

## Quantum States of the Trapped Electron for an Interstitial Ion\*

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The quantum states of the trapped electron for an interstitial ion in an ionic crystal are computed by a new method.

### INTRODUCTION

**I**N this paper we shall apply a new method to calculate the energy levels of the interstitial positive ion in an ionic crystal. The interstitial positive ion is predicated to trap electrons, but there is little experimental work on this center.

The energy levels of the electron trapped at an interstitial positive ion have been discussed by Simpson.<sup>1)</sup> The method used in this paper starts from the many-body point of view in the Hartree approximation and<sup>2)</sup> includes the electron-phonon interaction as outlined in the previous paper.<sup>3)</sup>

### CALCULATIONS

In the present calculation, the crystal is assumed to be a dielectric medium and the net point charge for the interstitial ion is positive and unity.

When the electron under discussion is moving in the region very close to the interstitial ion, its electric field is almost completely shielded by the interstitial ion. Furthermore, the electron moves relatively fast. Hence, the ions of the crystal do not follow the electronic motion and there are no temporary displacements of ions, *i.e.*, no phonons are created. On the other hand, when the electron is moving in the region far from the interstitial ion, it moves relatively slowly compared to its motion when nearby. In this case, the ions can follow its movements and temporary displacements corresponding to acoustic and optical lattice vibrations result. For this problem, only the long wavelength longitudinal optical modes are important.

From considering these two cases, it seems reasonable to divide the crystal into

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1) J. H. Simpson, *Proc. Roy. Soc. (London)* **A197**, 269 (1949); *Proc. Roy. Soc. (London)* **A231**, 308 (1955).

2) S. F. Wang, *Phys. Rev.* **132**, 573 (1963).

two parts: one consisting of a spherical region of radius  $R$  with center at the interstitial ion center and the other consisting of the remaining part of the crystal. The radius  $R$  is taken as a parameter of the problem.

Thus, the Hamiltonian of this system is

$$H = \frac{\mathbf{p}^2}{2m} + \left\{ \begin{array}{l} \epsilon_\infty r^2 \quad \text{or } r < R \\ \sum_k \hbar \omega_k a_k^* a_k + H_{cl} + H_{cl} \frac{e^2}{\epsilon_\infty} \quad \text{for } r > R \end{array} \right. \quad (1)$$

where  $m$  is the reduced effective mass of the interstitial ion and the electron, and the first term of (1) is the kinetic energy operator of them.  $-e^2/\epsilon_\infty r$  is the interaction of the electron with the interstitial ion.  $\sum_k \hbar \omega_k a_k^* a_k$  is the Hamiltonian for the phonons, which is written in terms of creation and annihilation operators,  $a_k$  and  $a_k^*$ .  $H_{cl}$  represents the interaction between the trapped electron and the phonons;  $H_{cl}$ , the interaction between the interstitial ion and the phonons. Thus,

$$H_{cl} = \sum_k (V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} + V_k^* a_k^* e^{-i\mathbf{k}\cdot\mathbf{r}}). \quad (2)$$

$$H_{cl} = - \sum_k (V_k a_k + V_k^* a_k^*). \quad (3)$$

Here, the origin of the position vector for the trapped electron,  $r$ , is taken at the interstitial ion center.  $V_k$  is given by the following:

$$V_k = -i \left( \frac{2\pi e^2 \hbar \omega_k}{K^2 V \epsilon^*} \right)^{1/2} \quad (4)$$

In Eq. (4),  $V$  is the volume of crystal,  $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_s$ , where  $\epsilon_\infty$  and  $\epsilon_s$  are the optical and static dielectric constants; and  $\omega_k$  is the frequency of the longitudinal optical modes for the crystal.

The wave function corresponding to Eq. (1) is written in the following form

$$\Psi = \phi(\mathbf{r}) \cdot \Phi, \quad (5)$$

where  $\phi(\mathbf{r})$  is the electronic part wave function.  $\Phi$  is the phonon wave function which is written in the Hartree form, that is,

$$\Phi = \prod_k f(K). \quad (6)$$

Here  $f(\mathbf{K})$  is the wave function of phonons of momentum  $\mathbf{K}$ . It can be found by the perturbation theory using the phonon part Hamiltonian in Eq. (1) as outlined in the previous paper.<sup>2)</sup> To a first order approximation the  $f(\mathbf{K})$  is given by

$$f(K) = \left[ 1 - \frac{V_k^*}{\hbar \omega_k} (\varphi_k^* - 1) a_k^* \right] |0\rangle. \quad (7)$$

Here  $|0\rangle$  represents the phonon vacuum state and the conjugate function of  $\varphi_k^*$  in Eq.

( 7 ) is

$$\varphi_k = \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) e^{i\mathbf{r}\cdot\mathbf{k}} d^3r. \quad (8)$$

The effective Hamiltonian for the trapped electron is

$$H_{eff} = \langle \Phi, H\Phi \rangle. \quad (9)$$

The energy of the trapped electron is given by

$$E = \langle \psi(\mathbf{r}), H_{eff}\psi(\mathbf{r}) \rangle. \quad (10)$$

A reasonable set of trial wave functions for the trapped electron under discussion is the series of hydrogen-like functions. Therefore the electronic wave function for the ground state is chosen as follows:

$$\psi_1 = \left( \frac{\lambda^3}{\pi} \right)^{1/2} e^{-\lambda r}, \quad (11)$$

where  $\lambda$  is a variational parameter. Then the effective Hamiltonian for the ground state becomes

$$H_{eff} = \frac{\mathbf{p}^2}{2m} + \left\{ \begin{array}{l} \frac{-e^2}{\epsilon_\infty r} \text{ for } r < R \\ \frac{e^2}{\epsilon^*} \left( \frac{5}{16} \lambda - \frac{1}{a} \right) - \frac{e^2}{\epsilon_\infty r} + \frac{e^2}{\epsilon^* r} (e^{-2\lambda r} + \lambda r e^{-2\lambda r}) \text{ for } r > R \end{array} \right\}. \quad (12)$$

The quantity  $a$  is twice the nearest neighbor distance.

The energy levels given in this work depend on two parameters:  $\lambda$ , the wave function exponent coefficient and  $R$ , the radius of the spherical region about the interstitial ion in which the adiabatic approximation holds. Those may be determined by the variational method, which, however, leads to transcendental equations. To simplify the calculations we choose to pick a convenient value of  $R$  and solve for  $\lambda$ . In view of the calculation for the  $F$  center<sup>2)</sup> a reasonable choice is to take  $R = d/2$ . Here  $d$  is the nearest neighbor distance for NaCl-type crystals.

Then the ground state energy is as follows:

$$E_1 \equiv \langle \psi_{1,1}, H_{eff} \psi_{1,1} \rangle = \frac{\lambda^2 \hbar^2}{2m} + \frac{e^2}{\epsilon^*} \left( \frac{5}{16} \lambda - \frac{1}{a} \right) e^{-2\lambda R} (2\lambda^2 R^2 + 2\lambda R + 1) - \frac{e^2}{\epsilon_\infty} \lambda + \frac{1}{8} \frac{e^2}{\epsilon^*} \lambda e^{-4\lambda R} (8\lambda^2 R^2 + 12\lambda R + 3). \quad (13)$$

Minimizing  $E_1$  by varying the parameter  $\lambda$ , the  $A$  for minimum energy and hence the ground state energy can be found.

The trial wave function,  $\psi_2$ , for the  $2p$  state is chosen as

$$\psi_2 = \left( \frac{\beta^5}{\pi} \right)^{1/2} r e^{-\beta r} \cos\theta, \quad (14)$$

where  $\theta$  is the polar angle of the position vector of the electron,  $\mathbf{r}$ . The effective Hamiltonian for this state is

$${}_{2}H_{eff} = \frac{\mathbf{p}^2}{2m} + \left\{ \frac{-e^2}{\epsilon_{\infty} r} + \frac{e^2}{\epsilon^*} \left( \frac{81}{512} \beta - \frac{1}{a} \right) - \frac{e^2}{\epsilon_{\infty} r} + \frac{e^2}{\epsilon^* r} e^{-2\beta r} \left( 1 + \frac{5}{4} \beta r + \frac{11}{6} \beta^2 r^2 + \beta^3 r^3 \right) \right\}. \quad (15)$$

Then the energy  $E_2$  corresponding to  $2p$  state is as follows:

$$E_2 \equiv \langle \psi_2, {}_{2}H_{eff} \psi_2 \rangle = \frac{\beta^2 \hbar^2}{2m} + \frac{e^2}{3\epsilon^*} \left( \frac{81}{512} \beta - \frac{1}{a} \right) e^{-2\beta R} (2\beta^4 R^4 + 4\beta^3 R^3 + 6\beta^2 R^2 + 6\beta R + 3) - \frac{e^2}{2\epsilon_{\infty}} \beta + \frac{e^2}{\epsilon^*} \beta e^{-4\beta R} (A\beta^6 R^6 + B\beta^5 R^5 + C\beta^4 R^4 + D\beta^3 R^3 + E\beta^2 R^2 + F\beta R + G). \quad (16)$$

The coefficients  $A, B, C, \dots, G$  are real numbers. Minimizing with respect to  $\beta$ , the true  $2p$  state energy can be found. Using the value of  $\beta$  for minimum energy we can determine the electronic wave function.

The  $-e^2/\epsilon^*a$  in Eq. (13) is the energy of the lowest state of the conduction band as outlined in the previous paper.<sup>2)</sup> Thus the energy levels of the  $1s$  and  $2p$  states with respect to the bottom of the conduction band are respectively  $E_1' = E_1 + e^2/\epsilon^*a$  and  $E_2' = E_2 + e^2/\epsilon^*a$ . The theoretical values for  $E_1'$  and  $E_2'$  as calculated for AgBr and NaCl are summarized in the table below. The values of the constants used are also given.  $m/m_e$  is the ratio of the effective mass to the free electron mass.<sup>3),4)</sup>

Table. Energy levels and constants for an interstitial ion

Substance	$m/m_e$	$\epsilon_{\infty}$	$\epsilon_s$	$a(\text{\AA})$	$E_1'(\text{eV})$	$E_2'(\text{eV})$	$\frac{e^2}{\epsilon^*a}(\text{eV})$	$\lambda(10^8)$	$\beta(10^3)$
AgBr	0.20	4.62	13.10	5.76	-0.041	-0.009	0.350	0.05	0.02
NaCl	1.00 (Approx.)	2.25	5.62	5.62	-1.709	-0.208	0.690	0.80	0.24

F. C. Brown and his co-workers (Department of Physics, University of Illinois, Urbana, Illinois, U.S.A.) have observed the energy levels of the interstitial ion for AgBr (Private communication). The results given in this paper are in accord with their findings.

3) G. Ascarelli and F. C. Brown, *Phys. Rev. Letters* **9**, 209 (1962).

4) R. P. Femman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, *Phys. Rev.* **127**, 1004 (1962).