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The Binding Energy for a Self-Trapped Electron in NaCl*

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A calculation has been made of the binding energy of a self-trapped electron in NaCl. The potential well, caused by the ionic displacements, was assumed to be a sawed-off Coulomb field, the sides being given by $(1/\kappa_0 - 1/\kappa)1/r$, where the κ's are the dielectric constants. The depth of the well was calculated by the method of Mott and Littleton. In the present problem, however, we require a self-consistent solution; that is, the initial wave function which is employed in calculating the depth of the trapping potential hole must be identical to the one obtained from this potential hole on solving the Schroedinger equation. The electron is smeared over a sphere whose radius equals approximately three interatomic distances. The outer displacements are calculated by a semicontinuum theory, whereas the dipoles of the three ions nearest the trapping center are calculated from the condition of equilibrium. The optical dissociation energy is found to be 0.68 ev, whereas the thermal energy is 0.13 ev. The low value of the second quantity presumably explains why self-trapping has not been observed to date. This energy should be about twice as large in LiF. These results suggest that self-trapping should be sought at a very low temperature.

I. INTRODUCTION

THE possibility that an electron can trap itself in a polar crystal was predicted by Landau. The trapping potential well is produced as a result of the ionic displacements induced by the field of the electron. Formerly this type of trapping was believed to be a possible explanation of the *F* centers studied by Pohl.[1] Experimental studies of the way *F* centers are produced, when there is stoichiometric excess of metal in an ionic crystal, indicate that they actually are caused by an alternate mechanism suggested by de Boer. He proposed that the electrons are trapped in the vacant negative lattice sites. Further rough estimates of the energy required to form an *F* center from a vaporized alkali metal implies that Landau's mechanism does not compete favorably with de Boer's on energetic grounds.

The problem remains, however, to calculate the binding energy of a self-trapped electron sufficiently accurately to be sure that this process does not compete with the other. Further, one might hope that by a calculation of this type sufficient information would be gained to predict under what conditions, if any, self-trapping would be observed.

A rough set of calculations of the binding energy of a self-trapped electron in ionic crystals has been made by Gurney and Mott,[2] and they report the binding energy to be several electron volts. Details of the calculations are not given, but the problem of a self-consistent solution does not appear to have been considered. These values seem extremely high and make it very difficult to understand why self-trapping has not been observed during some of the experimentation of Pohl or his co-workers. Recently, Pekar[3] has calculated this binding energy on the assumption of a continuous medium. His solution is self-consistent and gives an optical activation energy of -0.32 ev for NaCl. To calculate this value from his equations, we have placed the effective mass of the self-trapped electron equal to the free electron mass.

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[1] For a recent review of this field see F. Seitz, Rev. Mod. Phys. **18**, 384 (1946), where a more detailed bibliography is given.

[2] R. W. Gurney and N. F. Mott, Proc. Phys. Soc. **49**, 32 (1937).

[3] S. Pekar, J. Phys. U.S.S.R. **10**, 341, 347 (1946).

In view of the importance of self-trapping, we deemed it worth while to carry through a detailed calculation of the binding energy. In these calculations the method developed by Mott and Littleton[4] to calculate lattice defects was used. It is based on the simple and reliable theory of ionic crystal of Born with appropriate modifications. The electron wave function determines the field which causes the displacement of the ions in the crystal; these displacements determine the potential hole the electron is found in, and, finally, the hole determines the wave function. We thus require a self-consistent solution. Further, as we shall see, the electron is smeared out over several neighboring ions. This implies that the more distant ions may be more important than in the calculations of Mott and Littleton and that the total charge which determines the polarization of an ion varies with the distance from the trapping center.

II. THE WAVE FUNCTION

Let us now consider in detail the Schroedinger's wave equation for a self-trapped electron in a crystal, namely,

$$\frac{\hbar^2}{2m}\nabla^2\psi+(E_T-eV_T)\psi=0, \tag{1}$$

where E_T is the total energy of the electron and V_T is the total potential at r. The other terms have their conventional meaning. V_T is a combination of two terms, namely, the undisturbed potential, which is present whether or not there is a distortion of the lattice due to self-trapping, and an additional potential from the distortion. We may thus write it in the form

$$V_T=V_I+V, \tag{2}$$

where V_I is the ionic potential, which is essentially the Hartree potential of the ion corrected for the fact that the ion is in a perfect crystal and V is the potential due to the lattice distortion. In line with Eq. (2) we write

$$E_T=E_I+E. \tag{3}$$

We now make the assumption that we may write the wave function, ψ, as a product of two wave functions

$$\psi=\varphi\chi. \tag{4}$$

χ is taken as the undistorted wave function—a Bloch function for an electron in the conduction band. We may picture φ as modulating χ. Admittedly (4) is just a first-order approximation. We assume that V_I, E_I, and χ are related by the equation

$$(\hbar^2/2m)\nabla^2\chi+(E_I-eV_I)\chi=0. \tag{5}$$

Substituting back into (1) we obtain

$$(\hbar^2/2m)\nabla^2\varphi+(\hbar^2/m)\nabla\varphi\cdot(\nabla\chi/\chi)+(E-eV)\varphi=0. \tag{6}$$

Let us now examine Eq. (5) so that we may find a way to handle the second term in Eq. (6). Tibbs[5] has calculated χ for NaCl. His calculations follow the standard method of calculating Bloch functions in solids.[6] Tibbs employed the calculations of Prokofjew[7] on Na and of Hartree[8] on Cl to determine the ionic fields, but added a term to take care of the Ewald potential. Its form is

$$Ar^2+Br^3\pm1.748e^2/a,$$

where r is the radial distance, A and B are constants, different for Na and Cl, "a" is the distance between nearest neighbors, and 1.748 is Madelung's constant. The positive sign goes with Na, and the negative with Cl. A and B are evaluated so that the Ewald term is zero at the point where the ionic spheres (Tibbs replaced the ionic polyhedrons by spheres) are in contact, and the potential is due only to the overlapping ions. By numerical integration Tibbs found the energy for which the condition

$$\chi(\mathrm{Cl})/\chi(\mathrm{Cl})=-\chi(\mathrm{Na})/\chi(\mathrm{Na})$$

is satisfied at the boundary of the ionic spheres. Tibbs' value of E_I is 3.2 ev.

We recalculated χ using more recent ionic fields, which include exchange terms. We used the field of Fock and Petrachen[9] for Na and the field

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[4] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[5] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939). Also N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 69.

[6] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[7] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929).

[8] D. R. Hartree, Proc. Roy. Soc. **A141**, 282 (1933).

[9] V. Fock and Mary Petrachen, Physik. Zeits. Sowjet union **6**, 368 (1934).

of Hartree and Hartree[10] for Cl. The wave function obtained in this way is very similar to that found by Tibbs. However, E_I is 12.8 ev. Our value is considerably larger than Tibbs' for the following reason. He made a correction for the use of the self-consistent field calculations without exchange. The diamagnetic susceptibility for Cl^- calculated from the field he used is 25×10^{-6} cm^3, while the measured value for Cl^- is 41.3×10^{-6} cm^3. Therefore, he multiplied his ionic radii by $(41.3/25)^{\frac{1}{2}}$ and obtained approximately 4.0 atomic units. We did not make this correction and used for the atomic radius the value obtained directly from the lattice constant. In addition, of course, we used slightly different fields from those used by Tibbs.

In treating Eq. (6) we shall neglect the second term and use the simplified form of the equation, namely,

$$(\hbar^2/2m)\nabla^2\varphi+(E-eV)\varphi=0. \qquad (7)$$

The principal justification for this procedure rests on the fact that φ varies slowly in comparison with χ so that $\nabla\chi/\chi$ may be replaced by its mean value over any single cell of the lattice to a good approximation. This mean value is readily seen to be zero because χ is an even function relative to the center of symmetry represented by each ion in the lattice.

To determine the effect on the energy of omitting the second term of Eq. (6), we calculate its value by the mean value theorem. To do this, we assume that ψ is given by (4), where φ and χ are given by Eqs. (5) and (7). If H is the total Hamiltonian obtained from Eq. (1), we have

$$\begin{aligned} E_T &= \int \psi^* H\psi d\tau \\ &= E+E_I-(\hbar/m)\int \chi^*\varphi^* \operatorname{grad}\chi\cdot\operatorname{grad}\varphi d\tau. \qquad (3a) \end{aligned}$$

We shall see that φ is a slowly varying function of position, and therefore, the last term can be written as

$$\sum_{\text{ll cells}} -\frac{\hbar}{m}\langle\varphi^* \operatorname{grad}\varphi\rangle_{\text{Av}}\cdot\int \chi^* \operatorname{grad}\chi d\tau.$$

We have substituted an average (over a cell) for φ^* gradφ, taken it out of the integrand, and summed over all the cells. Since χ is an even function of position, the integral vanishes and one obtains Eq. (3).

This same argument can be used to show that the higher approximation in a perturbation scheme vanishes. The perturbation scheme can be built up of product functions of the type $\chi\varphi_i$ in which the φ_i are the excited states' wave functions going with the wave (7) (φ being the ground state of Eq. (5)). We may therefore consider the wave function (4) as the leading term of the actual function given by $\chi\sum_i \varphi_i$.

We note that E is the energy relative to the electron in the conduction band, and we are, therefore, interested in it, not E_T.

Equation (7) is the form that was used by Pekar, although, in principle at least, he made allowances for the band structure by substituting an effective mass for m.

III. THE DISPLACEMENT POTENTIAL

Since χ does not enter into the evaluation of Eq. (7), we may use Born's[11] model of an ionic crystal. Therefore, we assume that the crystal is made of ions, whose internal structure is of no interest here except for the fact that they may become polarized when placed in an electric field. There are two main types of forces in this crystal, the short-range Born-Mayer force and the long-range electric force which arises from the additional electron and the polarization associated with displacements of the ions from their equilibrium positions. The equilibrium electric forces have, of course, been taken into account in V_I.

To simplify the problem, we assume that it is possible to separate the polarization of the electrons in the ion core from the displacement polarization of the ions. This separation is necessary because of a difference in the time of relaxation. Thus, if by some mechanism the electron is held constant for a period which is long compared to the time of a single lattice oscillation, 10^{-12} sec., the surrounding ions would be displaced. Effectively then, the electron would be surrounded by dipoles. The displacements would not follow the rapid motion of the electron after it is released, because of the long period of relaxa-

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[10] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A156**, 45 (1936).

[11] See N. F. Mott and R. W. Gurney, reference 5, Chapter I; F. Seitz, reference 6, Chapter II.

tion. Thus the displacement polarization would create a potential hole to which the electron would be bound. The core electrons will, however, follow the detailed motion of the trapped electron, since the velocities of the electrons are roughly comparable. This means that the susceptibility of the core will not enter directly into the creation of the potential hole. Strictly speaking, these two effects are not entirely separable because the local field (field at a given ion site within the crystal) is affected by the state of polarization of the neighboring ions. Nevertheless, we shall start with the assumption that the two are separable, so as to simplify the problem.

To make this argument quantitative, we consider two cases—first, for static charges the field is given by $\mathbf{D}/\kappa$, where $\mathbf{D}$ is Maxwell's displacement vector and κ is the static dielectric constant. This implies that there is an induced dipole of strength per unit volume,

$$(1/4\pi)(1-1/\kappa)\mathbf{D}. \tag{8}$$

If, on the other hand, we have a rapidly varying field, which cannot be followed by the ionic displacements, the field is $\mathbf{D}/\kappa_0$, where κ_0 is the high frequency dielectric constant. For this case the induced dipole is

$$(1/4\pi)(1-1/\kappa_0)\mathbf{D}. \tag{9}$$

To separate the effect of core polarization from the effects of displacements, we may use a method of Mott and Littleton.[4] If we impress a uniform field on our crystal, the positive ions will be displaced a distance $a\xi$ in one direction, while the negative ions are displaced $a\xi$ in the other. For small displacements the equation of equilibrium is:

$$pa\xi = eE_{(\text{local})}, \tag{10}$$

where p is an elastic constant. If we assume that the repulsive forces are represented by a short-ranged potential of the form (Born-Mayer)

$$w(r) = A\epsilon^{-r/\rho}, \tag{11}$$

where $\rho = 0.326\times10^{-8}$ cm, and that these forces act only between nearest neighbors, we obtain

$$p = \frac{2(1.748)e^2}{3a^2}\left[\frac{1}{\rho}-2/a\right]. \tag{12}$$

The induced dipole due to the displacement is simply

$$(e^2/p)E_{\text{local}}.$$

Thus e^2/p behaves just like a susceptibility, whence we may set $\alpha = e^2/p$. For static fields, we may define

$$f_e = (\alpha_1+\alpha_2)/(\alpha_1+\alpha_2+2\alpha), \tag{13}$$

$$f_d = 2\alpha/(\alpha_1+\alpha_2+2\alpha), \tag{14}$$

where α_1 and α_2 are the core polarizations for the odd and even ions (see below). f_d is the fraction of polarization arising from the displacements of the ions, and f_e is the fraction resulting from core polarization. In the equation, we have omitted corrections for the overlap terms,[11] since Mott and Littleton's calculations indicate that this correction is small.

One may arrive at an alternate expression for the f's by regarding the difference between the expressions (8) and (9) as the displacement dipoles per unit volume. According to this viewpoint, it follows that

$$f_e = (1-1/\kappa_0)/(1-1/\kappa), \tag{15}$$

and

$$f_d = (1/\kappa_0-1/\kappa)/(1-1/\kappa). \tag{16}$$

The definitions (13) and (14) are not equivalent to (15) and (16). For NaCl, the first set gives

$$\begin{aligned} f_e &= 0.38, \\ f_d &= 0.62. \end{aligned} \tag{17a}$$

In calculating Eq. (17a) the polarization used for Na was 0.195×10^{-24} and for Cl, 3.41×10^{-24} in cm^3. These are averages of values quoted by Fajan and Joos, Born and Heisenberg, and Pauling (see reference 11). The second definition gives

$$\begin{aligned} f_e &= 0.68, \\ f_d &= 0.32. \end{aligned} \tag{17b}$$

That these definitions are not equivalent in general can be seen with the use of the Lorentz term[12] for the local fields $\mathbf{E}+(4\pi/3)\mathbf{P}$. According to this relation, κ is related to the polarizability per unit cell α_c by the equation

$$(\kappa-1)/(\kappa+2) = (4\pi/3)n_0\alpha_c. \tag{18}$$

Here α_c is the total polarizability per unit cell and n_0 is the number of molecules per unit vol-

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[12] See, for example, J. N. Van Vleck, *The Theory of Electric and Magnetic Susceptibility* (Oxford University Press, New York, 1932), p. 14ff.

ume. α_c may be replaced by the electron polarizability per unit cell when displacement does occur, in which case κ is to be replaced by κ_0. With the use of Eqs. (13), (14), and (18) we may conclude that

$$f_e=[(\kappa_0-1)/(\kappa_0+2)][(\kappa+2)/(\kappa-1)]. \quad (19)$$

The derivation of this equation uses the fact that the total polarizability per unit cell is proportional to $\alpha_1+\alpha_2+2\alpha$ and the electronic polarizability is proportional to $\alpha_1+\alpha_2$ with the same proportionality factor.

If the electron polarization were the same before and after displacement, we would expect the relation

$$[1-(1/\kappa_0)]=[1-(1/\kappa)]f_e$$
$$=[(\kappa_0-1)/(\kappa_0+2)][(\kappa+2)/\kappa]. \quad (20)$$

or

$$\kappa/\kappa_0=(\kappa+2)/(\kappa_0+2).$$

This evidently is not identically satisfied. However, the condition approximately valid is at least partly satisfied. It is interesting to note that the right-hand side of (20) is smaller than the left, which means that the electron polarization decreases somewhat when the displacement polarization occurs.

The actual calculations were carried through, using Eqs. (15) and (16). That is, with the assumption that the electron polarizability is unchanged by the displacement, it is difficult to tell what error this introduced without carrying through some lengthy calculations. To be exact, one should take account of the core polarization in a more careful manner than we have done. Undoubtedly, the calculations presented in this paper give values that are correct to within an order of magnitude.

Equations (15) and (16) give the usual expression for the displacement dipole per unit volume,[3,13] namely,

$$(1/4\pi)(1/\kappa_0-1/\kappa). \quad (21)$$

The use of this expression is equivalent to assuming a continuous medium and completely disregarding the detailed crystal structure. For distant lattice points, one may assume the foregoing relation to hold approximately, but for neighboring ions we will have to consider the crystal structure in detail.

Zeroth Approximation

Let us, for the moment, assume that (21) holds for all the ions. Thus the displacement dipole induced on an ion a distance r (to be measured in interionic units) from the self-trapping center is

$$ea\delta(r_i)=(a^3/4\pi)(1/\kappa_0-1/\kappa)\mathbf{D}(r_i), \quad (22)$$

where δ is the displacement of the r_ith ion in units of "a." Here the problem is to calculate Maxwell's displacement vector. As we shall see subsequently, the electron is smeared over a sphere whose diameter is approximately $10a$. At points outside this sphere, $\mathbf{D}$ clearly equals $e/a^2r_i^2$. Since we are only interested in the time average dipole, we may use the time average displacement vector obtained from the trapped electron's wave function for points inside the sphere. In general, we may write

$$ea\delta(r_i)=(a/4\pi r_i^2)(1/\kappa_0-1/\kappa)eQ(r_i), \quad (23)$$

where

$$Q(r)=4\pi\int_0^{ar}|\varphi(\xi)|^2\xi^2d\xi.$$

Here we used only the envelope of ψ—i.e., φ ignoring the modulating function χ in computing Q. At large distances, $Q(r)$ equals unity, and further, we note "a" appears only in the first power on the right-hand side because of the units selected. Equation (23) shows the nature of the problem to be solved. To calculate the dipoles we must know φ from Eq. (7), but to evaluate that equation we must know the δ's.

Using Eq. (23) one could calculate V at any point in the crystal. This procedure is too complicated for actual use. However, we approximate V as follows. At large distances, where the continuum approximation is applicable, the potential due to the displacement dipoles is the difference between the static and the high frequency potential,

$$(1/\kappa_0-1/\kappa)e/ar, \quad (24)$$

in which we have let $Q(r)$ equal unity. Near the center of trapping, the field undoubtedly is neither a simple function nor is it completely spherically symmetric. We believe, however, that

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[13] See N. F. Mott and R. W. Gurney, reference 2, p. 86.

we can obtain a sufficiently good approximation by cutting off expression (24) at a distance r_0, and assuming that for smaller values of r_0 the potential is a constant. That the self-trapping potential behaves approximately in this manner can be seen from the fact that the potential at the very center is finite. We shall let the constant value at which (24) is cut off be this constant value. Our problem thus reduces itself to finding the potential once φ is known.

From Eq. (23) we obtain the desired value of the potential which we call $V_0(0)$, namely,

$$V_0(0)=(e/4\pi a)(1/\kappa_0-1/\kappa)\sum_{\text{all ions}} Q(r_i)/r_i^4. \quad (25)$$

The subscript denotes the order of the approximation. The summation converges slowly, since the number of ions per shell increases as the square of the distance. Until now we have made no assumption concerning the geometric arrangement of ions near the center of the self-trapped electron. For simplicity, we shall assume the center coincides with a positive ion site. In the zeroth approximation one would obtain exactly the same value of wave function φ and energy by locating the center at a negative ion site. This may seem paradoxical at first sight, but it should be recalled that the detailed internal structure, even the total charge of the ions, enters into the problem only through χ. However, the wave function χ is approximately equally distributed between the two ions, that is $\int|\chi|^2d\tau$ over the negative ion approximately equals $\int|\chi|^2d\tau$ over the positive ion. This shows that the electron does not distinguish strongly between the two ions.

Sums of the type found in (25) have been carried out by Ingham and Jones[14] for $Q(r)=1$. When the origin is at a positive ion, their result may be stated as follows:

$$\begin{aligned}\sum_{\text{neg. ions}} 1/r_i^4&=10.1977,\\ \sum_{\text{pos. ions}} 1/r_i^4&=6.3346.\end{aligned} \quad (26)$$

We can evaluate (25) accurately by assuming $Q(r)=1$ for the outer ions and write

$$\sum_{\text{all}} Q(r_i)/r_i^4=\sum_{\text{near}} Q(r_i)/r_i^4+\sum_{\text{far}} 1/r_i^4. \quad (27)$$

The division between "near" and "far" ions depends on φ. At first the 25 nearest shells were considered "near." However, it was found subsequently that $Q(r)$ converged sufficiently rapidly that it is necessary to consider only about half that number.

We started by using Pekar's wave function with the assumption that the free electron mass may be used for the effective mass. His equation leads to a value 20.3×10^{-4} e.s.u. for $V_0(0)$ while Eq. (25) gives 20.1×10^{-4} e.s.u. This implies that to the zeroth approximation both methods give the same results, as might have been expected. We must go to higher approximations to include the details of the crystal structure.

Higher Approximations

Mott and Littleton found when calculating $V(0)$ for a missing ion site that one may assume that an equation analogous to (22) holds for all but the nearest ions. It is not clear that this approximation is valid in the present case, because the electric charge is spread out over neighboring ions. Therefore, to be on the safe side, we assumed that (22) does not hold for the three sets of nearest ions, namely the (1, 0, 0), the (1, 1, 0) and the (1, 1, 1) sets. The cases in which these sets are successively included were referred to as the first, second and third approximations respectively. The displacements of these ions (which we shall call ξ to distinguish them from the δ's obtained by (22)) are calculated from the equations of equilibrium,

$$F_r+eE_i=0, \quad (28)$$

where F_r is the repulsive (Born-Mayer) force due to the neighboring six ions and E_i is the local field at the point of equilibrium. Here we ignore all effects of lattice vibrations. Strictly speaking, Eq. (28) gives the equilibrium position about which the ion is vibrating. The electric field is caused, to a good approximation, only by the lattice dipoles and the extra charge. The Madelung field is virtually zero near an ion site and is included in χ.

As stated, the trapped electron is not affected by the polarization of the ion core. The field E_i, to be used in Eq. (28), however, must include two effects; the field due to the displacements of the surrounding ions and the average core polar-

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[14] A. E. Ingham and J. E. Jones, Proc. Roy. Soc. **A107**, 636 (1927).

ization of the surrounding ions. The latter must be included because of the relatively long relaxation time of the ions. The average core polarization is simply given by the average field E_i times the ionic polarization. Hence we have the additional set of equations,

$$m_i = \alpha_i E_i. \tag{29}$$

Here α_i is the susceptibility of the ith ion, m_i is the average core dipole, and E_i is the time average field. The subscript i on the ξ's and the α's refers to the inner ions in accordance with the following scheme:

1 for the (1, 0, 0) ion,
2 for the (1, 1, 0) ion,
3 for the (1, 1, 1) ion.

In the case of the third approximation, Eqs. (28) and (29) give six conditions between six unknowns. From the solution of these equations we obtain information needed to determine $V(0)$. We shall now derive explicit expressions for the E's and the F_r's in terms of the other variables.

The E's are composed of three parts:

(a) *The Outer Dipoles.*—This term includes those dipoles whose strength is given by the continuum theory. Thus for the third approximation this includes all ions outside of (1, 0, 0), (1, 1, 0) and (1, 1, 1). To calculate their contribution to the field, we note that the dipoles must be oriented radial relative to the center of the trapped electron. From the geometry of the lattice it follows that the net field at a lattice site arising from a shell of ions is also radial. By "shell of ions" we mean all the ions given by the permutation of (x, y, z) when the x, y, and z have both a positive and a negative sign. For NaCl, the ion is of one type if the sum of x, y, and z is odd and is of another type if the sum is even. For our case, an odd sum represents a negative (Cl) ion site. The outward field at about $R-$ having coordinates (X, Y, Z) due to a radial dipole of strength d at a point $r-$ having coordinates (x, y, z), can be calculated from the standard expression for the field due to a dipole. We find

$$\begin{aligned} E(R, r) = (d/rR|\mathbf{r}-\mathbf{R}|^5)\{[(Xy-Yx)^2 \\ +(Xz-Zx)^2+(Yz-Zy)^2] \\ -2[(r^2-Xx-Yy-Zz) \\ \times(Xx+Yy+Zz-R^2)]\}. \end{aligned} \tag{30}$$

TABLE I. Comparison of the various approximations used.

Approximation	Potential $\times 10^4$ e.s.u. at (000)	$\xi_1 \times 10^3$	$\xi_2 \times 10^3$	$\xi_3 \times 10^3$
0	35.8			
1	56.7	26.5		
2	67.2	23.6	18.3	
3	70.6	23.4	17.4	14.1

The strength d of the dipole includes the effects due both to the displacement and to the core susceptibility. In view of our discussion in connection with the derivation of Eqs. (13) and (14) it would seem logical to define the average total (displacement plus ionic core) dipole induced at an odd (Cl$^-$) site as

$$(M_1 a^3 eQ(r)/a^2r^2)(1/4\pi)(1-1/\kappa), \tag{31a}$$

and that for an even (Na$^+$) site as

$$(M_2 a^3 eQ(r)/a^2r^2)(1/4\pi)(1-1/\kappa), \tag{31b}$$

where

$$\begin{aligned} M_1 &= (\alpha+\alpha_1)/(\alpha+\tfrac{1}{2}(\alpha_1+\alpha_2)), \\ M_2 &= (\alpha+\alpha_2)/(\alpha+\tfrac{1}{2}(\alpha_1+\alpha_2)). \end{aligned} \tag{31c}$$

Here the α_1 and α_2 are the core susceptibilities of the odd and even ions.

Using Eqs. (12), (30), and (31), we obtain for the field from an odd (Cl$^-$) ion shell

$$-5.346\times 10^4 Q(r) I_{ij}/r_j^2, \tag{32a}$$

and from an even (Na$^+$) shell

$$-2.612\times 10^4 Q(r) I_{ij}/r^2 j. \tag{32b}$$

The I's relate the field at site i to the dipoles in the jth shell. The evaluation of the I's requires lengthy calculations using (30). Mott and Littleton calculated the net effect (for $Q(r)=1$) due to the 23 nearest rings at some sites. We used only the 17 nearest rings, since a comparison with their value indicated that our other approximations give a much larger error. The individual values of the I's for the inner rings are given in Mott and Littleton.

(b) *The Inner Dipoles.*—We consider the effect of the ions in the "near" shells where (22) no longer holds. Here the displacements are given by ξ_i and the core susceptibility by m_i. Their contributions follow directly from Eq. (30) and are

$$-(e/a^2)\xi_j I_{ij}, \tag{33a}$$

and

$$-(m_j/a^3) I_{ij}. \tag{33b}$$

TABLE II. Summary of data for third approximation.

V (assumed) 10^4 e.s.u.	$\xi_1\times10^{+3}$	$\xi_2\times10^{+3}$	$\xi_3\times10^{+3}$	$m_1\times10^{+20}$ e.s.u.	$m_2\times10^{+20}$ e.s.u.	$m_3\times10^{+20}$ e.s.u.	$\beta\times10^{-8}$ cm^{-1}	V (cal.) 10^4 e.s.u.
70	23.5	17.4	14.1	17.8	0.72	10.6	0.3311	70.57
75	24.7	18.2	14.3	18.7	0.75	10.7	0.3405	72.89
80	25.8	18.8	14.4	19.4	0.77	10.8	0.3489	74.81

(c) *The Electron Charge.*—Superposed on the effects described in (a) and (b) are those of the field due to the electron. This is given to a satisfactory approximation by

$$eQ(r_i)/a^2(r_i\pm\xi_i)^2=(eQ(r_i)/a^2r_i^2)(1\mp2\xi_i/r_i),\quad(34)$$

where we adopt a sign convention in which outward displacements are positive for odd ions but negative for even ions. Combining (a), (b), and (c), we can calculate E_i for Eqs. (28) and (29).

We turn now to describe the method used to obtain F_r. This term can be obtained from (11) by calculating the potential of the inner ions and differentiating with respect to the ξ's, with due regard to the sign convention adopted. This gives us for F_r:

$$\begin{aligned}F_r(100)=(-A/\rho)\exp(-a/\rho)[\xi_1(2a/\rho-4)\\+\delta(2,0,0)a/\rho-2\sqrt{2}\xi_2],\quad(35\text{a})\end{aligned}$$

$$\begin{aligned}F_r(1,1,0)=(-A/\rho)\exp(-a/\rho)\\\times[\sqrt{2}\xi_1+(4-a/\rho)\xi_2\\+4/(6)^{\frac{1}{2}}\xi_3 2/(10)^{\frac{1}{2}}\\+(1-2a/\rho)\delta(1,2,0)],\quad(35\text{b})\end{aligned}$$

$$\begin{aligned}F_r(1,1,1)=(-A/\rho)\exp(-a/\rho)\\\times[-(6)^{\frac{1}{2}}\xi_2+(2a/\rho-4)\xi_3\\+\sqrt{2}(a/\rho-1)\delta(2,1,1)].\quad(35\text{c})\end{aligned}$$

A is evaluated by requiring that the net force at the position of equilibrium be zero. This consideration gives

$$(1.748)e^2/a^2=(6A/\rho)\exp(-a/\rho).\quad(36)$$

To obtain (35) we have expanded terms of the type $\exp\{(1/\rho)(a+\xi_i)\}$. *A priori*, one would expect the leading term to be of the type $(a/\rho)\xi_i\times\exp(-a/\rho)$ and the next term of the type $(a/\rho)^2\xi_i^2\exp(-a/\rho)$. The geometry of the lattice clearly shows, upon detailed consideration, that terms of the order of $\exp(-a/\rho)$ will not appear. When one carries through the expansion, however, one sees that the next term after $(a/\rho)\xi_i\times\exp(-a/\rho)$ is of the type $(a/\rho)^2\xi_i\delta_j\exp(-a/\rho)$. Since actual calculations show that the δ's are considerably smaller than the ξ's, the second term is small enough to be neglected in this approximation. The physical reason for the cancellation of terms quadratic in $a/\rho\xi_i$ is not obvious. It is associated with the lattice structure and the approximation used. Had higher approximations been necessary, the terms of the type $(a/\rho)^2\xi_i\xi_j$ would have come in, and they might well have introduced a larger error.

We have all the necessary information to be able to substitute the appropriate terms into Eqs. (28) and (29). In the third approximation we thus have six unknowns and six equations. Using standard methods,[15] we solved these to evaluate the ξ's and the m's. Finally, to obtain the potential at (0, 0, 0) we subtract from (25) the contributions of the three inner shells and add

$$\sum_{i=1,2,3} n_i e a\xi_i/a^2r_i^2,$$

where n_i is the number of particles in the ith shell.

We have thus developed a method to calculate $V(0)$ to the desired approximation once φ is known.

IV. THE WAVE FUNCTION

We now require the wave function for a spherically symmetric well given by

$$\begin{aligned}V(r)&=V(0)\quad\text{for}\quad r<r_0,\\V(r)&=c/r\quad\text{for}\quad r>r_0,\end{aligned}\quad(37)$$

where

$$c=(1/\kappa_0-1/\kappa)e.$$

Further, we define r_0 by the relation

$$c/r_0=V(0).\quad(37\text{a})$$

It would be possible to solve the wave equation directly for the potential (37). However, since our solution will be only approximate and a series of

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[15] R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (Cambridge University Press, New York, 1938), p. 125.

TABLE III. Summary of data for first approximation.

V (assumed) $\times 10^{-4}$ e.s.u.	$\xi_1 \times 10^{+3}$	$m_1 \times 10^{+20}$ e.s.u.	$\beta \times 10^{-8}$ cm^{-1}	V (cal.) $\times 10^{4}$ e.s.u.
40	16.1	13.9	0.2572	42.0
61.4	23.9	20.2	0.3138	52.9
70	26.5	22.3	0.3311	56.7

wave functions will be required for various trial $V(0)$, we decided to use the standard variational method.[16] We approximated φ by the simple, normalized, wave function $(\beta^{\frac{3}{2}}/\pi)\exp(-\beta r)$. We desire the best β for the potential (37).

The energy calculated by this method is the optical activation energy,[17] that is, the energy to excite the trapped electron into the conduction band without causing any other effect. The energy released by the relaxation of the displacement dipoles is not included. By the Frank-Condon principle, this is the energy required to excite the self-trapped electron optically. The energy is given by

$$E_0 = (\beta^2\hbar^2/2m) - eV(0) \times \{1-(1+\beta r_0)\exp(-2\beta r_0)\}. \quad (38a)$$

The first term gives the kinetic energy of the electron, while the second term gives the potential energy. β is determined in such a way that E_0 has an extreme value.

When a charge induces a displacement on the neighboring ions, there are two potential energy terms. One arises from the fact that the charge finds itself in a potential hole. This is given by the second term of Eq. (38a). A second potential arises from the work required to displace the neighboring charges. If the displacements are small, Hooke's law will hold approximately, and it follows that the second term is just half the first term. If the trapped electron escapes, due to thermal vibrations, the energy stored in the surrounding dipoles will be released. The thermal activation energy is thus E_0 plus half the potential energy in Eq. (38a) or is given by

$$E_t = (\beta^2\hbar^2/2m) - \tfrac{1}{2}eV(0) \times \{1-(1+\beta r_0)\exp(-2\beta r_0)\}. \quad (38b)$$

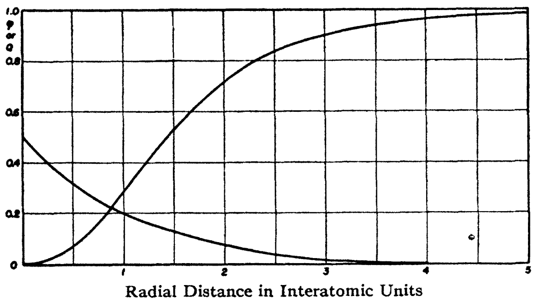

FIG. 1. Self-trapped electron's wave function "φ" (decreasing function) and charge distribution "Q" (increasing function) for NaCl.

For consideration of thermal equilibrium, we use (38b), but for the considerations of the optical properties we use (38a).

V. SUMMARY OF THE CALCULATIONS

On starting to make this calculation the first question one must answer is: To what order of approximation should one carry the calculation of $V(0)$? To answer this question, we calculated $V(0)$ by four approximations (starting with the zeroth), using the wave function corresponding to a well depth of 70×10^{-4} e.s.u. This value of $V(0)$ was selected because a preliminary calculation, starting with Pekar's wave function, indicated that that depth gives approximately a self-consistent solution. The values of a, κ_0, and κ used were 2.81×10^{-8} cm, 2.24, and 5.62, respectively. Table I gives the results. The value of V seems to converge rapidly after the second approximation. The sudden jump between the zeroth and first approximation is due, in part, to the use of Eqs. (15) and (16) in place of Eqs. (13) and (14). To be on the safe side, we carried the problem to the third. However, a great deal of labor would have been saved with little loss in accuracy had we used only the second approximation. The variations in the value of the ξ's which are larger than those in $V(0)$'s are of no importance for the problem at hand. Table II summarizes our calculations. This table contains three (assumed) values of $V(0)$, the calculated values of β, the ξ's, the m's, and the (computed) $V(0)$. From these values we obtained the self-consistent solution by plotting the difference between the two types of V's and the assumed V.

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[16] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 180.

[17] See N. F. Mott and R. W. Gurney, reference 5, p. 160.

The final values are:

$$\begin{aligned} V(0)&=71.2\times 10^{-4}\text{ e.s.u.},\\ \beta&=0.331\times 10^{8}\text{ cm}^{-1},\\ E_0&=-0.68\text{ ev}\\ E_t&=-0.13\text{ ev}. \end{aligned}$$

In Fig. 1 the final wave function φ and $Q(r)$ are plotted against r in interatomic units. Table III summarizes a similar calculation, but here only the ξ_1 and m_1 of the (1, 0, 0) ion are assumed unknown. In other words, this is the first approximation. The self-consistent values here are

$$\begin{aligned} V(0)&=44.7\times 10^{-4}\text{ e.s.u.},\\ \beta&=0.27\times 10^{8}\text{ cm}^{-1}, \qquad \text{(First approximation)}\\ E_0&=-0.56\text{ ev},\\ E_t&=-0.14\text{ ev}. \end{aligned}$$

It is difficult to estimate the relative errors introduced due to the various approximations made. One may check roughly the method used to find β from $V(0)$ by comparing our wave function with Pekar's, for the same depth of the potential hole. He also used the variational procedure. However, he had two parameters instead of one, his function being of the form

$$A(1+\beta r+\gamma r^2)\exp(-\beta r),$$

in which A is a normalizing factor. In his potential there is no abrupt cut-off like ours. For comparison we have plotted in Fig. 2 his $Q(r)$ against r for a free electron mass and the $Q(r)$ obtained by our method for $V(0)=20.3\times 10^{-4}$ e.s.u., the value of $V(0)$ he obtained. Pekar notes that γ does not affect his results appreciably, and concludes that his method is quite accurate. Further, Pekar's E_0 is 0.32 ev, while the value obtained by our approximation is 0.35 ev. There are, however, undoubtedly other errors in our method such as the use of Eq. (15) and (16) in place of (13) and (14), and one would hardly expect agreement with experimental results to higher accuracy than 25 percent. Actually, our results may be somewhat less accurate.

VI. CONCLUSION

We may now examine some of the conclusions that may be inferred from the calculated values of E_t and E_0. First let us examine the life-time of a self-trapped electron. Its magnitude is given approximately by

$$10^{-12}\exp(E_t/kT)\text{ sec.}$$

This yields a value of 10^{-10} sec. for room temperature ($kT=1/40$ ev). The self-trapped electron will have a very short lifetime even at the boiling point of oxygen (90°K), namely, about 10^{-5} sec. This means that if an electron were trapped it could not be observed unless one worked at very low temperatures.

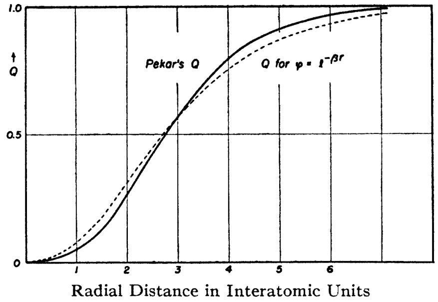

FIG. 2. Comparisons of $Q(r)$ obtained from Pekar's wave function, with that derived in this paper.

In an actual crystal, there are processes which compete with self-trapping, in particular the trapping of an electron in a vacant lattice site. We would like to know the differences between the energies involved in trapping an electron by the de Boer and Landau mechanisms. Let us consider the energy required to absorb a free sodium atom into the crystal, during which process the atom becomes an ion, and the extra electron gets trapped. This energy has been calculated for the de Boer process by Gurney and Mott[18] and is +0.23 ev. Let us now calculate this energy for a mechanism in which the positive ion is assumed to go into an interstitial position and the electron becomes self-trapped. We proceed as follows:

1. We ionize the free sodium atom; the necessary work is I, the ionization potential of sodium, namely 5.11 ev.
2. Next we place the electron into the conduction band; the energy E_c required to do this has been calculated by Mott[19] who obtains a value of -0.53 ev.

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[18] R. W. Gurney and N. F. Mott, Trans. Faraday Soc. **34**, 506 (1938); also ref. 12, p. 144.

[19] N. F. Mott, Trans. Faraday Soc. **34**, 500 (1938); also reference 13, p. 95.

3. The free sodium ion is placed in an interstitial site $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This process takes -1.71 ev.

4. Finally, we assume that the electron is trapped thermally, so that it gains 0.13 ev. Thus it takes $+2.74$ ev to form an F center by Landau's hypothesis, compared to 0.23 ev on the de Boer picture.

We may conclude that very few self-trapped electrons are formed during usual experimental procedures, and those trapped have a very short life. While some of the values used above and by Gurney and Mott may be questioned, there is little doubt that these calculations give values to an order of magnitude, and that the qualitative picture is correct.

One may wonder if self-trapping might be observed under reasonably static conditions in any crystal. In the zeroth approximation the quantity which determines the depth of the hole is primarily $(1/\kappa_0-1/\kappa)$. Further, in Pekar's treatment of this approximation the square of this is the only quantity which characterizes the crystal behavior provided it is assumed that the effective electron mass is about the same as the free value. Thus $(1/\kappa_0-1/\kappa)$ provides a rough measure of the relative ability of a crystal to trap an electron. We conclude that of the common ionic crystals LiF will have the largest energy for self-trapping, since $(1/\kappa_0-1/\kappa)$ is largest for it. The value for LiF is 0.41 compared to the value 0.27 for NaCl. If the energy parameters increase as the square of this quantity, we would expect E_0 to be about 1.6 ev and E_t about 0.3 ev. This second value means that the lifetime at the boiling point of oxygen is about 10^5 sec. Moreover the relatively large value of E_0 implies that Landau trapping could be observed in LiF with a relatively simple spectrograph if not visually. One would expect the nature of the absorption bands produced in LiF, when irradiated by x-ray, to be strongly temperature dependent in the neighborhood of 100°K. Of course, one would have to be careful to separate this effect from that caused by other trapping centers, which have their characteristic temperature dependence.

Little is known at present about the cross section for the process of self-trapping. Experimental studies of the capture of electrons by halogen ion vacancies in the formation of F centers, and of the capture of electrons by F centers in the formation of F' centers, show that the cross section for these processes is of the order of 10^{-15} cm^2. The experimental evidence concerning the formation of F centers also indicates that the initial trapping step which determines the magnitude of the trapping cross section rests on the transfer of energy from the electron to the lattice presumably by excitation of the polarization modes of vibration. This result strongly suggests that the cross section for self-trapping may also be of the order of 10^{-15} cm^2.

It should be pointed out that the electron need not be trapped about a sodium ion, although our calculations have been based on this premise. Undoubtedly there will be small variations in the trapping energy, depending upon the site which is chosen for the center of the trapping polarization. Since we have found that the trapped electron is distributed over a very large volume of the crystal, it seems reasonable to suppose that the trapping energy is relatively insensitive to the center chosen. This conclusion also suggests that the self-trapped electron may require only a small activation energy to move from one site to another. In other words, it is possible that at any but the very lowest temperatures the trapped electron may diffuse through the crystal with a velocity approaching sonic velocity. In this case, self-trapped electrons would find other trapping sites, such as halogen ion vacancies, in a time of the order of 10^{-8} sec. for normal densities of the latter.

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