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Polarization energy for core states of alkali halides

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The polarization energies for core states of alkali halides are discussed within the context of the theory developed by Hedin and Lundqvist. It emerges from the analysis that the choice of a particular $\vec{q}$-dependent dielectric function is more critical than the accuracy with which the core wave functions are described. We show that for very localized holes the use of a constant dielectric function leads to meaningless results. These results are compared with those obtained with other theoretical schemes. Comparison is also made between the theory of Hedin and Lundqvist and other theories, remarking on its more general character.

I. INTRODUCTION

The need of including correlation effects in Hartree-Fock calculations of energy bands in solids has long been recognized.[1] Although local-density-functional approaches provide a more conceptually clear way to treat correlation,[2] the method which consists of adding the polarization energy to the Hartree-Fock result is still very popular in band-structure calculations[3] and many other problems such as F centers[4] or any kind of electronic excitations in solids.[5]

Since the earlier classical model of Mott and Littelton,[6] two quantum-mechanical approaches to the calculation of polarization energies have been published. The first method was introduced by Toyozawa[7] and is based upon the concept of the electronic polaron. Although the method is physically clear it has some restrictive approximations—such as the description of the elementary excitations by a single exciton band—which have not been removed by the authors who have successively used the method to calculate the effect of the electronic polarization on the electron-hole interaction,[1] or upon a single electron in the conduction band,[8] or on band structures and core levels in solids.[9] A more general approach was lately developed by Hedin and Lundqvist.[10] This is the so-called Coulomb-hole plus screened-exchange approximation. This method was used by some authors[11,12] in calculating the effect of correlation upon energy bands and more recently by Gadzuk[13] in the study of polarization energies associated with electronic levels of atoms adsorbed on metallic surfaces. These three methods only include the extra-atomic relaxation due to the atoms surrounding a particular atom, and therefore the intra-atomic relaxation can be approximated by the polarization of the ion in which the hole or the electron is created.[3] It is therefore clear that the main shortcoming of the procedure which consists of calculating the electron properties within the Hartree-Fock approximation and then adding the short- and long-range correlation contributions is that the different quantities are calculated within different levels of approximation. Local-density-functional approaches avoid this difficulty and are, therefore, conceptually clearer.

Nevertheless, having the total energy split into different terms can be, in some cases, a great aid to understanding the physics of the problem we are faced with. This is the case of the chemical shifts which affect the core atomic levels when the atom is placed in a particular medium such as a bulk crystal[14] or a surface.[13] This reason, and the fact that the Hartree-Fock approximation is still very valuable, justify any investigation aimed at a better understanding of the calculation of polarization energies.

The purpose of the present paper is to explore the validity of different approximations made to calculate the polarization energy for core states of alkali halides. The study will be carried out by means of the Hedin-Lundqvist scheme.[10] This scheme has been recently rewritten by Gaszuk[13] performing some approximations which seem to work fairly well for core states. We shall investigate the relevance of two factors: (i) the dielectric screening (for this purpose we shall use different dielectric functions) and (ii) the description of the hole wave function. We shall show that the main factor in getting accurate enough polarization energies is the dielectric function used in the calculation. In particular, if the $\vec{q}$ dependence of this function is not included, the results for very localized holes are far from correct. The electronic polaron model of Toyozawa[7] assumes a constant dielectric function and, as we shall see, this forces one to perform the calculations by introducing a somewhat arbitrary cutoff in the $\vec{q}$ integrals.[1]

The rest of the paper is organized as follows. In Sec. II we shall discuss the model we use to calculate polarization energies and compare it with other models. Section III will be devoted to illustrate the discussion of Sec. II, by calculating polarization energies for different core levels of various crystals. Three dielectric functions will be used, and the hole wave function will be described within different approximations. Our results will be compared with other calculations. Finally, some concluding remarks are included in Sec. IV.

II. POLARIZATION ENERGY

The polarization energy in a hole state $\phi_n(\vec{r})$, with unrelaxed energy E_n, is written by Hedin[15] as

$$\Delta E_p = \int d^3r\, d^3r'\, \phi_n(\vec{r})\Sigma(\vec{r},\vec{r}\,',E)\phi_n(\vec{r}\,') . \qquad (1)$$

Hedin and Lundqvist[10] have written, within the random-phase approximation the nonlocal polarization self-energy $\Sigma(\vec{r},\vec{r}\,',E)$ for a quasiparticle with relaxed energy E as

$$\Sigma(\vec{r},\vec{r}\,',E) = \frac{i}{2\pi}\oint d\omega G_0(\vec{r},\vec{r}\,',E-w)\frac{\delta V(\vec{r}\,',\omega)}{\delta n(\vec{r},\omega)} , \qquad (2)$$

where $\delta V(\vec{r}\,',\omega)/\delta n(\vec{r},\omega)$ is the Fourier component of the potential induced at point $\vec{r}\,'$ by a charge at point $\vec{r}$, which can be readily calculated from classical electromagnetism. The propagator G_0 corresponds to the undressed quasiparticle. The integral runs over the spectrum of elementary excitations induced by the hole. Although in (1) the relaxed energy E of the hole state has to be used, a fairly good approximation is obtained by evaluating the self-energy and G_0 at the unperturbed energy E_n, provided that the Σ is a small correction to the total potential.

Assuming a nonpolarizable hole, which in fact is equivalent to restricting the sum over states needed to calculate G_0 to the actual state n, Gadzuk[13] arrived to the following expression for the polarization energy:

$$\Delta E_p \simeq \frac{1}{2}\int \frac{d^3q}{(2\pi)^3}\left(\frac{4\pi e^2}{q^2}\right)\left(\frac{1-\epsilon(\vec{q},0)}{\epsilon(\vec{q},0)}\right)|\rho_n(\vec{q})|^2 , \qquad (3)$$

where $\rho_n(\vec{q})$ is the Fourier transform of the charge associated with the n hole state and $\epsilon(\vec{q},0)$ is the static dielectric function. The assumption of a nonpolarizable hole made by Gadzuk has led to a formula (3) which only includes static effects. The consequences of this approximation are fully discussed by Gadzuk.[13]

In expression (3), the information on the hole state is contained in $\rho_n(\vec{q})$ and the particular medium where the hole is placed is described by means of $\epsilon(q,0)$. For both quantities we have to explore which approximations are significant.

It is worth noting that if one is interested in calculating polarization energies for band structures it will be necessary to calculate for an energy at a particular $\vec{k}$ of the Brillouin zone. The propagator G_0 is then calculated as a sum over bands and the wave number, and the final expression for ΔE_p is more complicated. Details for this case can be found in Refs. 11 and 12.

We want now to apply expression (3) to the analysis of the most simplified cases. We start with a 1s state described by means of a Gaussian function,[16]

$$\phi_{1s}(\vec{r}) = (2\alpha/\pi)^{3/4}e^{-\alpha r^2} . \qquad (4)$$

As regards the dielectric function we first choose a constant $\epsilon(\vec{q},0)=\epsilon_e$, where ϵ_e is the dielectric constant due to the electrons. We do not write ϵ_∞ to avoid confusion with the usual terminology in which $\epsilon_\infty=\epsilon(\vec{q},\infty)$. We only mean that the $\epsilon(\vec{q},w)$ only includes electronic screening. Here we should comment that for the problems we shall be studying, ionic screening does not need to be included. The reason is that the time required for the relaxation of the ions surrounding the one in which the hole is created (of the order of a lattice vibration), is much longer than the length of the photoejection process.[14] Nevertheless for the case of a constant dielectric function, including the ionic screening would simply mean substituting ϵ_e by ϵ_i (usually called ϵ_0). In the case of a $\vec{q}$-dependent dielectric functions some other problems would emerge. We shall come to this point later.

In this case we find for E_p the following expression:

$$\Delta E_p = (e^2/\pi)(2^{1/2}/\langle r\rangle)(1-\epsilon_e)/\epsilon_e , \qquad (5)$$

where $\langle r\rangle$ is the mean radius of the function $\phi_{1s}(\vec{r})$, which is equal to $(2/\pi\alpha)^{1/2}$. This formula has a general character and holds for any core state written in terms of a single Gaussian. In each case $\langle r\rangle$ would correspond to the mean radius of the particular state, 1s, 2p, 3d. It is interesting to note that Eq. (5) has the same form as the expression which is obtained from a classical calculation which assumes a charged sphere in a dielectric medium. This model was first used by Jost[17] although he wrote the formula corresponding to a sphere having a uniform surface distribution of charge instead of a volume distribution (which is the most approximate representation of the actual problem). Both cases can be obtained from Eq. (5) assuming either a $\delta(r-R)$ surface charge or a $\theta(r-R)$ volume charge.

There is a feature of Eq. (5) which must be noted, i.e., for very localized holes, that is, $\langle r\rangle \to 0$, the polarization energy tends to ∞. This is a characteristic of the model we are using, which derives from the infinite self-energy associated with the Coulomb interaction. This will be removed for a $\vec{q}$-dependent dielectric function. We first choose a very simplified dielectric function, that introduced by Inkson[18] which in fact is a simplification of the one presented by Penn,[9]

$$\epsilon_I(q,0) = 1 + \frac{\epsilon_e - 1}{1-(\epsilon_e - 1)(q^2/k_F^2)}\,, \tag{6}$$

where k_F is the Fermi wave vector of the solid. If we introduce this expression in (3) we arrive, for the case of a 1s state [Eq. (4)], at

$$\Delta E_p = e^2\alpha^{1/2}[(1-\epsilon_e)/\epsilon_e]e^{x^2}[1-\mathrm{erf}(x)]\,, \tag{7}$$

where

$$x = (k_F/2)\{(1/\alpha)[\epsilon_e/(\epsilon_e - 1)]\}^{1/2}$$

and erf is the error function. We want to study two limiting cases of (7). First we check its behavior for a very localized hole, that is for $\alpha\to\infty$; in this case Eq. (7) becomes

$$\lim_{\alpha\to\infty}\Delta E_p = -e^2(k_F/2)[(\epsilon_e - 1)/\epsilon_e]^{1/2}\,. \tag{8}$$

Now, ΔE_p is finite for a very localized hole. We have removed the infinity which appeared for a constant dielectric function. It is easy to check that for $\alpha\to 0$, we recover Eq. (5), that is for very delocalized holes the polarization energy is dominated by the shape of the wave function and the long distance dielectric screening, no matter how the $\vec{q}$ dependence of the screening is described. Our expression for ΔE_p has to behave in this way considering that, for long distances, the dielectric screening can be described by a constant dielectric function. We also note that if we wished to include ionic screening, since the q dependence of $\epsilon(\vec{q},0)$ is calculated for the electronic screening, we would have to add $\epsilon_i - \epsilon_e$ to $\epsilon(\vec{q},0)$ as a constant and then for $|\vec{q}|\to\infty$, $\epsilon(\vec{q},0)\to 1-\epsilon_i-\epsilon_e$, leading to problems similar to those discussed for the case of a constant dielectric function. Nevertheless, this problem could be solved by considering that the ionic screening is only effective at distances greater than the interatomic distance $(a/2)$, so that we could assume that the ionic part of the dielectric function $(\epsilon_i - \epsilon_e)$ vanishes for $q \geq 4\pi/a$. This cutoff is by no means justified for the electronic screening.

Although the particular values of ΔE_p depend on the way in which the dielectric function depends on $\vec{q}$ (see Sec. III), once the $\vec{q}$ dependence is introduced, the polarization energy behaves as discussed above. For instance, if we use the dielectric function calculated by Lipari[20] which includes a q^4 term, the result for ΔE_p can also be expressed in terms of error functions and its limits for $\alpha\to 0$ and $\alpha\to\infty$ are similar to those discussed above; in particular for $\alpha\to 0$ we also recover the case of a constant dielectric function. In Sec. III we shall show that for the core states of alkali halides, the choice of a $\vec{q}$-dependent dielectric function is more critical than the accuracy with which the wave function associated with the core state is described.

We turn now to compare the model we are using with the one which emerges from the analysis of Toyozawa.[7] Inoue *et al.*[8] have studied the Hamiltonian of Toyozawa by treating the interaction between the electron and the quasiparticle (exciton) in perturbation theory. Within their treatment, the polarization energy associated with a hole, in the second order of perturbation, can be written

$$\Delta E_p(\vec{k}) = -\sum_{\vec{q}}\frac{|V_{\vec{q}}|^2}{E(\vec{k}-\vec{q})+w-E(\vec{k})}\,, \tag{9}$$

where w is the exciton energy and $V_{\vec{q}}$ describes the interaction between the electron and the exciton and is given by

$$V_{\vec{q}} = e\left(\frac{2\pi w(1-1/\epsilon_e)}{V}\right)^{1/2}\frac{i}{|\vec{q}|}\rho_n(\vec{q})\,, \tag{10}$$

where V is the volume of the crystal. It is straightforward to show, by assuming flat bands (our case) and replacing the sum over $\vec{q}$ by an integral, that Eq. (9) coincides with Eq. (3) for the case of $\epsilon(q,0)=\epsilon_e$. We have then shown that in the case of flat bands (core states) and a constant dielectric function both theories lead to the same result. It is then clear that besides the approximations inherent to both methods, the one developed by Toyozawa has two further approximations, namely, it assumes a single exciton band and includes a screening which is static and $\vec{q}$ indepedent. In this paper, and due to the assumption of a nonpolarizable hole, we have also taken a static screening and reduced the quasiparticle spectrum to $w=0$ (Ref. 13). Nevertheless the method of Hedin and Lundqvist[10] provides a more general picture than the model introduced by Toyozawa.[7]

The $\vec{q}$ dependence of the dielectric screening can be easily included in the scheme of Toyozawa,[7] and has been done by Woo and Wang.[21] When this is done, the expression which is obtained from Eqs. (9) and (10) for the case of flat bands, exactly coincides with Eq. (3). Also, including this dependence allows one to avoid the cutoff in the $\vec{q}$ integrals which has been necessarily introduced[1] to avoid problems related to our discussion con-

TABLE I. Polarization energies (eV) for various metal core levels in alkali (A) halides. The results given in columns a, b, and c correspond to three different calculations in which three different dielectric functions are used, namely, a constant (a), the Inkson (b) (Ref. 18), and the Lipari (c) (Ref. 20) dielectric functions. The tabulated values correspond to $-\Delta E_p$ of Eq. (3) (see text).

		AF			ACl			ABr			AI		
		a	b	c	a	b	c	a	b	c	a	b	c
Li^+	1s	11.24	6.74	···	14.60	7.07	4.37	15.69	7.10	4.34	16.91	7.05	4.09
	1s	38.47	8.43	···	50.26	8.26	3.27	55.93	8.33	3.32	59.37	8.01	3.06
Na^+	2s	7.81	5.36	···	10.20	5.95	3.35	11.35	6.22	3.44	12.05	6.19	3.22
	2p	7.10	4.89	···	9.28	5.42	3.04	10.32	5.67	3.13	10.96	5.64	2.93

cerning the case of a constant dielectric function. It is not the purpose of this paper to show if there exists or not an equivalence between both theories, once the approximations of the theory of Toyozawa are removed.

III. CORE STATES OF ALKALI HALIDES

We turn now to apply Eq. (3) to some particular cases. We shall calculate the polarization energies for 1s, 2s, and 2p levels of the anion and cation of lithium and sodium halides. To describe the core wave functions we first choose a minimal set of Slater-type orbitals.[22] The radial wave functions corresponding to 1s, 2s, and 2p orbitals are written

$$\begin{aligned} R_{1s}(r) &= Ae^{-\alpha_1 r}, \\ R_{2s}(r) &= B_1 e^{-\alpha_1 r} + B_2 e^{-\beta_1 r}, \qquad (11) \\ R_{2p}(r) &= Cre^{-\gamma_1 r}, \end{aligned}$$

where the exponents α_1, β_1, and γ_1 are obtained from the expressions given by Clementi and Raimondi.[22,23] The coefficients A and C are used to normalize the wave functions, whereas one of the B coefficients is used to make the 2s orbital orthogonal to the 1s orbital, and the other to normalize the 2s orbital.

We have used the wave functions of Eq. (11) to describe the 1s orbital and the 1s, 2s, and 2p orbitals of Na^+, F^-, Cl^-, and Br^-. Three dielectric functions are chosen, a constant (ϵ_e), the one introduced by Inkson[18] and finally the more accurate of Lipari.[20] With all these ingredients we have calculated the polarization energies by means of Eq. (3). Our results are reported in Tables I and II. Several points are worthy of comment. (i) The choice of the dielectric function is very important. The large values obtained with a constant dielectric function are greatly reduced when the Inkson[18] dielectric function is used; a further reduction, nearly 50%, is found when the more accurate dielectric function of Lipari[20] is used. This behavior is in line with the discussion of Sec. IV. (ii) The polarization energies depend more noticeably on the crystal where the hole is created, than on the actual core level. In particular, the changes in the polarization energies found in going from lithium to sodium halides are specially important.

In order to look at the dependence of the polarization energies on the accuracy with which the wave functions are described, we have taken the local orbital description of the 1s orbital of Li^+, given by Kunz[24] for the lithium halide crystals. The results obtained with these wave functions differ by less than 1% from those reported in Table I. Similar results could be obtained for other levels.

We turn now to compare our results with other theoretical calculations.[9,25] First, the results obtained by means of the classical model of Mott and Littleton are the same for the different core levels of a particular ion, as the model does not include any information on the actual level. Moreover, the values for the polarization energies are somewhat lower than those of the present work, specially for the anion levels. For instance, our result for the 2s level of Br in lithium bromide is 3.3 eV higher than the one given by Du Pré

TABLE II. Polarization energies (eV) for 1s, 2s, and 2p cores levels of F^-, Cl^-, and Br^- ions in lithium and sodium halides (H). (See also caption of Table I.)

		LiH			NaH		
		a	b	c	a	b	c
	1s	35.98	9.89	···	31.24	8.13	···
F^-	2s	6.09	4.90	···	5.29	4.16	···
	2p	5.76	4.63	···	5.00	3.93	···
	1s	89.33	10.11	4.69	77.98	8.61	3.28
Cl^-	2s	18.57	8.33	4.94	16.21	7.15	3.50
	2p	20.45	8.02	4.54	17.85	6.87	3.20
	1s	198.9	10.23	4.62	179.9	8.98	3.31
Br^-	2s	46.3	10.28	5.21	41.88	9.05	3.75
	2p	52.41	9.35	4.59	47.41	8.23	3.30

et al.[25] As regards the values obtained by means of the scheme of Toyozawa,[9] we note that they are also lower than those of the present calculation, and do not depend on the particular level. The reason for the last feature could be the following. As remarked earlier in this paper the assumption of a constant dielectric function requires the introduction of a cutoff in the $\vec{q}$ integrals. This is usually assumed to be[1] $2\pi/a$, a being the lattice constant, and is of the order of 0.5–1.0 a.u. Then in the interval $0-2\pi/a$, the Fourier transforms of most of the core levels are constant and therefore the polarization energies so calculated do not depend on the particular orbital.

IV. CONCLUDING REMARKS

In this paper we have used the scheme of Hedin and Lundqvist,[10] as rewritten by Gadzuk,[13] to calculate the polarization energies for core states of alkali halides. Although many approximations have been made in order to obtain the self-energy associated with the hole, we think that they are justified for deep and highly localized states.[13] We have shown that the choice of the dielectric function is more critical than the accuracy with which the wave functions are described, showing that for very localized levels a constant dielectric function leads to meaningless results. Therefore, a good description of the electronic screening is needed in applying the present scheme to calculate polarization energies. The results we have obtained by means of the Lipari dielectric function,[20] have to be fairly accurate, as that dielectric function has been fitted to detailed band structure calculations.

Besides, we have proved that for core levels the polarization energy obtained from the scheme of Toyozawa[7] coincides, once a $\vec{q}$-dependent dielectric function is introduced, with the one obtained from the model of Hedin and Lundqvist.[10,13] The introduction of a $\vec{q}$-dependent dielectric function avoids the use of an *ad hoc* cutoff to perform the $\vec{q}$ integrals, which is the origin of most of the shortcomings of the calculations based upon the model of Toyozawa.[9] Moreover the introduction of the $\vec{q}$-dependent dielectric function directly in $V_{\vec{q}}$ [Eq. (10)] also avoids the use of the rather unjustified $\vec{q}$-dependent function used by Woo and Wang[21] to calculate the total screened interaction.

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