

TABLE I. Comparison of values of β^*/E_0 derived from these experiments and that deduced from diamagnetic susceptibility measurements.

	β^*/E_0 (gauss ⁻¹)
Thermal magnetoresistance	5.7×10^{-7}
Electrical magnetoresistance	6.1×10^{-7}
Magnetic susceptibility	5.9×10^{-7}

The parameter β^*/E_0 is a measure of the frequency of the de Haas-van Alphen oscillations and varies widely from metal to metal. The electron effective mass, m^* , is contained in β^* , an effective Bohr magneton, and

E_0 is the energy of overlap between the Fermi surface and the Brillouin zone boundary. As can be seen in Table I, the values of β^*/E_0 deduced from the present measurements are in good agreement with the results of Shoenberg⁵ using the diamagnetic susceptibility.

It is noted that the electrical data appear to exhibit a faint amplitude modulation, which suggests the presence of oscillations of a somewhat different frequency, but the effect is too indistinct for any definite conclusions to be drawn.

⁵ D. Shoenberg, Trans. Roy. Soc. (London) 245, 54 (1952).

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

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Qualitative arguments are presented, suggesting that the point-ion lattice model, first used by Gourary and Adrian for the F -center, should be generalized to all those states of electron-excess color centers in the alkali halide crystals which give rise to transitions, obeying the Ivey relations.

The point-ion lattice model is then postulated for Seitz's model of the M -center, and two sets of transition energies are obtained for a whole series of alkali halides. The A_1B_1 transition agrees with the M -band within some 15%. Its dipole matrix element has the [110] direction. The A_1B_2 transition lies at a shorter wavelength. In LiF and NaF it is close to the F -band. Its dipole matrix element has the [100] direction. Oscillator strengths are also given. There is some possibility, however, that the B_2 state may not be bound.

The contact term in the hyperfine structure is estimated for LiF and LiI, using an alternate form of wave function.

Experiments are suggested to verify the Ivey relations and the other predictions of the point-ion lattice model in suitably chosen sets of alkali halide crystals, which have almost identical interionic distances.

1. INTRODUCTION

ONE of the important absorption bands in x-rayed or otherwise colored alkali halide crystals is the M -band, named after its discoverer, Molnar.¹ It lies on the long-wavelength side of the F -band, and the wavelength of its peak in millimicrons is given quite well by Ivey's empirical formula²

$$\lambda_{\max} = 51.8a^{1.56}, \quad (1.1)$$

where a is the nearest neighbor distance in Bohr radii. It is believed to be due to an F -center which has captured a neutral vacancy pair.^{1,3} This model, which has been proposed by Seitz, has been tested to some extent by polarized light experiments,⁴ but thus far only one theoretical treatment of it has been attempted by Inui, Uemura, and Toyozawa.⁵ This calculation has

two weak points. First, the energy is obtained as the difference of several large quantities, each of which is computed only approximately. This is the usual difficulty experienced in the application of the molecular orbital technique in the LCAO (linear combination of atomic orbitals) approximation to the problems of electron-excess color centers. Secondly, Inui, Uemura, and Toyozawa have used wrong numerical values of the interionic distances. Thus both the method and the numerical results of that calculation leave room for considerable doubt.

Recently, Gourary and Adrian⁶ treated the F -center by a simplified Hartree method. They solved the wave equation for a lattice composed of *point ions*, and later estimated the effects of electronic polarization, lattice distortion, and exchange and overlap. It turned out that electronic polarization was not particularly important in the ground state and even in the first excited

and finds that because of the values of the interionic distance used in his work, his results should probably pertain to LiF and NaF, not to LiCl and NaCl, respectively. The observed M -bands then lie approximately halfway between the predicted A_1B_1 and A_1B_2 transitions.

⁶ B. S. Gourary and F. J. Adrian, Phys. Rev. 105, 1180 (1957).

* Work supported by the Bureau of Ordnance, Department of the Navy, under NOrd 73860.

¹ F. Seitz, Revs. Modern Phys. 18, 384 (1946).

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

³ F. Seitz, Revs. Modern Phys. 26, 7 (1954).

⁴ M. Ueta, J. Phys. Soc. Japan 7, 107 (1952); J. Lambe and W. D. Compton, Phys. Rev. 106, 684 (1957).

⁵ Inui, Uemura, and Toyozawa, Progr. Theoret. Phys. (Japan) 8, 355 (1952). Professor Inui has kindly checked his calculations

state. Lattice distortion was not too significant for the ground state binding energy, but it did change the transition energy by some 7% because it affected the energy of the first excited state. Exchange and overlap effects were estimated only roughly. They did not seem to affect the transition energy even though they changed the individual binding energies by an appreciable amount. In the calculation of the hyperfine structure, exchange and overlap effects became paramount. Gourary and Adrian managed to get a good wave function for the ground state by simply orthogonalizing to the core orbitals the wave function computed for the point-ion lattice. Their results agreed well with the experimental optical energies and observed hyperfine splittings for a whole series of alkali halides. Recently, double spin resonance experiments in KCl confirmed these predictions in an even more striking fashion.⁷

It now appears reasonable to postulate that the point-ion lattice model holds for all those states of electron-excess color centers in the alkali halide crystals which give rise to optical transitions obeying a formula of the Ivey type. The qualitative reasoning on which this generalization rests is the following. Ivey's formulas predict a smooth monotonic variation of the wavelength as a function of the interionic distance. It is plausible, therefore, to postulate that only quantities which vary smoothly with the interionic distance should be included in a model suitable for the calculation of wave functions for these states of the centers. Now, the high-frequency dielectric constant is not a smooth function of the interionic distance. The contribution to the cohesive energy, however, due to the repulsive potential r^{-n} acting between nearest neighbors, does decrease smoothly with increasing interionic distance. It follows that electronic polarization is probably not a relevant quantity while lattice distortion may be important. Similarly, exchange and overlap between the trapped electron and the core electrons of a given ion might be a smooth function of the ionic radius of the given ion. They can hardly be expected, however, to depend smoothly on the interionic distance since in almost every electron-excess color center, ions of one kind are closer to the trapped electron than are the ions of the other kind. Thus, if exchange and overlap do indeed play an important role, they must depend primarily either on the alkali or on the halide, but not on the interionic distance. It follows, therefore, that exchange and overlap probably do not influence these transitions greatly. They do determine the behavior of the wave function in the close proximity of each ion, but they do not affect its over-all shape. Thus the general behavior of the wave function can be obtained from the point ion lattice model, and its form inside the ionic cores can be calculated by subsequent orthogonalization

⁷ G. Feher, Phys. Rev. **105**, 1122 (1957); F. J. Adrian, Phys. Rev. **106**, 1356 (1957).

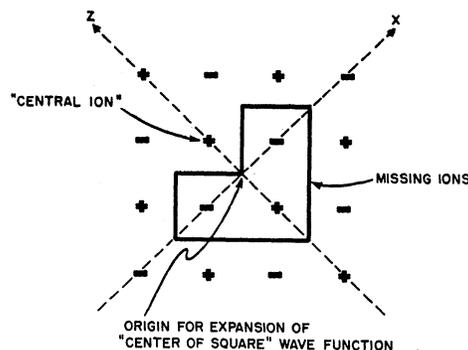


Fig. 1. Seitz's model of the M -center. Note that the y axis is perpendicular to the plane of the paper.

of the wave function to the core orbitals, provided that not too much of the charge is drawn inside the ionic cores by the orthogonalization procedure. The last proviso is important because, in the final analysis, the basic justification for the validity of the point ion lattice model is that most of the charge of the trapped electron stays *outside* of the ionic cores, where the correct potential is indeed closely approximated by the potential of the point-ion lattice. Most of the charge is, in fact, usually localized inside the vacancy, thus rendering the center electrically neutral and preventing any extensive polarization from taking place.⁸

The purpose of this paper is to apply the above procedure to Seitz's model of the M -center. Because of the lower symmetry, the computations are much more involved than for the F -center. Because of the large size of the resultant vacancy, lattice distortion can be expected to play a less important role. We shall, therefore, proceed to treat only a rigid point-ion lattice, neglecting lattice distortion.

2. "CENTER OF SQUARE" (CS) EXPANSION

Consider a point-ion lattice of the NaCl structure, from which two negative ions and one positive ion are missing. One electron is assumed to be trapped in the center. This center is shown in Fig. 1. Clearly the z axis is a twofold symmetry axis, and the xz and the yz planes are symmetry planes. The symmetry group corresponding to this center is C_{2v} . This group has

⁸ It is possible to extend this line of reasoning to speculate on the behavior of electrically charged centers where electronic polarization must play a role and the Ivey law may be expected to break down. A case in point is the F' -center, which consists of two electrons trapped at a single negative ion vacancy. If this band obeys an Ivey law, then an extrapolation of the straight line on a $\log\lambda$ - $\log\alpha$ plot requires that the F' -band in LiF should be at shorter wavelengths than the F -band. This is hardly believable, since the binding in the saturated system would be expected to be considerably less than in the unsaturated F -center. Unfortunately, no conclusive experimental evidence is available. The authors are indebted to Dr. W. Dale Compton for a discussion of this point.

It should be noted that Miessner and Pick [Z. Physik **134**, 604 (1953)] have shown that the position of the V_1 -band is determined by the anion, not by the interionic distance. This also seems to support the views expressed in this paper.

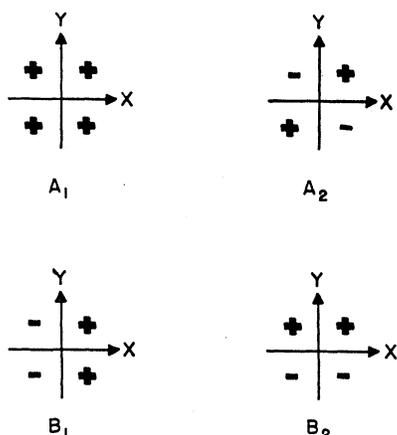


Fig. 2. Pictorial representation of the wave functions belonging to the several irreducible representations of C_{2v} .

four one-dimensional irreducible representations,⁹ whose properties can be visualized from Fig. 2, which shows the sign of a wave function belonging to a given representation at the following four points: (x, y, z) , $(-x, y, z)$, $(-x, -y, z)$, and $(x, -y, z)$.

The real spherical harmonics¹⁰ $S_{l,\mu}(\theta, \varphi)$ belong to the several irreducible representations according to the scheme shown in Table I. This table tells us what terms can arise in an expansion of the wave function in a series of real spherical harmonics. In this section, the origin for the expansion is taken (Fig. 1) at the center of the square, three of whose vertices lie at the vacant lattice sites. We call this the "center of square" expansion, and abbreviate it as CS. Thus

$$\Psi(\Gamma, n | \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{\mu} R(n, l, \mu | r) S_{l,\mu}(\theta, \varphi). \quad (2.1)$$

Here Γ denotes the representation, and n is an energy quantum number. (We shall be interested only in the lowest energy state of each symmetry; consequently, n will be omitted.) The $R(n, l, \mu | r)$ are variational trial functions. Since z belongs to A_1 , y to B_2 , and x to B_1 , electric dipole transitions can take place from a ground state of A_1 symmetry to all but a state of A_2 symmetry.

In the actual variational calculations, we have used the following trial functions:

TABLE I. Reduction of the real spherical harmonics according to the irreducible representations of C_{2v} .

μ	Representation
Positive, zero or even	A_1
Negative, even but not zero	A_2
Positive, odd	B_1
Negative, odd	B_2

⁹ Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 384.

¹⁰ C. C. J. Roothaan, *J. Chem. Phys.* **19**, 1445 (1951).

$$\psi(A_1 | \mathbf{r}) = A(4/7)^{1/2}(\mu/d')^{1/2}(1 + \mu r/d')e^{-\mu r/d'}S_{0,0}(\theta, \varphi) + B(4/3)^{1/2}(\nu/d')^{1/2}(\nu r/d')e^{-\nu r/d'}S_{1,0}(\theta, \varphi), \quad (2.2)$$

$$\psi(B_1 | \mathbf{r}) = (4/3)^{1/2}(\lambda_1/d')^{1/2}(\lambda_1 r/d')e^{-\lambda_1 r/d'}S_{1,1}(\theta, \varphi). \quad (2.3)$$

Here (B/A) , μ , ν , and λ_1 are variational parameters. $\psi(B_2 | \mathbf{r})$ differs from $\Psi(B_1 | \mathbf{r})$ only in having λ_2 instead of λ_1 , and $S_{1,-1}(\theta, \varphi)$ instead of $S_{1,1}(\theta, \varphi)$. Thus B_1 has a node in the yz plane while B_2 has a node in the zx -plane. The quantity d' is $a/\sqrt{2}$, where a is the nearest neighbor distance. The resulting energy functionals are given in the appendix, and the energy and parameter values are summarized in Table II, using Hartree atomic units. In Table II, f is the oscillator strength.

In Fig. 3, the logarithm of the wavelength of the predicted A_1B_1 and A_1B_2 transition is plotted against the logarithm of the nearest neighbor distance, giving straight lines in accordance with Ivey's formulas. Some

TABLE II. Term values, parameter values, oscillator strengths, and transition energies obtained by the center-of-square expansion.

Substance	LiF	NaF	NaCl	KCl
a	3.80	4.37	5.31	5.93
$E(A_1)$	-0.267	-0.247	-0.218	-0.203
$E(B_1)$	-0.174	-0.164	-0.148	-0.140
$E(B_2)$	-0.097	-0.092	-0.086	-0.082
μ	1.75	1.75	2.00	2.00
ν	1.75	2.00	2.00	2.25
B/A	0.493	0.501	0.560	0.563
λ_1	1.25	1.25	1.50	1.50
λ_2	1.00	1.00	1.25	1.25
$f(A_1B_1)$	0.22	0.26	0.24	0.27
$f(A_1B_2)$	0.37	0.44	0.43	0.49
$E(B_1) - E(A_1)$	0.093	0.083	0.070	0.063
$E(B_2) - E(A_1)$	0.170	0.154	0.132	0.121

of the available experimental data are also shown on the graph. Clearly, the A_1B_1 wavelength agrees with the observed M -band within 15% or better. For LiF and NaF, the A_1B_2 transition lies close to the F -band. Inclusion of exchange and overlap probably would not change the A_1B_1 transition much, but it would tend to concentrate the wave function more in the vacancy (away from the ions), and change the binding energy. This might result in a B_2 state which is not bound.

How good are our wave functions? Certainly they are not accurate in the immediate vicinity of the ions, because the ions are represented as point charges. Moreover, they are not even mathematically correct solutions of the point-ion lattice problem, because they do not have the freedom to behave like hydrogenic $1s$ orbitals in the vicinity of the cations. It is clear, however, that we do not want to solve the point-ion lattice problem too accurately in the immediate neighborhood of the ions, because the potential is incorrectly repre-

sented in this region. We do have to use variational wave functions that are reasonably flexible, but which cannot change too much in a volume of the order of the cube of the first Bohr radius. We have, therefore, tested our wave functions by two alternate procedures. First, we tried to add a term of the form

$$C[32(45)^{\frac{1}{2}}](\mu/d')^{\frac{1}{2}}(\nu r/d')^2 e^{-2\nu r/d'} S_{0,0}(\theta, \varphi) \quad (2.4)$$

to $\Psi(A_1|\mathbf{r})$. This led to an insignificant lowering of the energy. We have also considered adding some d -state to all the states, but the labor entailed was excessive. We have, therefore, resorted to the somewhat less satisfactory procedure of comparing our wave functions with analogous wave functions centered on the "central ion" (Fig. 1) (henceforth, "central ion" will be abbrevi-

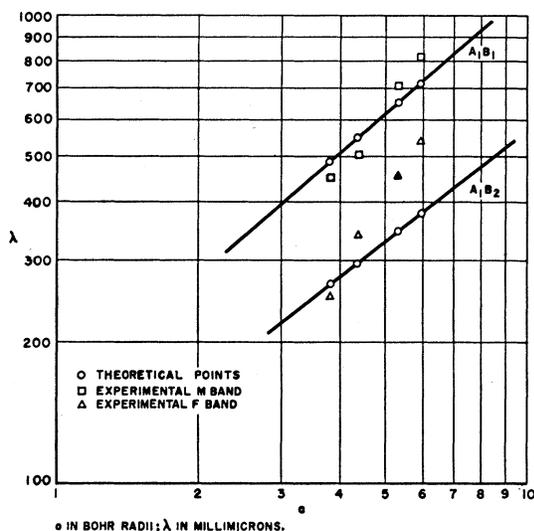


FIG. 3. The A_1B_1 and the A_1B_2 transitions: theoretical curves and their comparison with the experimental M -band and F -band data. The experimental data on NaCl and KCl are those of W. H. Duerig and J. J. Markham [Phys. Rev. **88**, 1043 (1952)]. The data on LiF are those of C. J. Delbecq and P. Pringsheim [J. Chem. Phys. **21**, 794 (1953)]. The NaF data are preliminary [N. W. Lord (private communication)]. It should be noted that few of these points have been taken at very low temperatures.

ated as CI), which had been computed in an earlier attempt and which are discussed in the following section. This comparison led us to the conclusion that the present wave functions were adequate for most purposes except hyperfine structure calculations.

3. "CENTRAL ION" (CI) EXPANSION

While the "center-of-square" (CS) wave functions are adequate for optical calculations, they do not have the requisite flexibility to permit the trapped electron to desert the central ion (Fig. 1) and to become localized in the negative ion vacancies. This leads to too high a density at the central ion. The natural remedy within the framework of the point-ion lattice model would be to add some d -state terms. Since this entails extensive

numerical calculations, we have postponed this project until further experimental work makes the calculation unavoidable. Meanwhile, we shall use some calculations, which have been made by us earlier in connection with another attempt to treat the M -center, in order to obtain estimates of the contribution of the central ion to the contact term of the hyperfine structure in the lithium halides.

These wave functions were obtained by centering an expansion of the form (2.1) on the central ion. The axes were taken parallel to the axes of Fig. 1, but with the origin at the central ion. In order to obtain correct behavior at the central ion, the trial functions were orthogonalized to the core orbitals of the central ion, and exchange and overlap with the core electrons of the central ion were included. Only lithium halides were treated in this manner. The trial functions were:

$$\begin{aligned} \varphi(A_1|\mathbf{r}) = & A[(4/3)^{\frac{1}{2}}(\mu/a)^{\frac{3}{2}}(\nu r/a)e^{-\nu r/a} \\ & - 2S(\mu_0/a)^{\frac{3}{2}}e^{-\mu_0 r/a}]S_{0,0}(\theta, \varphi) \\ & + B(4/3)^{\frac{1}{2}}(\nu/a)^{\frac{3}{2}}(\nu r/a)e^{-\nu r/a}S_{1,0}(\theta, \varphi), \end{aligned} \quad (3.1)$$

$$\mu_0 = 2.70a,$$

$$S = 8(3\mu_0^3\mu^5)^{\frac{1}{2}}/(\mu + \mu_0)^4,$$

$$\varphi(B_1|\mathbf{r}) = (4/3)^{\frac{1}{2}}(\lambda_1/a)^{\frac{3}{2}}(\lambda_1 r/a)e^{-\lambda_1 r/a}S_{1,1}(\theta, \varphi), \quad (3.2)$$

$$\varphi(B_2|\mathbf{r}) = (4/3)^{\frac{1}{2}}(\lambda_2/a)^{\frac{3}{2}}(\lambda_2 r/a)e^{-\lambda_2 r/a}S_{1,-1}(\theta, \varphi). \quad (3.3)$$

The resulting energies, parameter values, and densities of the square of the ground state wave functions at the central ion are given in Table III, using Hartree atomic units.

For LiF, we have computed the energy that would have been obtained if this "central ion" (CI) expansion were carried out in the strict point ion lattice model, i.e., with the central ion represented by a point charge and with a nonorthogonal wave function. These energy values are:

$$\begin{aligned} E(A_1) &= -0.225, & E(B_1) &= -0.152, \\ E(B_2) &= -0.099. \end{aligned} \quad (3.4)$$

TABLE III. Term values, parameter values, and the value of the square of the wave function at the central ion which are obtained by the central-ion expansion.

Substance	LiF	LiI
a	3.80	5.67
$E(A_1)$	-0.197	-0.170
$E(B_1)$	-0.153	-0.126
$E(B_2)$	-0.099	-0.082
μ	2.125	3.00
ν	2.125	2.75
B/A	0.532	0.581
λ_1	1.68	1.96
λ_2	1.32	1.61
$ \varphi(\text{CI}) ^2$	0.080	0.062

This ground state binding energy is smaller than the one given in Table II, and therefore the CS ground state function is better than the CI wave function. Parenthetically, it should be noted that one term in the CS expansion for the ground state gives an accuracy comparable to two terms in the CI expansion. It should also be noted that the orthogonalization and inclusion of exchange and overlap which is done in the CI expansion does not produce a superior wave function, except in the immediate vicinity of the central ion. This is so because exchange and overlap with the core electrons of other ions are not included, and an unsymmetric treatment of exchange and overlap usually leads to erroneous conclusions, even as far as the transition energy is concerned. For the B_1 state, the energy given by the CS expansion is the lower one, and the CS function is to be preferred somewhat. For the B_2 state, the CS and the CI functions are equally valid. We have used the CS function for convenience.

The density of the square of the orthogonalized wave function at the central ion is probably given more accurately by the CI function, because all that the CI function needs in order to attain greater accuracy is a few more terms in the spherical harmonics expansion. Although such a calculation is too cumbersome to be carried out in practice, it is not too difficult to see that its effect on the density of the wave function at the central ion would have to come through the normalizing factor. It would probably be rather small. The CS function, on the other hand, is too inflexible near the central ion to be reliable for this purpose. The density of the square of the orthogonalized wave function at the central ion given in Table III for LiF is about 3.5 times as large as the experimental density at the nearest neighbor alkali in the F -center in LiF. This leads to a contribution to the second moment of the paramagnetic resonance line which is about two times larger than the second moment for the F -center. Other ions may also contribute. This prediction is compatible with recent second-moment measurements by Lord.¹¹ It should be interesting to test this prediction further by the inherently more accurate double spin resonance technique for a whole series of lithium halides.

4. DISCUSSION

While the success of the point-ion lattice model in the calculations leading to the A_1B_1 transition energy is obvious, it is not so clear that the qualitative arguments presented in Sec. 1 and in reference 8 are correct; nor is it self evident that the B_2 state cannot be pushed up into the conduction band by exchange. It is essential, therefore, to supplement the present theoretical work with a series of experiments. First, it is necessary to verify the validity of the Ivey relations at liquid helium temperatures. These relations should be verified for all those electron-excess color centers which are believed

to be electrically neutral. This certainly includes F , R_2 , and M , and possibly R_1 . A particularly critical test of these relations and the degree of their validity should be provided by the study of sets of alkali halides with almost identical interionic distances. Several such pairs are: LiI and CsF, NaCl and RbF, NaI and KBr, etc. Electron spin resonance and double spin resonance data on such pairs of crystals should enable one to check the hypothesis that a wave function computed on the basis of the point-ion lattice model needs to be orthogonalized only to the core orbitals, since the unorthogonalized wave function would be practically identical for the two members of such a pair. Finally, a careful search for the A_1B_2 transition should be made optically in a series of different alkali halides, since the B_2 state may be bound in some crystals but not in others because of different exchange effects. Because of the diffuse nature of the B_2 state, electronic polarization may become important, and the A_1B_2 transition may deviate from the Ivey law towards longer wavelengths.

Such an experimental program could do much to clarify our understanding of the electron-excess color centers in alkali halide crystals. If the qualitative conjectures voiced in this article are confirmed, this would lead to more unified understanding of the subject. If they are disproved, we would have to look for an alternative explanation of the definite successes of the point ion lattice model.

5. ACKNOWLEDGMENTS

The authors are indebted to Professor F. Seitz for a stimulating discussion. They have had the benefit of numerous discussions with their colleagues Dr. F. J. Adrian, Dr. C. K. Jen, and Dr. N. W. Lord. Mrs. Mary E. Lynam has programmed parts of this calculation for the IBM Type 650 and has performed the rest manually. The authors are very grateful to her for her cooperation.

APPENDIX. ENERGY FUNCTIONALS FOR THE CENTER OF SQUARE EXPANSION

The Hamiltonian in the center of square expansion is

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + D(\mathbf{r}) + M(\mathbf{r}). \quad (\text{A.1})$$

Here the potential energy is separated into that due to the central ion, $M(\mathbf{r})$, and that due to the remainder of the lattice, $D(\mathbf{r})$.

$$M(\mathbf{r}) = -[x^2 + y^2 + (z - d')^2]^{-\frac{1}{2}},$$

$$D(\mathbf{r}) = \frac{1}{2} \sum'_{\xi, \eta, \zeta} [(-1)^\xi - (-1)^\eta] (-1)^\zeta [(x - \xi d')^2 + (y - \eta \sqrt{2} d')^2 + (z - \zeta d')^2]^{-\frac{1}{2}}.$$

The summation is over positive and negative integer values of ξ , η , and ζ . The prime denotes the omission of the points $(\pm 1, 0, 0)$ and $(0, 0, \pm 1)$. $D(\mathbf{r})$ belongs to the A_{1g} irreducible representation of the D_{2h} group; hence, it can be shown that an expansion of it in terms

¹¹ N. W. Lord, Phys. Rev. **106**, 1100 (1957).

of the $S_{l,\mu}(\theta, \varphi)$ can only contain terms with l even and $\mu \geq 0$ and even. Furthermore it is obvious that the $l=0$ term is missing.

The problem thus becomes that of varying the parameters in the wave functions [Eqs. (2.2) and (2.3)] so as to minimize the expression

$$E(\Gamma) = \int \psi(\Gamma|\mathbf{r})\mathcal{H}\psi(\Gamma|\mathbf{r})d\tau / \int [\psi(\Gamma|\mathbf{r})]^2d\tau. \quad (\text{A.2})$$

The resulting functionals are:

$$E(A_1) = \{[A^2T_{AA} + B^2T_{BB}(\nu)](2d'^2)^{-1} + B^2D_{BB}(\nu)(d')^{-1} + [A^2M_{AA} + 2ABM_{AB} + B^2M_{BB}](d')^{-1}\} \{A^2 + B^2\}^{-1}, \quad (\text{A.3})$$

$$E(B_1) = T_{BB}(\lambda_1)(2d'^2)^{-1} - D_{BB}(\lambda_1)(d')^{-1} + M_B(\lambda_1)(d')^{-1}, \quad (\text{A.4})$$

$$E(B_2) = T_{BB}(\lambda_2)(2d'^2)^{-1} + M_B(\lambda_2)(d')^{-1}, \quad (\text{A.5})$$

where

$$T_{AA} = 3\mu^2/7, \quad (\text{A.6})$$

$$T_{BB}(\nu) = \nu^2, \quad (\text{A.7})$$

$$D_{BB}(\nu) = \sum'_{\xi > \xi \geq 0, \eta \geq 0} 2^{3-\Theta} [(-1)^\xi - (-1)^\eta] (-1)^\eta \times [(\xi^2 - \eta^2)/\rho^2] \{9/(4\nu^2\rho^3) - (2/5)\nu^5\rho^4 \times [A_6(2\nu\rho) - A_1(2\nu\rho)]\}, \quad (\text{A.8})$$

$$M_{AA} = -1 + (4\mu^3/7) \{ \mu^2[A_4(2\mu) - A_3(2\mu)] + 2\mu[A_3(2\mu) - A_2(2\mu)] + [A_2(2\mu) - A_1(2\mu)] \}, \quad (\text{A.9})$$

$$M_{AB} = - (4/3) (\mu^3\nu^5/7)^{1/2} \{ 24(6\mu + \nu)(\mu + \nu)^{-6} - [A_4(\mu + \nu) - A_1(\mu + \nu)] - \mu[A_5(\mu + \nu) - A_2(\mu + \nu)] \}, \quad (\text{A.10})$$

$$M_{BB} = -1 - 3/\nu^2 + (4\nu^5/15) \{ 2[A_6(2\nu) - A_1(2\nu)] + 5[A_4(2\nu) - A_3(2\nu)] \}, \quad (\text{A.11})$$

$$M_B(\lambda_i) = -1 + 3/(2\lambda_i^2) + (4\lambda_i^5/15) \times \{ -[A_6(2\lambda_i) - A_1(2\lambda_i)] + 5[A_4(2\lambda_i) - A_3(2\lambda_i)] \}, \quad (\text{A.12})$$

$$A_n(x) = \int_1^\infty \xi^n e^{-x\xi} d\xi.$$

In Eq. (A.8), the prime on the summation denotes omission of the point (0,0,1), Θ is the number of zeros in (ξ, η, ζ) , and

$$\rho^2 = \xi^2 + 2\eta^2 + \zeta^2.$$

The term in Eq. (A.8) varying as ρ^{-3} was summed by the method of van der Hoff and Benson.¹²

In Eq. (A.3) the minimization was first done with respect to A and B for fixed values of μ and ν . Since Eq. (A.3) can be written as a homogeneous quadratic equation in A and B , differentiation and setting $\partial E(A_1)/\partial A$ and $\partial E(A_1)/\partial B$ equal to zero leads to a pair of homogeneous linear equations in A and B involving $E(A_1)$ as a parameter. This leads to a quadratic equation for $E(A_1)$. The lower root of this equation is obtained, and it is further minimized *numerically* as a function of μ and ν . The ratio (B/A) and the wave function can then be computed readily. Parenthetically it should be noted that the higher root of the quadratic gives the value of $E(A_{1,1})$, i.e., the energy for the first excited state of A_1 symmetry. Unfortunately, this excited state wave function is not orthogonal to the ground state wave function unless μ and ν are given the values which minimize the energy of the ground state. If this is done, however, the trial function for the excited state has only (B/A) as an effective variational parameter, and this is grossly inadequate. The only way to obtain a good wave function for the first excited A_1 state would be to start with a trial function containing several parameters and orthogonal to our $\psi(A_1|\mathbf{r})$. For the excited states, $E(B_i)$ is minimized *numerically* with respect to λ_i .

¹² B. M. E. van der Hoff and G. C. Benson, Can. J. Phys. **31**, 1087 (1953).