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Approximate Wave Functions for the *U* Center by the Point-Ion-Lattice Method*

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Wave functions for the ground state and the first excited state of the *U* center are calculated in the point-ion-lattice approximation, and the term values are obtained. The transition energy and the oscillator strengths are computed, and the former are compared with experimental data. They are approximately 20% smaller than the observed transition energies. A qualitative argument is presented, suggesting that this discrepancy can be removed by inclusion of the exchange energy.

I. INTRODUCTION

THIS is the third in a series of papers dealing with the calculation of approximate wave functions for electron-excess color centers in the alkali halides with the NaCl structure.[1] The point-ion-lattice method, first proposed in GA and further elaborated in GL, is applicable to the calculation of wave functions for those states of electron-excess color centers which give rise to transitions obeying Ivey's laws.[2] The problem of the *F* center was dealt with in GA, and the problem of the *M* center was treated in GL. The object of the present paper is to extend this technique to the *U* center, a simple two-electron center obeying an Ivey law. Since the general justification of the point-ion-lattice method has already been given in GL, this paper will treat only those aspects of the problem which are peculiar to two-electron centers in general or to the *U* center in particular.

The *U* center is thought to be a negative hydrogen ion, substitutionally replacing a halide ion. Mott and Gurney[3] give the following qualitative description of the optical absorption process: "There can be little doubt that the electronic transition responsible for the absorption band is one in which an electron is ejected from the hydrogen ion into a state extending over the neighboring metal ions and similar to the excited state of a halogen ion in the pure crystal." Our calculations support this view.

II. CALCULATIONS

In accordance with the usual procedure in the point-ion-lattice method, all ions will be represented by point charges and polarization effects will be neglected. This is legitimate here since the center (vacancy+proton +two trapped electrons) is electrically neutral and therefore incapable of producing long-range polarization effects. The Hamiltonian is, therefore,

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-1/r_1-1/r_2+1/r_{12}+V_L(r_1)+V_L(r_2), \quad (1)$$

where the origin is at the proton and the axes are parallel to the cube edges. The subscripts 1 and 2 refer to the two electrons, and $V_L(r_1)$ is the interaction of electron 1 with the rest of the lattice (i.e., excluding the proton). It is given by

$$V_L(r)=\sum_{\xi,\eta,\zeta=-\infty}^{+\infty}{}' (-1)^{\xi+\eta+\zeta}[(x-\xi a)^2+(y-\eta a)^2+(z-\zeta a)^2]^{-\frac{1}{2}}, \quad (2)$$

where a is the lattice parameter, i.e., the shortest anion-cation distance, and the prime indicates that the point (0,0,0) is omitted from the summation. We shall be interested in the ground state, which is a singlet state very similar to the ground state of the free H$^-$ ion. We shall also study the first excited state, which is a discrete singlet state and very much *unlike* the first excited state of the free H$^-$ ion which lies in the continuum.

For the ground state, we shall use the simplest wave function which is capable of predicting binding in the free ion, namely, Chandrasekhar's function[4]

$$\Psi=(N/4\pi)[e^{-\alpha r_1}e^{-\beta r_2}+e^{-\beta r_1}e^{-\alpha r_2}], \quad (3)$$

where N is the normalization constant, and α and β are variational parameters. For the free ion, the expectation value of the Hamiltonian [i.e., of the first five terms of Eq. (1)] is

$$E_{\mathrm{H}^-}(\alpha,\beta)=-\left[\tfrac{1}{2}+\tfrac{1}{2}\left(\frac{2\alpha}{\alpha+\beta}\right)^3\left(\frac{2\beta}{\alpha+\beta}\right)^3\right]^{-1}\left[\tfrac{1}{2}(\alpha+\beta)+\frac{11}{32}(\alpha+\beta)\left(\frac{2\alpha}{\alpha+\beta}\right)^3\left(\frac{2\beta}{\alpha+\beta}\right)^3-\tfrac{1}{4}(\alpha^2+\beta^2)-\frac{\alpha\beta}{2}\left(\frac{2\alpha}{\alpha+\beta}\right)^3\left(\frac{2\beta}{\alpha+\beta}\right)^3-\frac{\alpha\beta}{2}\left(\frac{\alpha^2+3\alpha\beta+\beta^2}{(\alpha+\beta)^3}\right)\right]. \quad (4)$$

The minimum of this energy functional occurs at

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[1] The first paper by B. S. Gourary and F. J. Adrian [Phys. Rev. **105**, 1180 (1957)] will be referred to as GA. The second paper by B. S. Gourary and P. J. Luke [Phys. Rev. **107**, 960 (1957); **108**, 1647 (E) (1957)] will be denoted by GL.

[2] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

[3] N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1948), second edition, p. 148.

[4] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

$\alpha=1.03925$ and $\beta=0.28309$. Its value is then

$$E_{\mathrm{H}^-}(1.03925,\,0.28309)=-0.51330 \text{ atomic unit,} \tag{5}$$

which is higher than the value of -0.5276 obtained with an eleven-parameter wave function by Henrich.[5] The required correction is -0.0143 atomic unit in the free ion.

For the U center, the energy functional obtained from the wave function (3) and the Hamiltonian (1) is

$$E_U(\mu,\nu)=E_{\mathrm{H}^-}(\mu/a,\nu/a)+(\Psi|\,V_L(r_1)+V_L(r_2)\,|\Psi), \tag{6}$$

where we have introduced the more convenient variational parameters $\mu=\alpha a$ and $\nu=\beta a$. The expectation value of the energy in the field of the point-ion-lattice is readily evaluated, and it yields the following expression:

$$\begin{aligned}(\Psi|\,V_L(r_1)+V_L(r_2)\,|\Psi)={}&-2\alpha_M/a\\ &+\frac{1}{a}\left[\tfrac{1}{2}+\tfrac{1}{2}\left(\frac{2\mu}{\mu+\nu}\right)^3\left(\frac{2\nu}{\mu+\nu}\right)^3\right]^{-1}\left[\frac{\mu}{2}S_2(\mu)+\frac{\nu}{2}S_2(\nu)\right.\\ &\left.+2\left(\frac{\mu+\nu}{4}\right)\left(\frac{2\mu}{\mu+\nu}\right)^3\left(\frac{2\nu}{\mu+\nu}\right)^3 S_2\left(\frac{\mu+\nu}{2}\right)\right],\end{aligned} \tag{7}$$

where the quantity $S_n(\mu)$ is defined by the following equation:

$$S_n(\mu)=\sum_{z_i\geqslant y_i\geqslant x_i\geqslant 0}{}' h_i(-1)^{z_i+y_i+x_i+1}(2\mu r_i)^n[A_n(2\mu r_i)-A_{n-1}(2\mu r_i)], \tag{8}$$

where the prime on the summation implies that the point (0,0,0) is omitted and where

$$r_i^2=x_i^2+y_i^2+z_i^2;\quad h_i=(3!/n_i!)2^{3-0_i}, \tag{9}$$

where n_i is the number of times any number occurs in the triplet (x_i,y_i,z_i) and where 0_i is the number of times zero occurs in this triplet. $A_n(x)$ is defined by

$$A_n(x)=\int_1^\infty t^n e^{-xt}dt, \tag{10}$$

and α_M is the well-known Madelung constant which is 1.747558 for the NaCl-type lattice.

TABLE I. Energies and parameter values for the ground state of the U center. All quantities are in Hartree atomic units. It should be noted that neither these energies nor the excited state energies are measured from the bottom of the conduction band.

Substance	a	$E_{\mathrm{H}^-}(\alpha,\beta)-2\alpha_M/a$	μ	ν	$E_U(\mu,\nu)$	$E_g(\mu,\nu)$
LiF	3.80	−1.433	3.8	2.2	−1.360	−1.374
NaF	4.37	−1.313	4.4	2.2	−1.263	−1.277
LiCl	4.86	−1.233	4.9	2.3	−1.195	−1.209
NaCl	5.31	−1.172	5.3	2.5	−1.142	−1.156
KCl	5.93	−1.103	6.0	2.6	−1.081	−1.095
RbBr	6.48	−1.053	6.6	2.6	−1.036	−1.050

If only the first term on the right-hand side of (7) is considered during the variational calculation, then the minimum occurs at the same values of the variational parameters as in the free ion, and the energy is altered from its value in the free ion only by the addition of the term $-2\alpha_M/a$. The effect of the other terms in (7) is to compress the negative hydrogen ion slightly, the degree of compression depending on the particular lattice concerned. Thus a numerical variational calculation must be carried out, to minimize E_U as a function of μ and ν. The results of such a variational calculation are given in Table I. Also listed is the quantity $E_{\mathrm{H}^-}(\alpha,\beta)-2\alpha_M/a$, computed for those values of α and β which minimize the energy of the free ion.

It should be noted that the wave function (3) is somewhat more extensive than the more flexible wave functions containing the interelectronic distance also considered by Chandrasekhar. Thus E_U computed using it is higher than the correct minimum value for two reasons: first, the unduly extended charge distribution resulting from this relatively inflexible variational function does not permit the electrons to fit themselves into the potential energy well of the lattice. Secondly, the variational function used does not give the correct result even in the case of the free ion. In the present paper, we shall attempt to correct only the second of these faults. This can be done approximately by adding to E_U the term -0.0143 atomic unit, which was obtained as the difference of (5) and Henrich's best energy value for the free H$^-$ ion. The other inaccuracy cannot be corrected without much more elaborate calculations. Its influence on the transition energy will be offset somewhat by the fact that the wave function for the first excited state will also be less than perfect, and consequently its computed energy will also be too high. Thus the two errors can be expected to cancel each other to some extent. We shall, therefore, use the quantity

$$E_g=E_U-0.0143 \tag{11}$$

as our calculated value for the energy of the ground state. This quantity is also listed in Table I.

TABLE II. Energies and parameter values of the $2p$ electron in an F center (in Hartree atomic units).

Substance	a	$\xi'=\delta a$	$[\frac{1}{2}\delta^2-\alpha_M/a+(\delta/12)S_4(\delta a)]$
LiF	3.80	2.00	−0.138
NaF	4.37	2.20	−0.137
LiCl	4.86	2.30	−0.135
NaCl	5.31	2.40	−0.133
KCl	5.93	2.50	−0.129
RbBr	6.48	2.60	−0.126

Let us now proceed to the calculation of the wave function for the first accessible excited state. Since the negative hydrogen ion has only one bound singlet

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[5] L. R. Henrich, Astrophys. J. 99, 59 (1943).

state,[6] it is clear that the excited state of the *U* center involves one electron bound to the proton while the other is held bound primarily by the potential well of the lattice. Since we are dealing with a singlet state, the spacial part of the wave function must be symmetric in the coordinates of the two electrons. Thus a reasonable trial wave function is

$$\Phi=(\tfrac{1}{2})^{\frac{1}{2}}[\phi(r_1)\psi(r_2)+\psi(r_1)\phi(r_2)], \tag{12}$$

where

$$\phi(r)=(1/4\pi)^{\frac{1}{2}}2\gamma^{\frac{3}{2}}\exp(-\gamma r), \tag{13}$$

and

$$\psi(r)=(3/4\pi)^{\frac{1}{2}}\cos\theta(\tfrac{4}{3})^{\frac{1}{2}}\delta^{\frac{5}{2}}r\exp(-\delta r), \tag{14}$$

where γ and δ are variational parameters. The expectation value of the Hamiltonian (1) becomes then

$$E_e=\tfrac{1}{2}\gamma^2-\gamma-\alpha_M/a+\gamma S_2(\gamma a)+\tfrac{1}{2}\delta^2-\tfrac{1}{2}\delta-\alpha_M/a \\ +(\delta/12)S_4(\delta a)+\tfrac{1}{2}\delta+g(\gamma,\delta). \tag{15}$$

Here, $\frac{1}{2}\gamma^2$ is the kinetic energy of the 1*s* electron; $-\gamma$ is its potential energy in the field of the proton; $-\alpha_M/a$ is the potential energy in the field of the lattice that the 1*s* electron would have if it were concentrated at the lattice site; and $\gamma S_2(\gamma a)$ is the correction to the preceding term due to the fact that the electron is not concentrated at the lattice site. The next term, $\frac{1}{2}\delta^2$, is the kinetic energy of the *p* electron; $-\frac{1}{2}\delta$ is its potential energy in the field of the proton; $-\alpha_M/a$ is the potential energy in the field of the lattice that the *p* electron would have if it were concentrated at the lattice site; and $(\delta/12)S_4(\delta a)$ is a correction to the preceding term due to the fact that the *p* electron is not concentrated at the lattice site. The last two terms are the effects of the electron-electron interaction. The first of these is the interaction of the *p* electron with a unit negative charge located at the lattice site. The second is a correction to the preceding term arising from the fact that the 1*s* electron is not a point charge, but has overlap and exchange interactions with the *p* electron.

TABLE III. Energies of the excited state in the *U* center (in Hartree units).

Substance	a	α_M/a	$\gamma S_2(\gamma a)$	$g(\gamma,\delta)$	E_e
LiF	3.80	0.460	0.0035	0.0109	−1.084
NaF	4.37	0.400	0.0011	0.0100	−1.026
LiCl	4.86	0.360	0.0004	0.0088	−0.986
NaCl	5.31	0.329	0.0002	0.0079	−0.954
KCl	5.93	0.295	0.0000	0.0067	−0.917
RbBr	6.48	0.270	0.0000	0.0059	−0.890

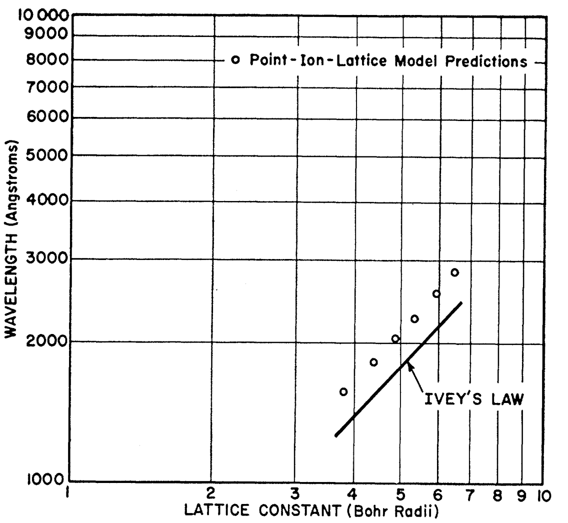

FIG. 1. The Ivey law for the *U* band and the point-ion-lattice model predictions.

It will now be assumed that the fourth and the last terms of (15) are small, and that they may, therefore, be neglected at first and then evaluated in first-order perturbation theory. This assumption will later be verified numerically. Thus, in zero order, the energy functional is

$$E_e{}^0=[\tfrac{1}{2}\gamma^2-\gamma-\alpha_M/a] \\ +[\tfrac{1}{2}\delta^2-\alpha_M/a+(\delta/12)S_4(\delta a)]. \tag{16}$$

The first square bracket contains the major contributions to the energy of the tightly bound electron. The second bracket contains the kinetic energy of the *p* electron; the statement that its interaction with the proton is, in this approximation, completely screened by the tightly bound electron; and finally the interaction of the *p* electron with the rest of the lattice. Thus the second bracket is identical with the expression for the energy functional of an *F*-center electron in a 2*p* state [i.e., it is identical with $E_F{}^{SH}$ appearing in Eq. (12) of GA. Their ξ' is equal to our δa]. The two brackets can now be minimized separately with respect to the two variational parameters. The minimization of the first bracket is trivial, and it yields the result $\gamma=1$. The minimization of the second bracket has already been carried out in connection with the *F*-center problem by GA. Their results are given in Table II.

The two correction terms are now evaluated in first-order perturbation theory. The explicit formula for g is

$$g(\gamma,\delta)=(28/3)\delta(\delta/\gamma)^4(1+\delta/\gamma)^{-7} \\ -(\delta/2)(\delta/\gamma)^4(3+\delta/\gamma)(1+\delta/\gamma)^{-5}. \tag{17}$$

The numerical results are given in Table III. A plot of the wavelength of the predicted transition as a function of the interionic distance is given in Fig. 1. This figure also gives the plot of the empirical Ivey formula for the *U* band. The calculated oscillator strengths are given

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[6] It has been shown by E. Hylleraas [Astrophys. J. 111, 209 (1950)] that another bound state of H⁻ exists. Since it is a triplet state, optical transitions to it from the ground state are forbidden, and it is not likely to play any role in the explanation of the optical spectrum of the *U* center. It may, however, be interesting to calculate the properties of such a center, consisting of an H^- ion in a $(2s)(2p)\ ^3P$ state, trapped in a negative-ion vacancy. It should have an absorption band at longer wavelengths, and be amenable to study by resonance techniques, provided that its lifetime in this metastable state be long enough.

TABLE IV. Theoretical oscillator-strength predictions for the U band.

LiF	NaF	LiCl	NaCl	KCl	RbBr
1.9	2.0	1.9	1.7	1.7	1.8

in Table IV. Comparison with experiment shows that they are somewhat too large.[7]

III. DISCUSSION

While the wave functions calculated above for the U center do provide a fair description of the general features of the center, they are by no means the "best" wave functions obtainable. A simple improvement would consist of using another p orbital for the excited state, namely, the type II function of GA. This would lead to a slight lowering of the excited state, which can be computed from Table III of GA. The effect of this on the transition energy is offset somewhat by the fact that a similar lowering would occur in the ground-state energy if a more flexible variational function were used there.

Since the electron spins are paired in the U center, paramagnetic resonance methods are not available for the detailed investigation of the ground state. Thus there is little point in attempting further refinements of the ground-state wave function by including exchange effects, and the detailed discussion of the exchange problem will be relegated to another paper dealing with the F center. It is quite easy, however, to provide a simple qualitative picture of the effects of exchange on the optical transition energy in highly symmetric centers, such as the U center and the F center. The basic effect of the exclusion principle is to surround each alkali nucleus with a spherical region from which the valence electron is virtually barred. Thus the effective radius of the negative-ion vacancy is not a, but somewhat smaller. The depth of the potential well at the center of the vacancy remains substantially the same. This can be expected to decrease the binding energy of both the ground state and the first excited state, but the effect on the energy of the more weakly bound excited state would probably be larger. The transition energy would thus be increased somewhat, leading to better agreement with experiment. This simple picture cannot be applied directly to the M center, because of the unsymmetric shape of the lattice defect.

In the excited state, the interaction between the excited electron and the neutral hydrogen atom it leaves behind is small and repulsive (it is equal to g). Thus the neutral atom should have no great difficulty in diffusing away, leaving behind an F center. This is also in accord with the arguments of Mott and Gurney.[3] The above discussion does not consider, however, the possible effects of the relaxation of the lattice on the interaction between the excited electron and the hydrogen atom.

In the present paper, we were able to avoid the calculation of a very accurate ground-state wave function by using the known binding energy of the free H^- ion to correct our computed ground-state energy. This is not possible in the more complicated two-electron centers, such as the F_2 center. Consequently, the calculation of an adequate ground-state wave function in those centers may present a more difficult computational problem. It is comforting to know, therefore, that the point-ion-lattice method can be expected to give reasonable results for the transition energy in some two-electron systems.

IV. ACKNOWLEDGMENTS

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[7] Preliminary measurements by Dr. H. Etzel indicate that the U-band oscillator strength in KCl is of the same order of magnitude as the F-band oscillator strength.