ortho-positronium in superconducting lead[15] and if its three-quantum decay rate were the same in superconducting lead as in vacuum ($1/\lambda_3=1.4\times10^{-7}$ sec), then the *ortho*-positronium must have a mean life ($\tau\approx1/\lambda_2$) greater than 5×10^{-10} sec in order for us to observe an effect.

ACKNOWLEDGMENTS

It is a real pleasure to acknowledge the contributions of V. L. Telegdi who worked with us in conceiving and designing the experiment.

---

[15] In most substances which show a long-lifetime component, about 30% of the positrons are responsible for it. [See R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).]

PHYSICAL REVIEW VOLUME 103, NUMBER 3 AUGUST 1, 1956

Electron-Nuclear Wave Functions in Multiphonon Processes

Jordan J. Markham
Research Division, Zenith Radio Corporation, Chicago 39, Illinois

(Received December 27, 1955)

For most purposes, the wave functions of a crystal with an electron trapped at an impurity are approximated by the product of two functions, one involving the lattice coordinates and the other the position of the electron. The electronic function may be determined for the equilibrium position of the lattice (static approximation) or one may assume that the electronic wave function continuously adjusts itself to the instantaneous position of the lattice (adiabatic approximation). The author relates the wave functions to Hamiltonian operators which do not have some of the most common operational properties. A comparison of the two approximations is made using the variational principle. The static underestimates the kinetic energy and overestimates the potential energy, while the second does just the reverse. Although the formal treatment is quite general and includes all the effects for harmonic vibrations, the actual terms were evaluated for a simple model. The calculations show that for extremely shallow traps the static approximation may be slightly superior, while for deep traps the adiabatic approach should be used. For traps of depths less than 0.1 ev the methods are essentially equivalent; in any actual calculations, other approximations must be made and they are of greater importance than the slight difference between either of these approaches.

1. INTRODUCTION

A GREAT many papers have appeared concerning electronic transitions which involve more than one phonon. The problem resolves itself into three parts. First, one must know what perturbation causes the transition; this requires a detailed knowledge of the electron-nuclear wave functions used. It is at this phase that one distinguishes between multiphonon and single-phonon processes. Second, we need to know the number of vibrational modes which enter into the transition; this depends on the energy distributions of the electrons and phonons. Finally, one must sum up the various individual probabilities.

In recent years progress has been made in the third phase of the problem[1] by assuming the validity of certain electron-nuclear wave functions. The calculations of Kubo[1] and Vasileff[1] use the so-called Born-Oppenheimer, or adiabatic approximation, which is presumably based on a paper of Born and Oppenheimer.[2] A search of the literature revealed, however, that the exact approximation first appeared in 1940.[3] The word "exact" is of utmost importance since one must know (in principle at least) precisely what wave functions are being used to carry through a multiphonon calculation. On the other hand, O'Rourke,[1] Frenkel,[4] Moglich and Rompe[4]; and Goodman, Lawson, and Schiff[4] used a second approach, originally formulated by Born and Oppenheimer.[5] The most appropriate name for the second approximation seems to be "static."[6–8]

There seems to be some feeling that the adiabatic approximation is "exact" (see Lax), and certainly superior to the static. With the possible exception of the book of Born and Huang,[7] the author has found nothing in the

---

[1] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950); R. Kubo, Phys. Rev. **86**, 929 (1952); M. Lax, J. Chem. Phys. **20**, 1752 (1952); R. C. O'Rourke, Phys. Rev. **91**, 265 (1953); H. D. Vasileff, Phys. Rev. **96**, 603 (1954), **97**, 891 (1955). See also the work of S. I. Pekar Uspekhi Fiz. Nauk. **50**, 197 (1953) (English translation by M. D. Friedman of W. Concord, Massashusetts) and references therein.

[2] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[3] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 470.

[4] J. Frenkel, Phys. Rev. **37**, 17 and 1276 (1931); F. Moglich and R. W. Rompe, Z. Physik **115**, 707 (1940); and Goodman, Lawson, and Schiff, Phys. Rev. **71**, 191 (1947).

[5] Strictly speaking, one need not assume that O'Rourke used the static approximation. In the notation to be developed, one need only assume that $\langle\varphi_{n'}(R)|\mathbf{M}|\varphi_n(R)\rangle$ is not a function of the nuclear coordinates. **M** is the electric moment operator for the system. This is not quite as restrictive as the static approximation. The above assumption is referred to as the Condon approximation. As will become evident shortly, the static approximation always leads to Condon's; the adiabatic may also in very special cases.

[6] Other names have been used in place of static, namely "harmonic" by Born and Huang[7] and "Hartree" by Lax.[8] One should not in any way relate this problem with the usual many-electron ones, where another Hartree approximation appears (reference 3, p. 234). The term "adiabatic" can have more than one meaning; the one used here agrees with Kubo, Vasileff, and Huang and Rhys. It does not agree, however, with the one used by Born and Huang.

[7] M. Born and K. H. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), p. 166.

[8] M. Lax, *Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956).

literature to justify this feeling. Frenkel[9] in 1932 showed clearly that the adiabatic approach is only an alternate approximation which need not be superior.

One object of this paper is to place the approximations in juxtaposition, so as to focus attention on the two ways to handle the problems involving electrons and nuclear wave functions. Then a short analysis of the properties of the wave functions and the associated Hamiltonian operators is made. The treatment is then redeveloped for an impurity center; it shows in a general manner, why the equilibrium positions and the vibrational frequencies are affected by electronic transitions.[10,11] In the following sections, the variation principle is applied to show when the adiabatic approximation is superior. These calculations are general, although a simplified model is used to obtain numerical results. The author does not believe this to be more extreme than the oft-quoted calculations of Pelzer and Wigner.[12] Finally, attempts are made to estimate the order of magnitude of the shifts in the equilibrium positions and in the frequencies.

2. STATEMENT OF THE PROBLEM

In this section, we shall write down in juxtaposition the two types of solutions generally used in these problems. Next, some of the properties of the operators and eigenfunctions will be explored.

A. General Solution

In a solid, one is allowed to disregard the six external coordinates; this greatly simplifies the problem in comparison to the rotating molecule.[13] Further, the problem will be simplified by disregarding the spins. Hence, the complete Hamiltonian H, for the monatomic solid of N_0 atoms with nuclear mass M, is

$$H=T_e+T+V(R), \tag{2.1}$$

where T_e is the kinetic energy operator for the electrons, T is the kinetic energy operator for the nuclei, V is the total potential energy, and R stands for all the positions of the nuclei. The components of R are $X_\alpha(k)$ $(\alpha=1,2,3;k=1,2,\cdots N_0)$. Thus,

$$T=\frac{-\hbar^2}{2M}\sum_k \nabla_k^2=\frac{-\hbar^2}{2M}\sum_{\alpha,k}\frac{\partial^2}{\partial X_\alpha^2(k)}, \tag{2.1a}$$

$\hbar$ being Planck's constant over 2π. V depends on R and the position of the electrons. The dependence of the latter is not explicitly stated, for reasons which should become clear as we develop the paper.

In general, one cannot solve directly for the wave function Ψ associated with H. One may assume that the complete wave function is of the form

$$\Psi_N=\sum\nolimits_{n,v} a_{Nnv}\varphi_n\chi_{nv}. \tag{2.2}$$

Here, $\varphi_n\chi_{nv}$ is a solution of a modified Hamiltonian H_0, and H_1 is defined so that $(H_0+H_1)\varphi_n\chi_{nv}=H\varphi_n\chi_{nv}$. The a's are so determined that Ψ_N is an eigenfunction of (2.1). In practice v stands for a set of eigenfunctions related to the vibrational energy, ϵ_v, of the nuclei, while n stands for a set related to the electronic eigenvalues, ϵ_n. N is a quantum number associated with the eigenvalue E_N of the whole system. H_0 can be formulated an infinite number of ways leading to different ϵ_n, ϵ_v and a_{Nnv}. In principle, as long as the $\varphi_n\chi_{nv}$ form a complete set in the coordinate space of all the electrons and nuclei, any formulation will give correct Ψ's.

To define the approximations actually used it will be convenient to define two auxiliary operators: First,

$$h_e(R)=T_e+V(R). \tag{2.3}$$

We require the eigenvalues, $\epsilon_n(R)$ and eigenfunctions $\varphi_n(R)$, of h_e for a fixed value of the nuclear coordinates, R.

The second operator is

$$h_v(R_n)=T+\tfrac{1}{2}\sum_{\alpha,\beta,k,k'}\left[\frac{\partial^2\epsilon_n}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n}\times\Delta X_\alpha(k)\Delta X_\beta(k'). \tag{2.4}$$

R_n is the fixed value of the nuclear coordinates, where

$$\partial\epsilon_n/\partial X_\alpha(k)=0 \tag{2.4a}$$

for every α and k. Further, $\Delta X_\alpha(k)=X_\alpha(k)-X_\alpha{}^0(k)$. [$X_\alpha{}^0(k)$ is a component of R_n.]

To complete the notation to be used throughout this paper, we also define

$$\langle\varphi_{n'}|\mathbf{O}|\varphi_n\rangle=\int\varphi_{n'}{}^*\mathbf{O}\varphi_n dr, \tag{2.5}$$

where the integration is over all positions of the electrons, and

$$\{\chi_{n'v'}|\mathbf{O}|\chi_{nv}\}=\int\chi_{n'v'}{}^*\mathbf{O}\chi_{nv}dR. \tag{2.6}$$

$\mathbf{O}$ is any operator. It will be omitted when $\mathbf{O}=1$.

For the static approximation:

$$H_0(S)=h_e(R_n)+h_v(R_n), \tag{2.7a}$$

$$H_1(S)=V(R)-V(R_n)-\tfrac{1}{2}\sum_{\alpha,\beta,k,k'}\left[\frac{\partial^2\epsilon_n}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n}\times\Delta X_\alpha(k)\Delta X_\beta(k'). \tag{2.7b}$$

---

[9] J. Frenkel, Z. Physik U.S.S.R. **1**, 99 (1932).

[10] On occasion, these shifts are assumed to be "phenomenological" (O'Rourke)[1] or derived from specialized Hamiltonians which indicate that one type of shift is independent of the other.[11] This conclusion is not supported by our calculations.

[11] K. Huang, "Phenomenological equation of motion for simple ionic lattices," British Electrical and Allied Industries Research Assoc. Leatherhead Surrey, England, reference *L/T* 239, 1950 (unpublished).

[12] H. Pelzer and E. Wigner, Z. physik. Chem. **15B**, 445 (1932).

[13] Reference 7, p. 172.

The eigenfunction in this case is assumed to be in the form $\varphi_n(R_n)\chi_{nv}$. On the other hand, in the adiabatic approximation:

$$H_0(A)\varphi_n(R)\chi_{nv}=\chi_{nv}h_e(R)\varphi_n(R)+\varphi_n(R)T\chi_{nv}, \quad (2.8a)$$

$$H_1(A)\varphi_n\chi_{nv}=\frac{-\hbar^2}{2M}\Big[\sum_k 2\nabla_k\varphi_n \cdot\nabla_k\chi_{nv}+\chi_{nv}\nabla_k{}^2\varphi_n\Big]; \quad (2.8b)$$

i.e., this approximation assumes that for H_0, $\varphi_n(R)$ permutes with T. The corresponding eigenfunctions are $\varphi_n(R)\chi_{nv}$.

Terms in $(\Delta X)^3$ are neglected. An elegant method of arriving at (2.7) has been given many years ago by Born and Oppenheimer.[2] This treatment is reproduced in a simpler form by Born and Huang[7] who have also found a systematic way to obtain the adiabatic approximation. Their χ's in the adiabatic case, however, contain higher order anharmonic terms and therefore are not equivalent to (2.8a) and (2.8b).

To obtain the eigenvalues of (2.8a), we may proceed as follows:

$$\begin{aligned}H_0(A)\varphi_n\chi_{nv}&=\varphi_n(R)[\epsilon_n(R)+T]\chi_{nv}\\&=\varphi_n(R)[\epsilon_n(R_n)+h_v]\chi_{nv}\\&=[\epsilon_n(R_n)+\epsilon_{nv}]\varphi_n(R)\chi_{nv}, \quad (2.9)\end{aligned}$$

where (2.4) and (2.4a) have been used. The eigenvalues of (2.7) and (2.8) are identical for

$$H_0(S)\varphi_n(R_n)\chi_{nv}=[\epsilon_n(R_n)+\epsilon_{nv}]\varphi_n(R_n)\chi_{nv}. \quad (2.10)$$

B. Properties of the Hamiltonians

The method of splitting H into parts is based on physical intuition and the fact that the nuclear mass is much heavier than the electron mass. Mathematically, the splitting has an unfortunate aspect, since some of the nicest mathematical properties do not hold for the H_0's. $H_0(S)$ does not define an orthogonal set of functions while $H_0(A)$ and $H_1(A)$ do not lead to a Sturm-Lionville equation since, in general, they are not Hermitian. This in no way is a violation of some quantum mechanical principle because $H_0(A)$ is not associated to a real variable. Since the usual proof of the method of the variation of parameters assumes Hermitian operators, it does not apply to $H_0(A)$. What restriction this puts on the problem of finding φ and χ the author is not ready to state. We shall now derive some of the properties of these operators.

1. The static eigenfunctions $\varphi_n(R_n)\chi_{nv}$ do not form an orthogonal set.

$\varphi_{n'}(R_{n'})$ is not an eigenfunction of $h_e(R_n)$. $\varphi_{n'}(R_{n'})$, however, is a function of the coordinates of the electrons and can be expanded in terms of $\varphi_n(R_n)$; thus,

$$\varphi_{n'}(R_{n'})=\sum_i\langle\varphi_{n'}(R_{n'})\,|\,\varphi_i(R_n)\rangle\varphi_i(R_n). \quad (2.11)$$

Only in very special cases would one expect that $\langle\varphi_{n'}(R_{n'})\,|\,\varphi_n(R_n)\rangle=0$ for every $n'(n\neq n')$. Hence, in general the $\varphi_n(R_n)$'s do not form an orthogonal set.

2. The adiabatic eigenfunctions form an orthonormal set for

$$\begin{aligned}\{\langle\varphi_{n'}(R)\chi_{n'v'}\,|\,\varphi_n(R)\chi_{nv}\rangle\}&=\{\chi_{n'v'}\langle\varphi_{n'}(R)\,|\,\varphi_n(R)\rangle\chi_{nv}\}\\&=\{\chi_{n'v'}\,|\,\delta_{nn'}\,|\,\chi_{nv}\}=\delta_{nn'}\delta_{vv'}, \quad (2.12)\end{aligned}$$

where δ is the Kronecker delta.

3. $$\begin{aligned}\{\langle\varphi_{n'}(R)\chi_{n'v'}\,|\,H_1(A)\,|\,\varphi_n(R)\chi_{nv}\rangle\}\\=\{\langle\varphi_n{}^*(R)\chi_{nv}{}^*\,|\,H_1(A)\,|\,\varphi_{n'}{}^*(R)\chi_{n'v'}{}^*\rangle\}. \quad (2.13)\end{aligned}$$

This is not the same as stating that $H_1(A)$ is Hermitian, for we are here greatly restricting the functions on which $H_1(A)$ operates. Since T is Hermitian, in general (2.13) will hold, if $T-H_1(A)$ is Hermitian with respect to the eigenfunctions of $H_0(A)$. The proof is divided into two parts: When $n\neq n'$,

$$\begin{aligned}\{\langle\varphi_{n'}(R)\chi_{n'v'}\,|\,T-H_1(A)\,|\,\varphi_n(R)\chi_{nv}\rangle\}&=\{\langle\varphi_{n'}(R)\chi_{n'v}\,|\,\varphi_n(R)h_v(R_n)\chi_{nv}\rangle\}\\&=\epsilon_{nv}\{\langle\varphi_{n'}(R)\chi_{n'v'}\,|\,\varphi_n(R)\chi_{nv}\rangle\}=0, \quad (2.14)\end{aligned}$$

where we have used the fact that

$$\{\chi_{n'v'}\langle\varphi_{n'}(R)\,|\,f(R)\,|\,\varphi_n(R)\rangle\chi_{nv}\}=0$$

for $n\neq n'$. f is not a function of the electronic coordinates. When $n=n'$,

$$\begin{aligned}\{\langle\varphi_n(R)\chi_{nv'}\,|\,\varphi_n(R)T\chi_{nv}\rangle\}\\-\{\langle\varphi_n{}^*(R)\chi_{nv}{}^*\,|\,\varphi_n{}^*(R)T\chi_{nv'}{}^*\rangle\}\\=(\epsilon_{nv}-\epsilon_{nv'})\{\chi_{nv'}\,|\,\chi_{nv}\}=0. \quad (2.15)\end{aligned}$$

We have added and subtracted $\{\langle\varphi_n(R)\chi_{nv'}\,|\,\epsilon_n(R)-\epsilon_n(R_n)\,|\,\varphi_n(R)\chi_{nv}\rangle\}$ to go from the first to second step.

This property assures one that laws of detail balance will hold for both approximations. The probability of emitting n phonons during a downward electron jump equals the probability of absorbing n phonons during an upward jump. Of course, this statement does not include effects due to the Boltzmann temperature factor.

4. It can be shown that[14]

$$\left[\frac{\partial\epsilon_n}{\partial X_\alpha(k)}\right]_{R_n}=\left\langle\varphi_n(R_n)\,\middle|\left[\frac{\partial V}{\partial X_\alpha(k)}\right]_{R_n}\middle|\,\varphi_n(R_n)\right\rangle. \quad (2.16)$$

C. Impurity Center

The foregoing calculations will now be applied to an impurity center. Consider the case where we have one electron trapped at an imperfection. Here, T_e consists of one term while V can be split into two parts. The first part, V_1, consists of the potential energy between the

---

[14] See reference 7, p. 189; also R. P. Feynman, Phys. Rev. **56**, 340 (1939).

atoms.[15] For a simple ionic crystal this part of V includes the Coulomb and the repulsive (Born-Mayer) terms as well as the higher order terms, such as the Van der Waal forces. In a pure homopolar crystal, such as diamond or germanium, it will be composed of the potential which is related to the position of the atoms. V_2 includes the part which is related to the position of the electron. When an electron is very near an atom, it is no longer correct to average over the position of the bound electrons; these corrections, however, will be neglected.

We may thus rewrite (2.1) in the form:

$$H=(-\hbar^2/2m)\nabla^2+T+V_1(R)+V_2(R,r), \quad (2.17)$$

where r is the position of the electron while here R is related to the atoms.

The static approximation is obtained as follows:

1. φ_n is a solution of the equation

$$[(-\hbar^2/2m)\nabla^2+V_2(R_n,r)-\epsilon_n(R_n)]\varphi_n(R_n)=0. \quad (2.18)$$

2. R_n is determined from the condition

$$\left\{\frac{\partial}{\partial X_\alpha(k)}[\epsilon_n(R)+V_1(R)]\right\}_{R_n}=0. \quad (2.19)$$

3. The nuclear motion (in this case ionic or atomic) is governed by the equation

$$\left\{T+\tfrac{1}{2}\sum_{\alpha,\beta,k,k'}\left[\frac{\partial^2}{\partial X_\alpha(k)\partial X_\beta(k')}(\epsilon_n+V_1)\right]_{R_n}\Delta X_\alpha(k)\Delta X_\beta(k')-\epsilon_{nv}\right\}\chi_{nv}=0. \quad (2.20)$$

The appearance of ϵ_n in (2.19) and (2.20) is of considerable importance. ϵ_n affects the equilibrium position through (2.19), and the atomic frequency through (2.20). In general, there is no theoretical justification for considering these effects separately, although cases may occur where one type is more important than the other. This separation, however, occurs in several of the published treatments.

The adiabatic approximation is obtained from (2.18) and (2.20) except that φ_n is evaluated at R, not R_n, i.e., the wave function is $\varphi_n(R)\chi_{nv}$.

3. EIGENVALUE SPACE—CRITERION FOR BEST APPROXIMATION

For illustrative purposes we consider the hydrogen atom where for simplicity the eigenstates will be defined only by n and l. We may describe any state by a "distribution" in quantum number space—that is, n and l are plotted along the x and y axis and $a_{Nnl}(n,l)$ of Eq. (2.2) along the z axis. If only one a_{Nnl} is different from zero, Ψ would be an eigenstate of H_0 as well as H. The above idea may be expanded by imagining a space where all the v's and n's are coordinates. The eigenfunctions Ψ_N are distributions. As long as the φ's and χ's form a complete set, any selection is permissible; and one may go from one approximation to another by a transformation from one eigenvalue coordinate system to another.

Any actual state in the solid will be represented as a "wave packet" in the above eigenvalue space. If the φ's and χ's were selected so that $H_1=0$, the value of the a's would be independent of time. We are assuming, as is done in Eq. (2.1), that the system does not interact with its environment. Unfortunately, when the χ's are pure harmonic functions and the φ's pure electronic functions, $H_1\neq 0$. Then a_{Nnv} varies with time, indicating that some electronic energy is transformed into vibrational energy, or vice versa. For many problems, mathematical simplicity requires one to assume that an initial a_{Nnv} equals one, and since the $\varphi\chi$'s are normalized, all the other a's are zero. Further, from the work of Born and Fock,[16] one may assume that the time dependent perturbation theory can be used only when the rates of change are slow.

Since, at present, no way is known to fulfill this requirement, one may make the assumption that the better φ's and χ's are selected, the more closely will Ψ_N be represented by a single product, and the smaller will H_1 be. Hence, the variational principle suggests that the choice between two approximations can be made by calculating,

$$\{\langle\varphi_n\chi_{nv}|H|\varphi_n\chi_{nv}\rangle\};$$

the more negative being superior. Unfortunately, this criterion only states which of two is superior. It does not justify the use of the perturbation method nor the use of a single product. In this paper we shall neglect these last important points.

Born and Huang arrived at these approximations by a method which suggests that the adiabatic is always superior if nonharmonic terms are included. This occurs because the adiabatic approximation includes additional terms in their expansion. The author feels that the criterion suggested is superior than simply including additional terms without a careful study of the convergence.

One may present a physical argument to show that the adiabatic approximation is not necessarily superior. $\varphi_n(R)$ at all times gives the minimum value of ϵ_n; to achieve this, however, the electron has to acquire a

---

[15] The word "atom" will include the ionized state as well as the neutral state. The splitting of the potential is not a necessary step in the derivation. In a subsequent paper, the author will start with Eq. (2.1) and by using the technique of Born and Oppenheimer arrive at (2.17).

[16] M. Born and V. Fock, Z. Physik **51**, 165 (1928). See also P. Guttinger, Z. Physik **73**, 169 (1931); R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, Oxford, 1938), p. 395 ff., or L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 207 ff.

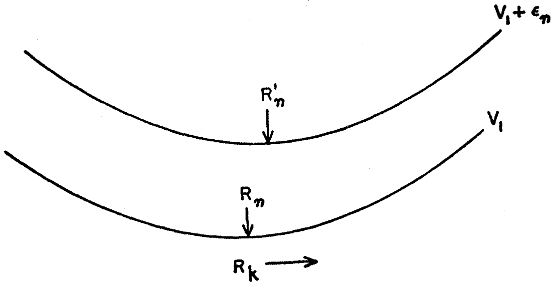

FIG. 1. Plot of V_1 and $V_1+\epsilon_n$ against X_k. Note the shift in the minimum.

slightly additional kinetic energy of readjustment. In the static approach the electron does not adjust itself to the position of the nuclei, hence acquires additional potential energy. The question as to what is larger depends on the depth of the potential well and the amplitude of the vibrations, which are determined primarily by V_1. We shall make detailed calculations on a simple model in Sec. 5.

4. COMPARISON OF THE TWO APPROXIMATIONS

In this section, we shall calculate the integral $\{\langle\varphi\chi|H|\varphi\chi\rangle\}$ for both approximations, using the imperfection model. The criterion suggested in 3 can then be applied.

A. Static Approximation

Using (2.17) (but denoting the kinetic energy of the electron by T_e and omitting the argument R_n of φ) and the eigenfunction associated with static approximation, we obtain

$$\begin{aligned} H_s&=\{\langle\varphi_n\chi_{nv}|H|\varphi_n\chi_{nv}\rangle\} \\ &=\int\int\varphi_n{}^*\chi_{nv}{}^*[T_e+T+V_1+V_2(R,r)] \\ &\qquad\times\varphi_n\chi_{nv}drdR. \end{aligned}\tag{4.1}$$

Now adding and subtracting

$$\frac{1}{2}\sum_{\alpha,\beta,k,k'}\left[\frac{\partial^2(\epsilon_n+V_1)}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n}\Delta X_\alpha(k)\Delta X_\beta(k')$$

to the operator, it follows that:

$$\begin{aligned} H_s=&\{\chi_{nv}\langle\varphi_n|T_e+V_1(R_n)+V_2(R_n)|\varphi_n\rangle\chi_{nv}\} \\ &+\langle\varphi_n\{\chi_{nv}|h_v|\chi_{nv}\}\varphi_n\rangle \\ &+\left\langle\varphi_n\left\{\chi_{nv}\middle|\Delta V_1+\Delta V_2-\frac{1}{2}\sum_{\alpha,\beta,k,k'}\left[\frac{\partial^2(\epsilon_n+V_1)}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n}\right.\right. \\ &\qquad\left.\left.\times\Delta X_\alpha(k)\Delta X_\beta(k')\middle|\chi_{nv}\right\}\varphi_n\right\rangle, \end{aligned}\tag{4.2}$$

where

$$\Delta V_i=V_i(R)-V_i(R_n).\tag{4.3}$$

In view of (2.19), the last term of (4.2) can be written as:

$$\int\varphi_n{}^2\chi_{nv}{}^2\Delta V_2dRdr-\int\chi_{nv}{}^2[\Delta\epsilon_n+\Delta V_1-\Delta V_1]dR.\tag{4.4}$$

Using the properties of the Hermite function, i.e.,

$$\{\chi_{nv}|\Delta X_\alpha(k)|\chi_{nv}\}=0,\tag{4.5}$$

we may write expression (4.4) in terms of two factors, namely:

$$\begin{aligned} S_1=\frac{1}{2}\sum_{\alpha,\beta,k,k'}&\left[\frac{\partial^2\langle\varphi_n(R_n)|V_2(R)|\varphi_n(R_n)\rangle}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n} \\ &\times\{\chi_{nv}|\Delta X_\alpha(k)\Delta X_\beta(k')|\chi_{nv}\} \end{aligned}\tag{4.6}$$

and

$$\begin{aligned} S_2=\frac{1}{2}\sum_{\alpha,\beta,k,k'}&\left[\frac{\partial^2(\epsilon_n+V_1)}{\partial X_\alpha(k)\partial X_\beta(k')}-\frac{\partial^2V_1}{\partial X_\alpha(k)\partial X_\beta(k')}\right]_{R_n} \\ &\times\{\chi_{nv}|\Delta X_\alpha(k)\Delta X_\beta(k')|\chi_{nv}\}. \end{aligned}\tag{4.7}$$

First, let us consider the meaning of S_2. We consider an Einstein model of a solid and pick one term in the sum; namely,

$$\begin{aligned} s_2=\frac{1}{2}&\left[\left(\frac{\partial^2(\epsilon_n+V_1)}{\partial X_\alpha{}^2(k)}\right)_{R_n}-\left(\frac{\partial^2V_1}{\partial X_\alpha{}^2(k)}\right)_{R_n}\right] \\ &\times\{\chi_{nv}|\Delta X_\alpha{}^2(k)|\chi_{nv}\}. \end{aligned}\tag{4.8}$$

The first part is just the average potential energy of the ion along $X_\alpha(k)$, for $\partial^2(\epsilon_n+V_1)/\partial X_\alpha{}^2(k)$ equals $4\pi^2M\nu_n{}^2$. Since the average square of the displacement is $\frac{1}{2}(2v+1)/\gamma$ (where $\gamma=2\pi M\nu_n/\hbar$),[17] the first term of (4.8) equals $\frac{1}{4}(2v+1)h\nu_n$. To evaluate the second part of S_2, we refer to Fig. 1, where ϵ_n+V_1 and V_1 are plotted against $X_\alpha(k)$. It follows that

$$\partial^2V_1/\partial X_\alpha{}^2(k)=4\pi^2M\nu^2,\tag{4.9}$$

where ν is the frequency when the imperfection is ionized. Actually, in (4.8), $\partial^2V_1/\partial X_\alpha{}^2(k)$ is evaluated at R_n determined by (2.19), not from $\partial V_1/\partial X_\alpha(k)=0$. Since this shift is very small, it will be disregarded. Hence, the second term of (4.8) is $\frac{1}{4}(2v+1)h\nu^2/\nu_n$ and, to a good approximation,

$$s_2=\frac{1}{2}(2v+1)h\nu\delta,\tag{4.10}$$

where

$$\delta=(\nu_n-\nu)/\nu.\tag{4.11}$$

Above the Debye temperature, the average value of this expression becomes

$$s_2=(\tfrac{1}{2}h\nu+kT)\delta,\tag{4.12}$$

---

[17] This statement can be checked by referring to the development by H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), pp. 122 and 342. In the notation of that book, Eq. (11-41), $\{\chi_{nv}|\Delta X_\alpha{}^2(k)|\chi_{nv}\}=\int\Psi^2(x)X^2dx=\frac{1}{2}(2v+1)/\gamma$. We have replaced their β by γ.

where T is the temperature and k in this equation is Boltzmann's constant.

On the other hand, S_1 contains the additional potential energy which arises because $\varphi_n(R_n)$ does not follow the motion of the nuclei.

Substituting (2.18), (2.20), (4.6), and (4.7) into (4.2),

$$H_e=\epsilon_n(R_n)+V_1(R_n)+\epsilon_v+S_1-S_2. \tag{4.13}$$

Now consider the adiabatic approximation. Here

$$\begin{aligned}H_a&=\{\langle\varphi_n\chi_{nv}|T_e+T+V_1(R)+V_2(R)|\varphi_n\chi_{nv}\rangle\}\\&=\{\chi_{nv}|\epsilon_n(R)+V_1(R)|\chi_{nv}\}+\{\chi_{nv}|T|\chi_{nv}\}\\&\quad\frac{-\hbar^2}{2M}\sum_k\int\int\varphi_n{}^*(R)\chi_{nv}{}^*(R)\\&\quad\times[2\nabla_k\varphi_n\cdot\nabla_k\chi_{nv}+\chi_{nv}\nabla_k{}^2\varphi_n]drdR.\end{aligned} \tag{4.14}$$

Further,

$$\begin{aligned}H_a=\epsilon_n(R_n)+V_1(R_n)+\int\chi_{nv}{}^*\Bigg[T+\tfrac{1}{2}\sum_{\alpha,\beta,k,k'}&\\\times\left(\frac{\partial^2(\epsilon_n+V_1)}{\partial X_\alpha(k)\partial X_\beta(k')}\right)_{R_n}\Delta X_\alpha(k)\Delta X_\beta(k')\Bigg]\chi_{nv}dR&\\-\frac{\hbar^2}{2M}\sum_k\int\chi_{nv}{}^2\left[\int\varphi_n{}^*\nabla_k{}^2\varphi_ndr\right]dR&\\-\frac{\hbar^2}{M}\sum_k\int\chi_{nv}{}^*\nabla_k\chi_{nv}\cdot\left[\int\varphi_n{}^*\nabla_k\varphi_ndr\right]dR.&\end{aligned} \tag{4.15}$$

If φ_n is real and normalized, $\int\varphi_n{}^*\nabla_k\varphi_ndr=0$; hence, the last term in (4.15) drops out. Finally, one obtains the desired expression,

$$H=\epsilon_n(R_n)+V_1(R_n)+\epsilon_v+D, \tag{4.16}$$

where

$$D=\int\left[\chi_{nv}{}^2\int\varphi_n{}^*T\varphi_ndr\right]dR. \tag{4.17}$$

Equations (4.13) and (4.16) are exact for harmonic vibrations, so one needs only to evaluate D and the S's, to use the suggested criterion. This will be done in the next section for a very simple model.

5. SIMPLIFIED MODEL OF AN IMPURITY CENTER

A. Evaluation of the S and D

We shall use a "hard hydrogenic impurity" to evaluate the S and D. This crude model has been used on several previous occasions. Indeed, Pelzer and Wigner[12] based their often-referred-to calculations on it. Of course more elaborate calculations would be desirable.

TABLE I. Values of S_1 for various v's.

v	$\langle\Delta Z^2\rangle_{\text{Av}}$	$\langle\Delta Z^2\rangle_{\text{Av}}^{\frac{1}{2}}A$	S_1 (ev)
0	$1/2\gamma$	0.058	$0.22q^4$
1	$3/2\gamma$	0.10	$0.66q^4$
2	$5/2\gamma$	0.13	$1.1q^4$

TABLE II. Values of S_1 for various binding energies.

ϵ_n (ev)	q	S_1 ($v=0$)	S_1 ($v=1$)	S_1 ($v=2$)
13.6	1	0.22	0.66	1.1
1.36	0.316	0.0022	0.0066	0.011
0.136	0.1	0.000022	0.000066	0.00011

We assume that the impurity is a foreign nucleus whose effective charge is qe (q will be varied so as to change the binding energy of the center) and whose mass is 30 M_p (M_p is the proton mass). Further, the impurity is assumed to vibrate along the Z axis about a rest position at $Z=0$. The rest positions of the surrounding ions are determined from (2.19). They appear implicitly in the value of q.

Consider first the static approximation. The normalized wave function of an electron in the ground state is

$$\varphi_1(R_n,r)=\frac{q^{\frac{3}{2}}}{(\pi a_0{}^3)^{\frac{1}{2}}}\exp\left\{-\frac{q}{a_0}r\right\}, \tag{5.1}$$

where $a=\hbar^2/me^2$, the Bohr radius, and r is measured from R_n. Substituting into (4.6)

$$S_1=\tfrac{1}{2}\{\chi_{nv}|(\Delta Z)^2|\chi_{nv}\}\times\left[\frac{\partial^2}{\partial Z^2}\int\varphi_1{}^2(r)\frac{-e^2q}{[x^2+y^2+(z-Z)^2]^{\frac{1}{2}}}d\tau_r\right], \tag{5.2}$$

where $d\tau_r$ is an element of volume in r space. Substituting z_1 for $z-Z$, we obtain

$$\begin{aligned}S_1&=-\tfrac{1}{2}\langle\Delta Z^2\rangle_{\text{Av}}qe^2\frac{q^3}{\pi a_0{}^3}\Bigg[\frac{\partial^2}{\partial Z^2}\int\int\frac{1}{r}\\&\quad\times\exp\left\{\frac{-2q}{a_0}[x^2+y^2+(z_1+Z)^2]^{\frac{1}{2}}\right\}2\pi r^2\sin\theta d\theta dr\Bigg]_{Z=0}\\&=-\frac{2}{3}\frac{e^2q^4}{a_0{}^3}\langle\Delta Z^2\rangle_{\text{Av}}\\&=65q^4\langle\Delta Z^2\rangle_{\text{Av}}.\end{aligned} \tag{5.3}$$

In the final expression, S_1 is in ev, while ΔZ is in angstroms.

One may obtain the results given in Table I for S_1 by using an average square displacement. For our model, $\nu_n=5\times10^{12}$ sec^{-1} and $\gamma=148$ A^{-2}. The binding energy of the center is given by $\epsilon_n=13.6q^2$ ev. Hence, the relation between S_1 and ϵ_n is as shown in Table II.

The author believes that one is justified in setting $S_2=0$ for the reason that the s's of Eq. (4.8) are small and of both signs. The wave function (5.1) is too crude an approximation to show this. We shall shortly return to this problem in an attempt to justify this statement. Hence, S_1 of Table II gives the difference between H_s and $\epsilon_n(R_n)+\epsilon_v+V_1(R_n)$.

We now turn to the adiabatic approximation. To evaluate D of Eq. (4.17), Eq. (5.1) is replaced by

$$\varphi_1=\frac{q^{\frac{3}{2}}}{(\pi a_0^3)^{\frac{1}{2}}}\exp\left\{\frac{-q}{a_0}[x^2+y^2+(z-Z)^2]\right\}. \quad (5.4)$$

It continuously adjusts itself to the position of the ion. Substituting into (4.17):

$$D=\int\chi_{nv}{}^2dZ\left[\frac{-\hbar^2q^3}{2M\pi a_0^3}\int\exp\left\{\frac{-q}{a_0}[x^2+y^2+(z-Z)^2]^{\frac{1}{2}}\right\}\right.$$
$$\left.\times\frac{\partial^2}{\partial Z^2}\exp\left\{\frac{-q}{a_0}[x^2+y^2+(z-Z)^2]^{\frac{1}{2}}\right\}. \quad (5.5)$$

By the proper selection of $d\tau_r$ one may evaluate the expression by elementary means, and one obtains

$$D=\tfrac{1}{6}(e^2/a_0)(m/M)q^2=8.3\times10^{-5}q^2 \text{ ev}. \quad (5.6)$$

It may seem a little surprising that D is independent of v, the quantum state of the vibration energy. This seems to arise because we are using a hard hydrogenic impurity, and thus $\langle\varphi_n(R)|\nabla_k{}^2|\varphi(R)\rangle$ is independent of R.

In Fig. 2, we have plotted D and S_1 against q or ϵ_n. We shall discuss the curves in the conclusion of the paper.

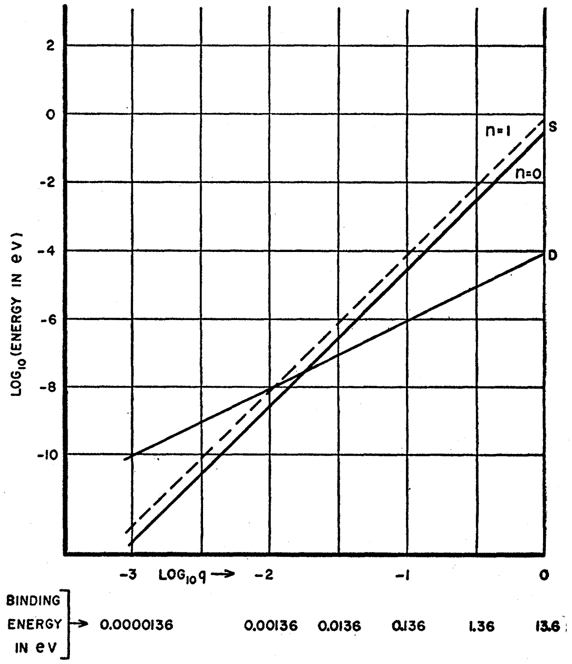

FIG. 2. Plot of $\log_{10}S_1$ and $\log_{10}D$ against $\log q$.

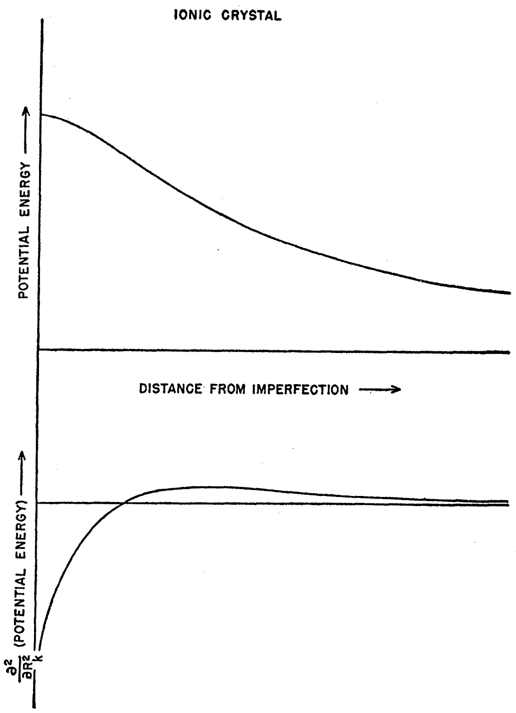

FIG. 3. Plot of $\langle\varphi_1|V_3|\varphi_1\rangle$ and $(\partial^2/\partial R^2{}_k)\langle\varphi_1|V_3|\varphi_1\rangle$ against R_k for an ionic crystal. The lower curve indicates that δ changes signs for small q's.

B. Equilibrium Position and Frequency Shifts for Ionic Crystals

An attempt will now be made to estimate the shifts in the equilibrium positions and in the frequency caused by the trapping of an electron at an imperfection. The calculations will be limited to ionic crystals.

Consider a negative ion located at a distance R_k from the center. It is convenient to subdivide V_2 further into V_3, the potential caused by this ion, and V_4, the potential resulting from all the other ions. Using (2.16), we may write

$$\frac{\partial}{\partial R_k}(\epsilon_n+V_1)=\frac{\partial V_1}{\partial R_k}+\left\langle\varphi_1\left|\frac{\partial V_3}{\partial R_k}\right|\varphi_1\right\rangle$$
$$+\left\langle\varphi_1\left|\frac{\partial V_4}{\partial R_k}\right|\varphi_1\right\rangle. \quad (5.7)$$

Since only radial displacements are going to be considered, $X_\alpha(k)$ is replaced by R_k. The last term is zero, since V_4 is independent of R_k. The first term should be evaluated when the surrounding ions are at their equilibrium positions; hence, it depends on φ_n and varies with the state of the electron. To obtain an order of magnitude value, we shall ignore this variation. If the dependence of φ on R_k is also neglected, we obtain the following relation for the equilibrium position of the

kth ion:

$$\frac{\partial}{\partial R_k}\langle\varphi_1|V_3|\varphi_1\rangle=-\left(\frac{\partial V_1}{\partial R}\right)_{R_k}. \tag{5.8}$$

The left-hand term is evaluated at the rest position in the trapped state.

Equation (5.1) reduces the evaluation of $\langle\varphi_n|V_3|\varphi_n\rangle$ to an electrostatic problem of calculating the potential at a point in a nonuniformly charged sphere. The calculations give

$$\langle\varphi_1|V_3|\varphi_1\rangle=(qe^2/a_0)f(qR/a_0) \tag{5.9}$$

for our model, where

$$f(\rho)=\frac{1}{\rho}[1-(1+\rho)e^{-2\rho}]. \tag{5.9a}$$

Using a very simple Einstein ion model, where one of the ion's vibrational modes is radial, we obtain

$$V_1=\tfrac{1}{2}M\omega^2(\Delta R_k)^2+\text{const}. \tag{5.10}$$

ΔR_k is the radial displacement from the equilibrium position for the ionized state. It follows from (5.8) that the shift in the equilibrium position, r_k, is

$$r_k=\frac{-q^2}{M\omega^2}\frac{e^2}{a_0^2}\frac{\partial f}{\partial\rho}=-16.7q^2\frac{\partial f}{\partial\rho}, \tag{5.11}$$

in angstroms. The value of $f(\rho)$ does not depend critically on very small displacements; hence, it can be evaluated at the equilibrium position of either the trapped or ionized states.

Next, we would like to evaluate δ of Eq. (4.11). From Eq. (2.20):

$$4\pi^2\nu^2M=\frac{\partial^2V_1}{\partial R_k^2} \tag{5.12}$$

and

$$4\pi^2\nu_1^2M=\frac{\partial^2}{\partial R_k^2}(V_1+\epsilon_n). \tag{5.13}$$

Now $\partial^2\epsilon_n/\partial R_k^2$ is composed of two effects. One arises because the kth ions move relative to the center, while the second occurs because the electron wave function changes with changes in R_k. Accurate estimates of $\partial^2\epsilon_1/\partial R_k^2$ thus require detailed calculations. As a crude estimate, we shall set

$$\frac{\partial^2\epsilon_n}{\partial R_k^2}=\frac{\partial^2}{\partial R_k^2}\langle\varphi_1|V_3|\varphi_1\rangle, \tag{5.14}$$

TABLE III. Values of δ for ions surrounding a center.

Ion	No. of ions	δ	$\Sigma\,\delta$
100	6	−0.068	−0.410
110	12	+0.047	+0.560
111	8	−0.032	−0.257
200	6	+0.023	+0.139

and make no allowances for changes of φ_1 with R. Hence,

$$4\pi^2M[\nu^2(1+\delta)^2-\nu^2]=\frac{\partial^2}{\partial R_k^2}\langle\varphi_1|V_3|\varphi_1\rangle, \tag{5.15}$$

or for small δ,

$$\delta=\frac{1}{8\pi^2\nu^2M}\frac{\partial^2}{\partial R_k^2}\langle\varphi_1|V_3|\varphi_1\rangle$$
$$=\frac{e^2}{8\pi^2\nu^2Ma_0^3}q^3\frac{\partial^2f}{\partial\rho^2}=15.8q^3\frac{\partial^2f}{\partial\rho^2}. \tag{5.16}$$

In Fig. 3, we have plotted $\langle\varphi_1|V_3|\varphi_1\rangle$ and $(\partial^2/\partial R_k^2)\times\langle\varphi_1|V_3|\varphi_1\rangle$ against R_k for a negative ion. Equation (5.16) and Fig. 3 indicate that for large q's, δ is always positive but may have either sign for smaller q's and R's. Figure 4 gives δ as a function of q for several values of R_k.

Returning to Eq. (4.12) and assuming that only the radial modes vary, the following equation is obtained for S_2:

$$S_2=(\tfrac{1}{2}h\nu+kT)\textstyle\sum_k\delta_k, \tag{5.17}$$

where k is summed over all the ions. In Table III, we give δ and $\sum\delta$ as a function of R_k for $q=0.316$.

Equation (5.16) applies to a negative-ion and a trapped electron. The table assumes that an electron is trapped at a negative-ion vacancy (F-center); hence, the ions in the sites 100 are positive. This is the reason for the negative sign. The last column is the product of the number of ions times the δ's. The sum of all the δ's shown is $+0.032$. If we include all the 280 positive and negative ions within a radius of $\sqrt{(17)}$, the sum is

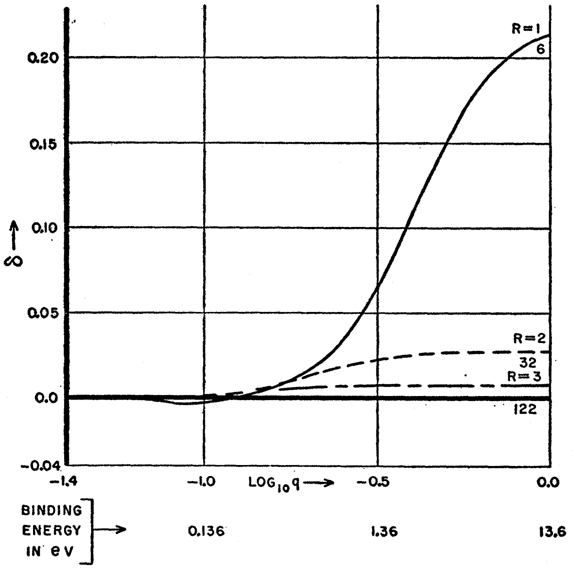

FIG. 4. Plots of frequency shift against binding energy for various R_k. The curve marked $R=1$ is for the nearest neighbor. The curve marked $R=2$ is for the 200 ion; there are 32 ions within this distance. For simplicity δ has been assumed to be positive for large binding regardless of the sign of the ion.

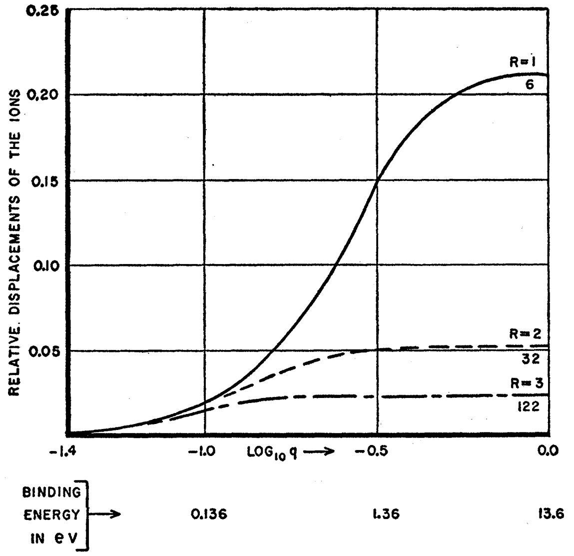

FIG. 5. Plots of displacements of ions during trapping against binding energy for various R_k. The notation and sign convention is the same as in Fig. 4. The relative displacement is the displacement in distances of nearest neighbors which was assumed to be 2.8 A.

-0.086. For a NaCl lattice, the number of positive ions within the radius happens to equal the number of negative ions.[18] The calculations seem to indicate that the sum over an equal number of positive and negative ions is about ± 0.05.

The sums would have the opposite sign if the electron were attached to a divalent ion at a positive-ion site. This gives a value of ± 0.001 ev for S_2, which is smaller than S_1 for the same value of q. We have set $\frac{1}{2}h\nu + kT = 0.025$ ev.

For $q=0.1$, the sum over the same set of ions is ± 0.013, giving a value of ± 0.0003 ev. If one neglects kT in (5.16) (low temperature) and sets $\frac{1}{2}h\nu = 0.01$, the value is 0.00013 ev, which is larger than the corresponding S_1 even for $n=2$. This seems to reflect the oversimplified method used to obtain the results. The contributions of the nearer ions to the sum of δ is most important and they depend on the second derivative of the electronic distribution. Thus, changes in φ_n will greatly effect δ and S_2. We also note that a term was omitted in order to obtain Eq. (5.14). The author suspects that correct calculations will always give $H_s > \epsilon_n + \epsilon_v$, and that S_1 will always be the leading term.

These incomplete arguments are the justification for omitting S_2 and for relying on Fig. 2, which most probably indicates a trend, although its details are not to be taken seriously.

In Fig. 5 we have plotted r_k against q for several values of R_k. The values seem to be larger by a factor of about two when compared with similar calculations made by Mott and Littleton,[19] Williams,[19] or Markham and Seitz.[19] This is not surprising since no allowance is made for the readjustment of the surrounding lattice. While Fig. 5 gives an estimate of the displacements, its reliability is not greater than a factor of two or three.

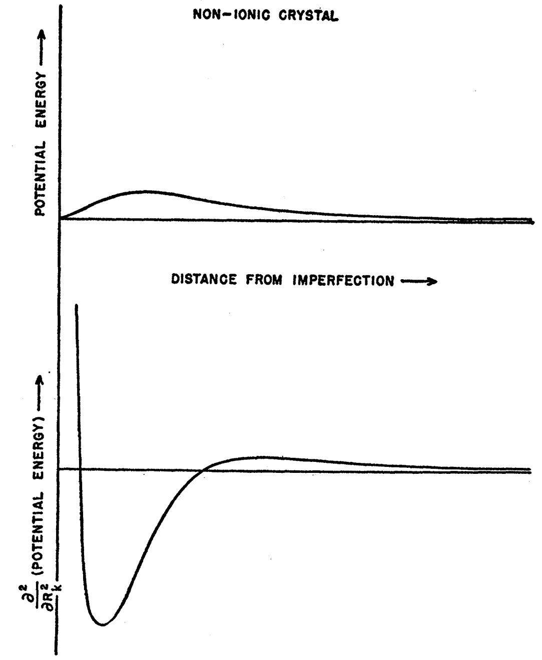

FIG. 6. Plot of $\langle\varphi_1|V_3|\varphi_1\rangle$ and $(\partial^2/\partial R_k^2)\langle\varphi_1|V_3|\varphi_1\rangle$ against R_k for a non-ionic crystal. The lower curve again indicates that the δ's change signs for small q's.

The estimation of r_k, δ, and S_2 for a non-ionic crystal seems more difficult. The electronic field polarizes the atom, and one might suspect that $\langle\varphi_n|V_3|\varphi_n\rangle$ would be proportional to the square of the field due to the electron cloud. Hence, in Fig. 6 we have plotted the square of this field and its second derivative against R_k. The s's are again of both signs. Since the s's are much smaller (although D and S_1 are not) one is probably justified again in neglecting S_2.

6. CONCLUSION

We may summarize this paper with the following conclusions:

1. The wave function chosen for the electrons in a solid determine the perturbation potential to be used. Although in principle this can be done in an infinite number of ways, only two types of approximations, the "adiabatic" and "static," have been used extensively in the past. There seems to be nothing in the literature to justify the assumption that one approximation is "exact."

2. Equations (2.7b) and (2.8b) are the expressions which enter into a perturbation scheme for the inter-

---

[18] There are two sets of 24 ions at a radius of $\sqrt{(17)}$ from the center, namely, the 410 and the 322 set. The above statement is true only if one set is omitted.

[19] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938); F. E. Williams, J. Phys. Chem. **57**, 780 (1953); J. J. Markham and F. Seitz, Phys. Rev. **74**, 1014 (1948).

action of electrons and phonons. Note that the last term of (2.7b) usually does not appear.

3. The adiabatic approximation overestimates the kinetic energy, while static approach overestimates the potential energy.

4. Electron transitions affect the equilibrium positions of the ions and the frequency of the normal modes. One cannot, in general, justify the consideration of these effects independently.

5. The splitting of the Hamiltonian leads to several mathematical difficulties. The static approximation gives non-orthogonal wave functions while the adiabatic gives non-Hermitian operators.

6. The adiabatic approach is superior for deeper traps. A rough estimate indicates that it should be used when the binding energy is greater than 0.1 ev.

7. For very shallow traps the static approach may be superior at low temperatures. Actually, the difference between the two for depths of about 0.1 ev or less is so small that there is little choice, and other approximations made in a calculation will be of greater importance.

ACKNOWLEDGMENTS

The author would like to acknowledge some very helpful discussions with his colleagues. Particular mention should be made of Professor F. Seitz, who read the first draft, Dr. P. Clavier, who suggested some of the proofs in Sec. 2, and Dr. H. J. G. Meyer of Eindhoven for valuable criticism. The assistance of Mrs. M. Parker with the calculation and of Mrs. H. Pietrini with the manuscript is also gratefully acknowledged.

PHYSICAL REVIEW VOLUME 103, NUMBER 3 AUGUST 1, 1956

Radio-Frequency Spectra of Li^6Cl by the Molecular Beam Electric Resonance Method[*]

D. T. F. Marple[†] and J. W. Trischka
Syracuse University, Syracuse, New York

(Received January 16, 1956)

Transitions between the hyperfine structure levels of the rotational state of Li^6Cl with $J=1$ were studied by the molecular beam electric resonance method. The electric quadrupole interaction constant, $(eqQ)_{Cl}$, and the spin-rotation interaction constant, c_{Cl}, of the chlorine nucleus, and the product of the square of the molecular dipole moment, μ^2, and moment of inertia, A, were determined in several different vibrational states. These constants, and the ratios derived from them are:

for Li^6Cl^{35}	$v=0$	$v=1$	$v=2$	$v=3$
$(eqQ/h)_{Cl}$ (kc/sec)	-3071.72 ± 0.61	-3479.3 ± 1.7	-3873.0 ± 1.8	-4250 ± 11
c/h_{Cl} (kc/sec)	2.07 ± 0.10	2.22 ± 0.20	2.19 ± 0.21	...
μ^2A ($\times10^{76}$ cgs)	1774.26 ± 0.28	1840.26 ± 0.40	1909.3 ± 0.6	1980.6 ± 0.9
for Li^6Cl^{37}				
$(eqQ/h)_{Cl}$ (kc/sec)	-2419.9 ± 2.4	-2736.6 ± 5.4	...	...
c/h_{Cl} (kc/sec)	1.88 ± 0.30	1.60 ± 0.34	...	...
μ^2A ($\times10^{76}$ cgs)	1788.24 ± 0.40	1854.9 ± 0.6	1924.7 ± 0.7	...
$(eqQ)_{Cl^{35}}/(eqQ)_{Cl^{37}}$	1.2694 ± 0.0013	1.2714 ± 0.0025	...	...
$\mu^2A(Li^6Cl^{37})/\mu^2A(Li^6Cl^{35})$	1.00788 ± 0.00027	1.0081 ± 0.001	...	...

The random errors in μ^2A are given in the foregoing. The systematic error was $\pm1.1\times10^{-76}$ cgs.

The vibrational constant, ω_e, was found to be 536 ± 60 cm^{-1} from a study of line intensities. The magnetic field at the chlorine nucleus, H_R, was calculated to be 4.96 ± 0.23 gauss from c_{Cl} for Li^6Cl^{35} in the zeroth vibrational state. μ, and the internuclear distance, r, were found from beam deflection data to be 5.9 ± 1.3 Debye units 2.4 ± 0.4 A, respectively.

A static electric field was used to study the Stark effect. When the static field was weak or absent, line frequencies were found to depend on the magnitude of the radio-frequency field used to produce transitions. This effect is termed "radio-frequency Stark effect." A theory for this effect was developed and accounts for the observations.

INTRODUCTION

RADIO-FREQUENCY spectra of Li^6Cl^{35} and Li^6Cl^{37} were studied by the molecular beam electric resonance method.[1–3] Transitions were induced between the electric hyperfine structure levels of the rotational state with $J=1$ by an oscillating field applied in the region between two inhomogeneous fields which selected the initial and final states to be observed. Stark effect was produced by a static electric field superimposed on the oscillating field.

Two nuclear-molecular interactions, the electric quadrupole interaction and the spin-rotation interaction of the Cl nuclei, were required to explain the observed spectra. The product of the square of the molecular

---

[*] This work was supported in part by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[†] Present address: General Electric Research Laboratory, Schenectady, New York.

[1] H. K. Hughes, Phys. Rev. **72**, 614 (1947).

[2] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

[3] Lee, Fabricand, Carlson, and Rabi, Phys. Rev. **91**, 1395 (1953).