

Variational Calculation of the Polarizability of an Electron Trapped by a Point Defect

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A variational method is used to determine the polarizability of an electron trapped by a positive point defect in an ionic crystal. The model Hamiltonian describing the interaction between the point defect and an electron in an ionic crystal is related to the model introduced by Simpson to calculate the charge distribution and energy levels of trapped electrons in ionic crystals. However, in the problem considered here, an applied electric field is also present, and consequently a somewhat different model is proposed. The polarizabilities are calculated for both the new model and Simpson's original model, and the results are compared with the results of a theoretical calculation by Adamov, Ledovskaya, and Rebane of the polarizability of an F center in alkali halide crystals. In atomic units, the polarizabilities obtained for the new model range from 227 for NaF to 4280 for LiI.

I. INTRODUCTION

The polarizability of the hydrogen atom (expressed in a.u.) is 4.5.¹ The continuum model of an electron trapped by a positive point charge in a homogeneous dielectric of dielectric constant ϵ yields a value of $4.5\epsilon^4$ for the polarizability of the resulting hydrogenlike system. However, if the dielectric is polar and characterized by low- and high-frequency dielectric constants ϵ_s and ϵ_∞ , then the wave function, energy, and polarizability of the trapped electron are no longer related in any simple fashion to the hydrogen-atom problem. The essential point is that in a polar dielectric the charge distribution associated with the trapped electron plays a major role in determining the total polarization of the medium.

The object of this paper is to calculate the polarizability of an electron trapped by a unit positive point charge (we shall use a.u. throughout) in a polar dielectric continuum and subject to a uniform external electric field $\mathbf{F} = F\hat{\mathbf{k}}$. Our treatment of this problem is an extension of the work of Simpson,² who calculated the energy and the wave function for such an electron in the absence of any external field.

Owing to the presence of the external electric field, the wave function will not be spherically symmetric, and we assume an initial wave function of the form

$$\psi_0(\lambda, \alpha) = A \exp(-\lambda r)(1 + \alpha z). \quad (1.1)$$

Here the normalization constant A is related to λ and α by the requirement that the norm of $\psi_0(\lambda, \alpha)$ be equal to unity:

$$A^2 = \lambda^3 [1 + (\alpha/\lambda)^2] / \pi. \quad (1.2)$$

Following Simpson, the Hamiltonian for the system under consideration is given by

$$H = -\frac{1}{2}\nabla^2 - (1/\epsilon_s r) - V(\lambda, \alpha) + Fz, \quad (1.3)$$

where $V(\lambda, \alpha)$ is the electrostatic potential due to the polarization of the dielectric caused by the trapped electron, whose wave function is given by Eq. (1.1). Here it should be noted that the parameters λ and α are

field dependent (i.e., functions of the external field F), and therefore $V(\lambda, \alpha)$ is an implicit function of F . The calculation of the potential $V(\lambda, \alpha)$ is described in Sec. II.

The next step in applying Simpson's method to the present problem is to calculate the expectation value of the energy using the trial wave function

$$\psi_1(\mu, \beta) = B \exp(-\mu r)(1 + \beta z), \quad (1.4)$$

yielding a result

$$E = E(\lambda, \alpha, \mu, \beta), \quad (1.5)$$

which depends on all four parameters λ , α , μ , and β . Simpson's variational method then involves the minimization of $E(\lambda, \alpha, \mu, \beta)$ with respect to μ and β ,

$$(\partial/\partial\mu)E(\lambda, \alpha, \mu, \beta) = (\partial/\partial\beta)E(\lambda, \alpha, \mu, \beta) = 0, \quad (1.6)$$

and then one finally sets $\lambda = \mu$ and $\alpha = \beta$ and uses Eqs. (1.6) to determine μ and β explicitly. Simpson actually used this variational method only for the spherically symmetric case when no external electric field is present (i.e., α and β do not appear in his treatment).

Once μ and β have been explicitly determined, the polarizability p can be obtained from the coefficient of the F^2 term in the expansion of E in powers of the external field

$$E = W_s - \frac{1}{2}pF^2 + \dots, \quad (1.7)$$

where W_s denotes Simpson's result for the energy in the absence of an applied field.

It is much easier to evaluate the polarizability by calculating that part of the expectation value of z which is proportional to the field F [i.e., $pF = \langle \psi_1 | (\text{charge})z | \psi_1 \rangle / \langle \psi_1 | \psi_1 \rangle$, where the charge equals -1 a.u.]. Using the wave function (1.4) normalized to unity, one can easily verify that

$$pF = -2\beta/[1 + (\beta/\mu)^2]. \quad (1.8)$$

Since β is a measure of the distortion of the wave function in the direction of the applied field, we can write

$$\beta = b_1 F + b_3 F^3 + b_5 F^5 + \dots \quad (1.9)$$

Furthermore, since reversing the direction of the z axis cannot change the value of μ , it is clear that we can also write

$$\mu = \mu_S + a_2 F^2 + a_4 F^4 + \dots, \quad (1.10)$$

where μ_S denotes Simpson's result for μ . Hence from the induced dipole moment we find

$$p = -2b_1/\mu_S^2. \quad (1.11)$$

It can be shown that the two results for p , viz., that determined from the expansion of the energy in powers of the field by (1.7), and that determined by direct calculation of the polarization by (1.11), do not agree for Simpson's variational procedure.^{3,4}

In Sec. III we present a modified version of Simpson's model which does lead to the same result for the polarizability whether it is calculated from the induced dipole moment or from the coefficient of F^2 in the expression for the energy. The model proposed in Sec. III is based on calculating the expectation value of the total Hamiltonian (1.3) by using the same wave function (1.1) originally used to determine the electrostatic potential associated with the trapped electron's charge density. The expectation value of the energy then depends on only the two parameters λ and α . One then chooses λ and α to minimize $E(\lambda, \alpha)$, i.e., the variational parameters are determined from the equations

$$(\partial/\partial\lambda)E(\lambda, \alpha) = (\partial/\partial\alpha)E(\lambda, \alpha) = 0. \quad (1.12)$$

In the absence of an applied field, our model leads to the result

$$W_0 = -\frac{1}{2}\lambda_0^2, \quad (1.13a)$$

where

$$\lambda_0 = 3/8\epsilon_s + 5/8\epsilon_\infty. \quad (1.13b)$$

On the other hand, Simpson's original model yields

$$Ws = \frac{1}{2}\lambda_S\{\lambda_S - 5/4\epsilon_\infty - 3/4\epsilon_s\}, \quad (1.14a)$$

where

$$\lambda_S = 11/16\epsilon_s + 5/16\epsilon_\infty. \quad (1.14b)$$

The simplest comparison one can make of the two models is to note that for various alkali halides our model leads to binding energies of the trapped electron which are approximately 10% higher than Simpson's results. The two models lead to appreciably different values of the polarizabilities; the main advantage of our model is that it avoids the ambiguity encountered in Simpson's model in regard to using Eq. (1.7) or (1.11) to determine the polarizability.

Our conclusions are briefly discussed in Sec. III. We also compare our results with the computed values for the F -center polarizabilities of alkali halide crystals given by Adamov, Ledovskaya, and Rebane.⁵ It should be emphasized, of course, that the two calculations are for different systems: Our calculations are based on Simpson's model of an interstitial positive ion whereas

an F center involves a vacancy. Nevertheless, it is of interest to find that the values of Adamov, Ledovskaya, and Rebane are in essential agreement with ours for traps of equal binding energies. For a given alkali halide crystal the polarizabilities of the interstitial ions are larger than the values of Adamov, Ledovskaya, and Rebane for the F -center polarizabilities, but this discrepancy can be attributed to the large difference in the binding energies (the deeper the trap, the more the wave function tends to be pulled into it, and the smaller the resulting polarizability).

II. CALCULATION OF POTENTIAL

Owing to the presence of the applied electric field, the electrostatic potential due to the trapped electron's charge density has cylindrical symmetry rather than spherical symmetry, and is consequently somewhat more difficult to calculate than in Simpson's² case.

Let us begin by using the phenomenological equations of Born and Huang⁶ to find the potential due to a unit point charge imbedded in a polar dielectric medium and surrounded by an arbitrary electronic charge distribution $-\psi(\mathbf{r})$. The equations are

$$\ddot{\mathbf{u}}(\mathbf{r}) = a_{11}\mathbf{E}(\mathbf{r}) + a_{12}\mathbf{u}(\mathbf{r}), \quad (2.1)$$

$$\mathbf{P}(\mathbf{r}) = a_{21}\mathbf{E}(\mathbf{r}) + a_{22}\mathbf{u}(\mathbf{r}), \quad (2.2)$$

where \mathbf{P} and \mathbf{E} denote the polarization and electric field vectors, respectively, and \mathbf{u} denotes the ionic displacement vector. The coefficients are related to the properties of the medium by

$$a_{11} = -\omega_0^2, \quad (2.3a)$$

$$a_{12} = a_{21} = \omega_0[(\epsilon_s - \epsilon_\infty)/4\pi]^{1/2}, \quad (2.3b)$$

$$a_{22} = (\epsilon_\infty - 1)/4\pi, \quad (2.3c)$$

where ω_0 is the infrared dispersion frequency. The procedure will be to calculate $\mathbf{u}(\mathbf{r})$ due to both the point charge and the surrounding charge density of the trapped electron, and then to use the result to find the electric field (in the sense of the correspondence principle) acting on the electron.

If $\mathbf{u}(\mathbf{r})$ is assumed to be constant over the time interval corresponding to the orbital period of the trapped electron, then by averaging Eq. (2.1) over this period we obtain

$$0 = a_{11}\langle\mathbf{E}(\mathbf{r})\rangle + a_{12}\mathbf{u}(\mathbf{r}), \quad (2.4)$$

which shows that $\mathbf{u}(\mathbf{r})$ is an irrotational vector field. Now let $\mathbf{E}_{\text{ext}}(\mathbf{r})$ be the field of the unit positive charge and the point electron in the absence of a dielectric; then since the calculation of \mathbf{D} due to point charges in a dielectric is the same as the calculation of \mathbf{E} in the absence of the dielectric, we have from (2.2) and the definition

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}, \quad (2.5)$$

the result

$$\mathbf{E}(\mathbf{r}) = (1 + 4\pi a_{21})^{-1}[\mathbf{E}_{\text{ext}}(\mathbf{r}) - 4\pi a_{22}\mathbf{u}(\mathbf{r})]. \quad (2.6)$$

TABLE I. Values of the polarizabilities of alkali halide crystals in a.u. Values for ϵ_s and ϵ_∞ are taken from Ref. 7, Table V, p. 147. λ_0 and λ_s are in a.u. The theoretical values of the F -center polarizability are the results given by Adamov, Ledovskaya, and Rebane.⁴ The experimental values for the F -center absorption maxima are taken from Ref. 6, Table 3.2, p. 10.

	ϵ_s	ϵ_∞	λ_0	New model W_0 (eV)	p_0	λ_s	Simpson's model W_s (eV)	p_s	Theoretical values of F -center polarizability	Experimental values for F -center absorption maxima (eV)
NaF	6.0	1.74	0.422	-2.42	227	0.294	-2.19	783	95.1	3.65
KF	6.05	1.85	0.400	-2.17	275	0.283	-1.98	902	145	2.72
RbF	5.91	1.93	0.387	-2.04	303	0.278	-1.87	936	170	...
KCl	4.68	2.13	0.374	-1.90	299	0.294	-1.81	672	235	2.20
LiF	9.27	1.92	0.366	-1.82	462	0.237	-1.59	2 110	64.1	4.96
RbCl	5.0	2.19	0.360	-1.76	352	0.280	-1.68	821	265	1.98
KBr	4.78	2.33	0.347	-1.63	390	0.278	-1.57	819	270	1.97
NaCl	5.62	2.25	0.345	-1.61	440	0.261	-1.52	1 120	169	2.67
RbBr	5.0	2.33	0.343	-1.60	415	0.272	-1.53	911	309	1.72
RbI	5.0	2.63	0.313	-1.33	569	0.256	-1.28	1 105	372	1.60
KI	4.94	2.69	0.308	-1.29	592	0.255	-1.25	1 110	333	1.81
NaBr	5.99	2.62	0.301	-1.23	722	0.234	-1.17	1 690	201	2.30
NaI	6.60	2.91	0.272	-1.00	1090	0.212	-0.952	2 520	256	2.11
LiCl	11.05	2.75	0.261	-0.927	1650	0.176	-0.827	6 490	130	3.22
LiBr	12.1	3.16	0.229	-0.711	2750	0.156	-0.638	10 400	158	...
LiI	11.03	3.80	0.198	-0.535	4280	0.145	-0.495	12 600	205	...
AgCl	12.3	4.01	0.186	-0.472	5650	0.134	-0.434	17 500
AgBr	13.1	4.62	0.164	-0.365	9110	0.120	-0.339	26 200
ZnS	8.8	5.2	0.163	-0.360	7310	0.138	-0.351	12 600

Averaging (2.6) over an orbital period yields

$$\langle \mathbf{E}(\mathbf{r}) \rangle = (1 + 4\pi a_{21})^{-1} [\langle \mathbf{E}_{\text{ext}}(\mathbf{r}) \rangle - 4\pi a_{22} \mathbf{u}(\mathbf{r})], \quad (2.7)$$

where $\langle \mathbf{E}_{\text{ext}}(\mathbf{r}) \rangle$ is identified as the vacuum field of the unit positive charge and the trapped electron's charge distribution $-|\psi(\mathbf{r})|^2$. Substituting (2.7) into (2.4), we obtain

$$\mathbf{u}(\mathbf{r}) = \frac{(1 + 4\pi a_{21})^{-1} \langle \mathbf{E}_{\text{ext}}(\mathbf{r}) \rangle}{4\pi a_{22} / (1 + 4\pi a_{21}) - a_{12} / a_{11}}. \quad (2.8)$$

However, \mathbf{E}_{ext} contains the fields of both the central point charge and the electron; the latter is spherically symmetric about the electron and thus contributes a part of the electric field which does not affect the electron motion at all. We therefore write the following expression for the field acting on the electron:

$$\mathbf{E}'(\mathbf{r}) = (1 + 4\pi a_{21})^{-1} [\mathbf{E}_{\text{ext}}'(\mathbf{r}) - 4\pi a_{22} \mathbf{u}(\mathbf{r})], \quad (2.6')$$

where $\mathbf{E}_{\text{ext}}'(\mathbf{r})$ denotes the field of a unit positive charge located at the origin in the absence of a dielectric. Substituting (2.8) into (2.6') and also using (2.3), we finally obtain

$$\mathbf{E}'(\mathbf{r}) = -\langle \mathbf{E}_{\text{ext}}(\mathbf{r}) \rangle / \bar{\epsilon} + [\mathbf{E}_{\text{ext}}'(\mathbf{r}) / \epsilon_\infty], \quad (2.9)$$

where

$$\bar{\epsilon}^{-1} = \epsilon_\infty^{-1} - \epsilon_s^{-1}. \quad (2.10)$$

The electrostatic potential for this field is

$$V(\mathbf{r}) = \bar{\epsilon}^{-1} \{ \int [\psi(\mathbf{r}')^2 d\mathbf{r}' / |\mathbf{r} - \mathbf{r}'|] - r^{-1} \} + (\epsilon_\infty r)^{-1}. \quad (2.11)$$

Assuming that the wave function is given by Eq. (1.1), we calculate the integral appearing in (2.11) by first evaluating it when the point \mathbf{r} lies on the axis of cylindrical symmetry, and then using the uniqueness theorem of electrostatics to determine the potential at any other point. Thus, the first step is to calculate

$$\phi(z\hat{\mathbf{k}}) = \int |\psi(\mathbf{r}')|^2 d\mathbf{r}' / |\mathbf{r}' - z\hat{\mathbf{k}}|, \quad (2.12)$$

where

$$|\psi|^2 = A^2 \exp(-2\lambda r') [(1 + \frac{1}{3}\alpha^2 r'^2) P_0(\cos\theta') + 2\alpha r' P_1(\cos\theta') + \frac{2}{3}\alpha^2 r'^2 P_2(\cos\theta')], \quad (2.13)$$

$$|\mathbf{r}' - z\hat{\mathbf{k}}|^{-1} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos\theta'). \quad (2.14)$$

In the last equation, $r_{<} = z$ if $z < |\mathbf{r}'|$, etc. Using the well-known orthogonality properties of the Legendre

polynomials, one finds

$$\begin{aligned}\phi(z\hat{\mathbf{k}}) = & \frac{4\pi A^2}{z} \int_0^r \exp(-2\lambda r') r'^2 dr' \\ & + \frac{8\pi A^2 \alpha}{3z^2} (1 + \frac{1}{2}\alpha z) \int_0^r \exp(-2\lambda r') r'^4 dr' \\ & + \frac{8\pi A^2 \alpha^2}{15z^3} \int_0^r \exp(-2\lambda r') r'^6 dr' \\ & + 4\pi A^2 (1 + \frac{2}{3}\alpha z + \frac{2}{15}\alpha^2 z^2) \int_r^\infty \exp(-2\lambda r') r' dr' \\ & + \frac{4}{3}\pi A^2 \alpha^2 \int_r^\infty \exp(-2\lambda r') r'^3 dr'. \quad (2.15)\end{aligned}$$

Since the potential for a problem possessing azimuthal symmetry has the general form

$$\sum_{l=0}^{\infty} \{A_l r^l + B_l r^{-l-1}\} P_l(\cos\theta), \quad (2.16)$$

the potential at any arbitrary point (r, θ) is obtained from expression (2.15) by replacing z^n by $r^n P_n(\cos\theta)$ and z^{-n-1} by $r^{-n-1} P_n(\cos\theta)$. Making these substitutions and carrying out the integrations, the electrostatic potential due to the trapped electron is

$$V(\lambda, \alpha) = V_0 + \alpha V_1 + \alpha^2 V_2, \quad (2.17)$$

where

$$\begin{aligned}V_0 = & (\pi A^2 / \bar{\epsilon} \lambda^3) [r^{-1} - (r^{-1} + \lambda) \exp(-2\lambda r)], \quad (2.18) \\ V_1 = & \frac{\pi A^2}{\bar{\epsilon} \lambda^3} \left[\frac{2}{\lambda^2 r^2} - \left(\frac{2}{\lambda^2 r^2} + \frac{4}{\lambda r} + 4 + 2\lambda r \right) \exp(-2\lambda r) \right] \\ & \times P_1(\cos\theta), \quad (2.19)\end{aligned}$$

and

$$\begin{aligned}V_2 = & \frac{\pi A^2}{\bar{\epsilon} \lambda^3} \left[(\lambda^2 r)^{-1} - \left((\lambda^2 r)^{-1} + \frac{3}{2\lambda} + r + \frac{1}{3}\lambda r^2 \right) \exp(-2\lambda r) \right] \\ & + \frac{\pi A^2}{\lambda^3} \left[\frac{3}{\lambda^4 r^3} - \left(\frac{3}{\lambda^4 r^3} + \frac{6}{\lambda^3 r^2} + \frac{6}{\lambda^2 r} \right. \right. \\ & \left. \left. + \frac{4}{\lambda} + 2r + \frac{2}{3}\lambda r^2 \right) \exp(-2\lambda r) \right] P_2(\cos\theta). \quad (2.20)\end{aligned}$$

The Hamiltonian for the problem is now given by (1.3) with the help of Eqs. (2.17)–(2.20).

III. VARIATIONAL CALCULATION

The expectation value of the Hamiltonian (1.3) is easily found by using the trial wave function (1.1) and expression (2.17) for the potential. The result can be written

$$E = \frac{1}{2}\lambda^2 + \frac{N}{1 + (\alpha/\lambda)^2}, \quad (3.1)$$

where

$$\begin{aligned}N = & -\frac{\lambda}{\epsilon_s} - \frac{\alpha^2}{2\epsilon_s \lambda} + \frac{2F\alpha}{\lambda^2} \\ & - \frac{\lambda}{\bar{\epsilon}[1 + (\alpha/\lambda)^2]} \left(\frac{5}{8} + \frac{7\alpha^2}{6\lambda^2} + \frac{501}{5 \cdot 2^8} \frac{\alpha^4}{\lambda^4} \right). \quad (3.2)\end{aligned}$$

Equation (1.12) then yields simultaneous algebraic equations for λ and α which are of seventh and fourth order, respectively. They are

$$\begin{aligned}\lambda \left[1 + \left(\frac{\alpha}{\lambda} \right)^2 \right] - \epsilon_s^{-1} - \frac{5\alpha^2}{2\epsilon_s \lambda^2} - \frac{\alpha^4}{2\epsilon_s \lambda^4} \\ - \bar{\epsilon}^{-1} \left[\frac{5}{8} - \frac{7\alpha^2}{6\lambda^2} - \frac{1503}{5 \cdot 2^8} \frac{\alpha^4}{\lambda^4} + \left(1 + \frac{\alpha^2}{\lambda^2} \right) \right. \\ \left. \times \left(\frac{5\alpha^2}{2\lambda^2} + \frac{14\alpha^4}{3\lambda^4} + \frac{501\alpha^6}{5 \cdot 2^6 \lambda^6} \right) \right] - \frac{4F\alpha}{\lambda^3} = 0 \quad (3.3)\end{aligned}$$

and

$$\begin{aligned}\alpha^4 - \left(\frac{737}{15 \cdot 2^7 \bar{\epsilon}} + (2\epsilon_s)^{-1} \right) \frac{\lambda^3 \alpha^3}{F} \\ - [(12\bar{\epsilon})^{-1} + (2\epsilon_s)^{-1}] \frac{\lambda^5 \alpha}{F} - \lambda^4 = 0. \quad (3.4)\end{aligned}$$

Formal solution of these equations would present enormous difficulty, but successive approximations in powers of the electric field F are easily found. Using expansions of the form (1.9) and (1.10) the first approximation to the solution of the simultaneous equations (3.3) and (3.4) is readily found to be given by (1.13b) and

$$\begin{aligned}\alpha = b_1 F \\ = -F/\lambda_0 [(12\bar{\epsilon})^{-1} + (2\epsilon_s)^{-1}]. \quad (3.5)\end{aligned}$$

Substitution of (1.13b) and (3.5) into (3.1) yields for the energy

$$E = W_0 + f_2 F^2 + \dots,$$

where

$$W_0 = -\frac{1}{2}\lambda_0^2$$

and

$$\begin{aligned}f_2 = & - \left[\lambda_0^3 \left(\frac{1}{12\bar{\epsilon}} + \frac{1}{2\epsilon_s} \right) \right]^{-1} \\ = & - \frac{3}{2} \frac{(8\epsilon_s \epsilon_\infty)^4}{(\epsilon_s + 5\epsilon_\infty)(3\epsilon_\infty + 5\epsilon_s)^3}, \quad (3.6)\end{aligned}$$

and it is readily verified that the solutions (1.13b) and (3.5) for λ and α include the entire term in the energy which is proportional to F^2 . Using the definition of polarizability arising from (1.7), we find

$$\begin{aligned}p_0 = & -2f_2 \\ = & \frac{3(8\epsilon_s \epsilon_\infty)^4}{(\epsilon_s + 5\epsilon_\infty)(5\epsilon_s + 3\epsilon_\infty)^3}. \quad (3.7)\end{aligned}$$

It is readily checked that substitution of (1.13b) and

(3.5) into (1.11) yields the same result for the polarizability. Note that (1.11) is true whether one uses Simpson's variational method or the modified procedure described in this section; the results will differ because the values of b_1 and λ will be different. In fact using Simpson's variational method and the definition (1.11), one readily finds

$$p_s = \frac{3(16\epsilon_s\epsilon_\infty)^4}{(\epsilon_s + 11\epsilon_\infty)(5\epsilon_s + 11\epsilon_\infty)^3}. \quad (3.8)$$

Values of the polarizabilities are given in Table I for a series of 16 alkali halides and two silver halides. The values computed by Adamov *et al.*⁵ for the F -center polarizabilities are also shown in the table, along with the experimental F -center absorption maxima according to Markham.⁷

It is clear from the table that the results for the polarizabilities are extraordinarily sensitive to the choice of model; the difference in energies between the two models amounts to 10% or less, but the polarizabilities calculated on Simpson's model are greater by a factor of 3 or 4. On both models the polarizability in lithium salts seems anomalously high. The reason for this can be seen by writing (3.7) as

$$p_0 = \epsilon_\infty^4 \frac{3(8x)^4}{(x+5)(5x+3)}, \quad (3.7')$$

where $x = \epsilon_s/\epsilon_\infty$. Then if ϵ_∞ were constant, (3.7') would be a rapidly increasing function of x ; the large value of the ratio $\epsilon_s/\epsilon_\infty$ is thus the chief contributing factor to the high polarizabilities in the lithium salts as compared with the other alkali halides.

The deficiencies of the point-defect model are well known (see, for example, a discussion on this point by Gourary and Adrian⁸); however, a simple analytic result has been found which correlates well with computed values in a certain sense. Since the F -center model of Adamov *et al.*⁵ is different from the point-defect model, it yields different values for the energy, and the polarizabilities are also different. However, an examination of Table I shows that roughly equal polarizabilities are associated with approximately equal values of trap depth and dielectric constants.

It should also be noted that our result (3.7) reduces to 4 for the hydrogen atom [to verify this, set $\epsilon_s = \epsilon_\infty = 1$ in (3.7)]; so also does the polarizability (3.8). One can obtain the correct result 4.5 for the polarizability of the hydrogen atom by using the trial wave function

$$\psi = A \exp(-\lambda r) (1 + \alpha z + \beta rz)$$

instead of (1.1). We anticipate that this will change the values given in Table I for the polarizability by 10% or less.

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¹ N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Oxford U. P., Oxford, England, 1948), pp. 166-168.

² J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

³ One can easily verify that in Simpson's model the result for the polarizability given by Eq. (1.7) will depend on the value of a_2 . To see this, let us make a Taylor's series expansion of $W(\lambda, \alpha, \mu, \beta)$ about the point $\lambda = \mu = \lambda_s, \alpha = \beta = 0$,

$$\begin{aligned} W(\lambda, \alpha, \mu, \beta) = & W_s + (\partial W/\partial \lambda)_0 a_2 F^2 + (\partial W/\partial \mu)_0 a_2 F^2 \\ & + (\partial W/\partial \alpha)_0 b_1 F + (\partial W/\partial \beta)_0 b_1 F + \frac{1}{2} (\partial^2 W/\partial \alpha^2)_0 (b_1 F)^2 \\ & + \frac{1}{2} (\partial^2 W/\partial \beta^2)_0 (b_1 F)^2 + \dots \end{aligned}$$

In Simpson's model the variational procedure amounts to choosing μ and β to minimize W , but the other two partial derivatives, $(\partial W/\partial \lambda)_0$ and $(\partial W/\partial \alpha)_0$, do not vanish. Hence one finds a term proportional to $a_2 F^2$ in the expansion of W in powers of the field. On the other hand, in the new model proposed here the analogous expansion takes the form

$$\begin{aligned} W(\lambda, \alpha) = & W_0 + (\partial W/\partial \lambda)_0 a_2 F^2 + (\partial W/\partial \alpha)_0 b_1 F \\ & + \frac{1}{2} (\partial^2 W/\partial \alpha^2)_0 (b_1 F)^2 + \dots \end{aligned}$$

but now the variational principle guarantees that $(\partial W/\partial \lambda)_0$ and $(\partial W/\partial \alpha)_0$ both vanish.

⁴ It is somewhat surprising that the two results for the polariz-

ability are not the same in Simpson's prescription since in principle one expects them to be identical. It has been pointed out that the trouble lies in the fact that the model Hamiltonian (1.3) is not the Hamiltonian of the entire system. The system consists of the polarizable crystal plus the electron, whereas Eq. (1.3) describes the Hamiltonian of the electron after taking an expectation value and integrating over all the crystal coordinates. In other words, the total energy (or Hamiltonian) is the sum of (a) the internal energy of the crystal, (b) the electron's energy of binding to the point charge, (c) the crystal polarization-electron interaction, (d) the interaction of the crystal polarization with the field, and (e) the interaction of the electron polarization with the field. Expression (1.3) contains items (b), (c), and (e). Thus, when the energy corresponding to the Hamiltonian (1.3) is found, terms quadratic in the field arising from items (c) and (e) occur. The latter is due to the electronic polarizability, the former to that component of the total system polarizability which is due to energy stored in the electron-crystal polarization interaction; it cannot be ascribed to either the electron or crystal separately.

⁵ M. N. Adamov, E. M. Ledovskaya, and T. K. Rebane, Fiz. Tverd. Tela **8**, 3173 (1966) [Soviet Phys. Solid State **8**, 2541 (1967)].

⁶ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, England, 1954), pp. 82-89.

⁷ J. J. Markham, Solid State Phys. Suppl. **8** (1966).

⁸ B. S. Gourary and F. J. Adrian, Solid State Phys. **10**, 127 (1960).