left(\sum_{\vec{k}}\overleftrightarrow{G}_n(\vec{k},\vec{k})+\frac{1}{2}\sum_{\vec{k},\vec{k}'}\overleftrightarrow{G}_n(\vec{k},\vec{k}')\overleftrightarrow{G}_n(\vec{k}',\vec{k})+\cdots\right). \tag{13}$$

The properties of the medium enter through $\overleftrightarrow{G}_n$, which is governed by its dielectric response.

The shift in the relatively sharp spectral lines of an atom or ion when it is inserted into a medium as an impurity can be obtained, as indicated in an earlier work,[3] by taking the difference in the dispersion self-energies of the atom in the two levels between which the optical transition occurs. We shall, however, be dealing with the spectral properties of the system as a whole, which can be described in terms of the spectral density function $g_n(\omega)$

$$g_n(\omega)=\mathrm{Im}\left[\left(\frac{1}{\pi}\right)\frac{d}{d\omega}\ln D_n(\omega+i0^+)\right]=-\mathrm{Im}\left\{\left(\frac{1}{\pi}\right)\mathrm{Tr}\left[\frac{d}{d\omega}\sum_l\left([\hat{G}_n(\omega+i0^+)]^l/l\right)\right]\right\}. \tag{14}$$

In this form, the poles $\hat{G}_n$ arising out of the dielectric response of the medium, as also those from α_n will automatically be included.

In a homogeneous dielectric medium with no spatial dispersion, $\overleftrightarrow{G}(\vec{r},\vec{r}';\omega)$ has the simple form

$$\overleftrightarrow{G}(\vec{r},\vec{r}';\omega)=-(\nabla\nabla')\frac{1}{\epsilon(\omega)|\vec{r}-\vec{r}'|}=-\frac{4\pi}{(2\pi)^3\epsilon(\omega)}\int\frac{(\vec{k}\vec{k})}{k^2}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}d^3k\,, \tag{15}$$

where $\epsilon(\omega)$ is the dielectric constant of the medium at the frequency ω. In this case, Eq. (10) becomes

$$\overleftrightarrow{G}_n(\vec{k},\vec{k}'';\omega)=-\frac{(4\pi)(2\pi)^2}{V\epsilon(\omega)}\left(\frac{\vec{k}\vec{k}}{k^2}\right)\times\alpha_n(\vec{k}-\vec{k}'';\omega)e^{-i(\vec{k}-\vec{k}'')\cdot\vec{R}}. \tag{16}$$

A point to note here is that the representation in $\vec{k}$ space implied by Eqs. (15) and (16) is strictly valid in a truly continuous medium. In a real situation when k exceeds various critical values (corresponding to shorter wavelengths), the graininess of the medium will appear, and the continuum picture will break down. A natural cutoff from this point of view is $k_L\approx2\pi/d$, where d is the interatomic distance in the medium.

A more important cutoff in k space arises from the polaron effect which we shall discuss in Sec. III. This is the value of k beyond which the coupling of the dielectric medium with an electron in it disappears. These cutoffs in k space render the sums in Eq. (13) finite.

III. ENERGY OF A FREE ELECTRON IN A DIELECTRIC: THE POLARON PICTURE

A free electron in a dielectric medium of a special type, i.e., an ionic crystal, has been studied in great detail within the framework of the polaron picture.[5-7] We shall indicate here the connection between the polaron concept and that of the dispersion self-energy, and shall also indicate a way of generalizing the polaron concept to apply to the electron in a general dielectric medium.

The polaron concept is based on two tenets.

(i) The electron lowers its energy in a dielectric medium by an amount

$$\Delta E\approx(e^2/R)(1/\epsilon-1)\,, \tag{17}$$

where R is the size of the polarization charge induced by the electron.

(ii) If the medium has a characteristic frequency ω_0 of polar oscillations, the coupling of the electron with that mode can be assumed to reduce sharply at velocities exceeding that at which the distance travelled within the period $(2\pi/\omega_0)$ exceeds its de Broglie wavelength (which is a measure of the extent of the localization of the electron and hence of the polarization cloud).

This critical velocity v_p gives a cutoff wave number k_p satisfying the equation

$$k_p = \omega_0/v_p = m\omega_0/\hbar k_p$$

or (18)

$$k_p = (m\omega_0/\hbar)^{1/2}.$$

For an electron in a plane-wave state corresponding to a wave number $k < k_p$ we can assume that the energy of interaction is

$$V_{\text{int}} = +\frac{e^2 k_p}{2\pi}\left(\frac{1}{\epsilon} - 1\right) = -\frac{e^2}{2\pi\bar{\epsilon}}\left(\frac{m\omega_0}{\hbar}\right)^{1/2} = -\gamma\hbar\omega_0;$$
$$\gamma = \frac{e^2}{2\pi\bar{\epsilon}\hbar}(m/\hbar\omega_0)^{1/2}. \tag{19}$$

Here $1/\bar{\epsilon}$ stands for $1 - (1/\bar{\epsilon})$. γ is the coupling constant which Fröhlich has evaluated[5]—in his notation it is denoted by α.

The shift in the energy of the free electron due to its coupling with the phonons corresponding to the polar oscillations of the medium of frequency ω_0 is a particular case of the problem of its energy shift in a general dielectric medium. This shift can be evaluated from its dispersion self-energy in the following manner.

From Eq. (8), using box-normalized plane-wave states, we get, for the free electron,

$$\alpha(\vec{k}, \omega) = (e^2/Vm\omega^2)\delta(\vec{k}). \tag{20}$$

Using this in Eqs. (16) and (13), we get for the dispersion energy difference between vacuum and the medium the expression

$$\Delta E \approx -\frac{\hbar}{4\pi i}\oint d\omega \sum_{\vec{k}}\left(\frac{1}{\epsilon(\omega)} - 1\right)\left(\frac{4\pi}{V}\right)\left(\frac{e^2}{m\omega^2}\right). \tag{21}$$

In view of the situation explained at the end of Sec. II, we expect the $\vec{k}$ sum to have cutoffs. If the medium has one polar frequency ω_0, as in I we can write $\epsilon(\omega)$ in the form (as is consistent with a low-density crystalline medium)

$$\epsilon(\omega) = 1 + \frac{4\pi N e^{*2}}{M}\,\frac{1}{\omega_0^2 - \omega^2}, \tag{22}$$

where N is the number of cells per unit volume, e^* and M are the effective charge and mass of the oscillator in each cell. The pole of $(1/\epsilon) - 1$ in Eq. (21) will be very close to ω_0 in this low-density approximation. Taking this approximation and replacing the $\vec{k}$ sum by an integral over a sphere of radius $k_p = (m\omega_0/\hbar)^{1/2}$, we get the result

$$\Delta\epsilon \approx -\frac{e^2}{6\pi\bar{\epsilon}\hbar}\left(\frac{m}{\hbar\omega_0}\right)^{1/2}\hbar\omega_0 = -\gamma\hbar\omega_0. \tag{23}$$

Here

$$\frac{1}{\bar{\epsilon}} = \frac{4\pi N e^{*2}}{M\omega_0^2} \approx \left(1 - \frac{1}{\epsilon(0)}\right). \tag{24}$$

The constant γ here differs from that in Eq. (19) by an unimportant numerical factor. This result, which has already been alluded to in I, indicates that the energy shift occurring in Frohlich's polaron problem is implicitly contained in the dispersion self-energy of an electron in a dielectric medium.

If there are several characteristic frequencies in $\epsilon(\omega)$, i.e., if $\epsilon(\omega)$ has the form

$$\epsilon(\omega) = 1 + 4\pi N\left(\frac{e^2}{m}\right)\sum_l \frac{f_l}{\omega_l^2 - \omega^2}, \tag{25}$$

where f_l is the oscillator strength associated with the lth frequency, a procedure similar to the above leads to the result

$$\Delta\epsilon \approx -\sum_l \gamma_l \hbar\omega_l, \tag{26}$$

where

$$\gamma_l = \frac{e}{6\pi\bar{\epsilon}_l\hbar}\left(\frac{m}{\hbar\omega_l}\right)^{1/2}; \quad \frac{1}{\bar{\epsilon}_l} = \frac{4\pi N e^2 f_l}{m\omega_l^2}. \tag{27}$$

IV. IMPURITY IN A DIELECTRIC MEDIUM: BINDING ENERGY AND FREQUENCY SHIFTS

We shall consider here only those impurities which form hydrogenic bound states in the solid, with the electron wave functions spread out over a few lattice cells so that local-field corrections are negligible. The coupling of the impurity with the medium is complicated, but it can be split up in the following manner. Firstly, the formation of the hydrogenic system takes into account the dielectric screening of the impurity-ion potential which forms the bound state with the electron. Secondly, after the bound state is formed, the impurity interacts with the medium through its polarization fluctutations. The former interaction is included in the effective Bohr radius a_0 that characterizes the impurity ground state. The latter interaction can be studied in the dispersion self-energy formalism.

As in I, we make the assumption (for the impurity in its ground state)

$$\alpha(\vec{k}, \omega) = \alpha(\omega) f(\vec{k}). \tag{28}$$

The explicit form of $f(\vec{k})$ is not as important as the fact that it is a peaked function with a spread of the order of $1/a_0$. As indicated in Sec. II we are concerned with the secular determinant $D_0(\omega)$ of Eq. (11), using

$$\overleftrightarrow{G}_n(\vec{k}, \vec{k}''; \omega) = -\frac{(4\pi)(2\pi)^3\alpha(\omega)}{V\epsilon(\omega)}\left(\frac{\vec{k}\vec{k}}{k^2}\right) f(\vec{k} - \vec{k}'')$$
$$\times e^{-i(\vec{k}-\vec{k}'')\cdot\vec{R}}. \tag{29}$$

The energy shifts can be computed in exactly the same way as in Sec. III, the only difference being the occurrence of the form factor $f(\vec{k}-\vec{k}'')$, which introduces a cutoff in the $\vec{k}$ sums occurring in Eq. (13) at about $1/a_0$ in the second- and higher-order terms. We shall give here the results (in the first two orders) for the shift in the binding energy of a loosely bound impurity

$$\Delta E = -\sum_l \gamma_l \hbar\omega_l \left[1 + \frac{45\pi^4}{16}\gamma_l\left(\frac{\hbar}{m\omega_l a_0^2}\right)^{3/2}\right]. \tag{30}$$

This result is entirely analogous to that obtained for an impurity in an ionic crystal in I by direct estimation of the frequency shift of the polar mode of the crystal.

Of some interest is the change in the spectral-density function of the system consisting of the medium and the impurity due to the latter. This is obtained from Eq. (14) substituting for $\vec{G}_n(\vec{k}, \vec{k}''; \omega)$ from Eq. (29). For a small concentration of impurities, the optical absorption of the system would be given approximately by Eq. (14) multiplied by the concentration in the right-hand side.

The shifts in the principal absorption frequencies of the medium due to the impurity can be estimated with reasonable accuracy from an approximate relation

$$D_0(\omega) \approx 1 - \mathrm{Tr}\left[\hat{G}_n(\omega)\right] = 0$$

or (31)

$$1 + \frac{4\pi\alpha(\omega)}{V\epsilon(\omega)}\sum_{\vec{k}} = 0 .$$

If the summation over $\vec{k}$ is cut off in the manner discussed earlier, Eq. (31) can be written

$$1 + \frac{4\pi\alpha(\omega)}{\epsilon(\omega)(2\pi)^3}\left(\frac{4\pi}{3}\right)\left(\frac{\hbar}{m\omega}\right)^{-3/2} = 0 .$$

When the above formulas are applied to the case of an impurity in an ionic crystal (as in I), the results already stated in I are readily obtained. But this formalism is obviously of wider applicability to any type of medium.

V. SURFACE EFFECTS

In this section we calculate the self-energy of an electron in a dielectric slab of thickness L using the result (13). The Green's function $\overleftrightarrow{G}(\vec{r}, \vec{r}'; \omega)$ for this case[4] consists of two parts—the first part is the same as Eq. (15), while the second part arises due to the finite size of the medium

$$\overleftrightarrow{G}(\vec{r}, \vec{r}', \omega) = -\frac{\nabla\nabla'}{\epsilon(\omega)}\left(\frac{1}{|\vec{r}-\vec{r}'|} + \frac{\Delta}{2\pi}\int \frac{d^2k \, \exp[i\vec{k}\cdot(\vec{\rho}-\vec{\rho}')]}{k[1-\Delta^2\exp(-4kL)]} \right.$$
$$\times\{\exp[-k(z+z')-2kL] + \Delta\exp[-k(z-z')-2kL]$$
$$\left. + \exp[+k(z+z')-2kL] + \Delta\exp[k(z-z')-2kL]\}\right), \tag{32}$$

where $\Delta = [\epsilon(\omega)-1]/[\epsilon(\omega)+1]$, $\vec{\rho}$ is the position vector of $\vec{r}$ in the plane parallel to the surface of the slab, and z is the corresponding perpendicular coordinate with the center of the slab as the origin. In the limit of L going to infinity the second term in Eq. (32) vanishes as is expected. Substituting Eq. (32) into Eq. (7) and utilizing the result in Eq. (13) enables us to calculate the self-energy following the procedure of the earlier sections. For simplicity, considering only the first term in the expansion (13) and restricting to lowest order terms in $1/L$, allows us to write

$$\Delta E = -\sum_l \gamma_l \hbar\omega_l \left[1 - \left(\frac{\hbar}{m\omega_l L^2}\right)^{1/2} C\right], \tag{33}$$

where C is an unimportant numerical factor of the order of unity. For large L the second term in Eq. (33) becomes negligible while for L small but larger than $(\hbar/m\omega_l)^{1/2}$, the effect of the slab thickness can become significant.

VI. CONCLUSION

The main purpose of this paper has been to illustrate the various ways in which the concept of dispersion self-energy can be used to analyze the properties of an impurity in a dielectric medium. This is in the same framework as the semiclassical treatment of interaction of radiation with matter which was the basis of I. It may be emphasized here, however, that in this framework the problem is analogous to other impurity problems in solid state physics, notably the lattice dynamics of crystals with impurities. Instead of dealing with atomic displacements we are dealing with polarizations in the lattice cells, and the impurity introduces additional correlations among the polarizations leading to new absorption frequencies obtained from a secular equation of the type given in Eq. (11). It is also demonstrated that many of the features of the polaron picture are implicit in this approach.

At the moment, apart from the work of Dean, Manchon, and Hopfield[8] not much detailed experimental work has been done on the optical properties of dielectrics with impurities. Such experiments would be extremely useful, since the way in which polarization correlations in the medium and in the impurity affect the optical properties would be clarified through analysis of the experimental data within the theoretical framework outlined in this paper.

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