

## $F^{19}$ Hyperfine Interaction in the Paramagnetic Resonance Spectrum of $Mn^{++}$ Ions in $ZnF_2$

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The observation of a predominantly isotropic fluorine hyperfine interaction in the paramagnetic resonance of  $Mn^{++}$  ions dissolved in a  $ZnF_2$  crystal has been interpreted in terms of the contact interaction of the unpaired  $d$  electrons of the  $Mn^{++}$  ion at the fluorine nucleus. The distortion produced in the free-ion orbitals of the  $Mn^{++}$   $3d$  electrons due to the electrons of the  $F^-$  ion has been considered. The calculated value of the isotropic hyperfine interaction constant is 10 oersteds, which is about half the experimental value of 19 oersteds. The quadrupole interaction of the  $Mn^{++}$   $d$  electrons with the crystalline field gradient, calculated on the point charge model, is found to produce a very small change in the theoretical value. The principal causes which contribute to the quantitative disagreement between the theoretical and the experimental values are also discussed.

### INTRODUCTION

TINKHAM<sup>1</sup> has recently studied the paramagnetic resonance spectrum of  $Mn^{++}$  ions dissolved in  $ZnF_2$ . He found a fine-splitting of the resonance spectrum which could only be explained by postulating an interaction of the form  $A_F \mathbf{I}_F \cdot \mathbf{S} + B_F (3I_{Fz} S_z - \mathbf{I}_F \cdot \mathbf{S})$  between the electronic spin of the  $Mn^{++}$  ion and the spin  $\mathbf{I}_F$  of each of the nearest-neighbor  $F^{19}$  nuclei. Shulman and Jaccarino<sup>2</sup> and later Baker and Hayes<sup>3</sup> studied the  $F^{19}$  nuclear magnetic resonance spectrum in a number of iron group fluorides including  $MnF_2$  and found large paramagnetic shifts for the  $F^{19}$  resonance frequency in each case. They explained this shift by assuming the same interaction as that proposed by Tinkham. Since the electron-spin relaxation time was short compared to the  $F^{19}$  Larmor precession frequency, each of the  $F^{19}$  nuclei "saw" a Boltzmann distribution among the spin levels of adjacent  $Mn^{++}$  electronic spins. Hence they experienced an effective magnetic field due to the latter. Bleaney<sup>4</sup> has made an interesting correlation between the data of Tinkham and those of Shulman and Jaccarino. All these authors have pointed out that each of the  $Mn^{++}$   $d$  electrons spends an appreciable fraction of time near the neighboring  $F^{19}$  nuclei and hence leads to the above interaction. Tinkham<sup>5</sup> made use of the observed values of  $A_F$  and  $B_F$  to estimate the effective  $2s$  and  $2p$  characters of each nearest-neighbor  $F^-$  ion in the  $Mn^{++}$  unpaired electrons.

In this paper we attempt to calculate  $A_F$  from a purely theoretical standpoint and compare it with experiment. The problem is the following. A  $Mn^{++}$  ion is placed at a lattice point normally occupied by a  $Zn^{++}$  ion in the  $ZnF_2$  lattice. We have to compute the charge density at the positions of the nearest-neighbor  $F^{19}$  nuclei due to the unpaired electrons on the  $Mn^{++}$  ion.

The  $Mn^{++}$  unpaired electron orbitals get deformed from their free-ion forms by interaction with the surrounding  $F^-$  ions. There are two kinds of distortion. The first distortion may be termed a Pauli distortion of the type emphasized by Gourary and Adrian<sup>6</sup> in their paper on the hyperfine interactions of  $F^-$ -center electrons. Thus, in computing the electron densities at the  $F^{19}$  nuclei we have to consider a determinant consisting not only of the  $Mn^{++}$  unpaired electrons but also the closed-shell electrons of the neighboring  $F^-$  ions. It may be shown, as in I, that this is equivalent to considering the unpaired electrons alone but with their orbitals orthogonalized to the closed-shell orbitals of the  $F^-$  ions. This distorts the unpaired electron orbitals from the free-ion  $Mn^{++}$   $d$  orbitals. In Sec. I it will be shown that using Hartree-Fock orbitals for  $Mn^{++}$  and  $F^-$  ions, a consideration of the Pauli distortion effect leads to an isotropic hyperfine interaction of the unpaired electrons with the  $F^{19}$  nucleus which is about half the observed value. The second distortion arises out of the electrostatic interaction of the  $Mn^{++}$   $d$  electrons with the nuclei of the nearest-neighbor  $F^-$  ions and the Coulomb and exchange interactions with the electrons of the  $F^-$  ions. The evaluation of the effects of the Coulomb and exchange interactions of the  $F^-$  ion electrons on the  $Mn^{++}$  electrons would need evaluation of a number of complicated two-center integrals termed the resonance and exchange integrals. These integrals are not only difficult to compute but are also likely to be very inaccurate unless calculated by a self-consistent procedure.<sup>7</sup> In molecular orbital calculations it is the usual practice, for interactions between  $p$  electrons, to use semiempirical approximations for these integrals. In view of these difficulties, we shall only speculate in Sec. II on the qualitative effects of the distortion of this latter type. A small part of this distortion may be evaluated using a point charge model for the crystalline field around the  $Mn^{++}$  ions. It has been found that the

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<sup>1</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956).

<sup>2</sup> R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956).

<sup>3</sup> J. M. Baker and W. Hayes, Phys. Rev. **106**, 603 (1957).

<sup>4</sup> B. Bleaney, Phys. Rev. **104**, 1190 (1956).

<sup>5</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956).

<sup>6</sup> B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957). (Hereafter referred to as I.)

<sup>7</sup> W. Moffitt, Proc. Roy. Soc. (London) **A196**, 510 (1949).

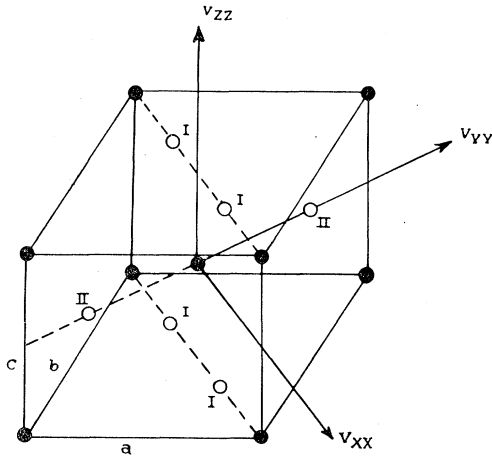


FIG. 1. Unit lattice of  $\text{ZnF}_2$  crystal. Hollow circles denote negative ions and full circles denote positive ions. Arrows indicate the principal axes (in reversed direction) of the field gradient tensor at the nucleus of the body-center positive ion.

distortion produced by the quadrupole component of this crystalline field is negligible. The effects of electron-electron correlation not taken into account in the Hartree-Fock picture will also be considered qualitatively.

### I. ESTIMATION OF $A_F$ DUE TO THE PAULI CORRELATION EFFECT

$\text{ZnF}_2$  has a rutile structure. The unit cell is tetragonal, but the environment around each  $\text{Zn}^{++}$  ion has only orthorhombic symmetry. The nearest-neighbor  $\text{F}^-$  ions are arranged as follows: There are four equivalent  $\text{F}^-$  ions (type I) at the corners of a rectangle around the  $\text{Zn}^{++}$  ion (Fig. 1), each at a distance of 2.03 Å from the latter. Another pair of  $\text{F}^-$  ions (type II) are situated symmetrically about the  $\text{Zn}^{++}$  ion (each at a distance of 2.04 Å from it) on a straight line through it perpendicular to the plane of the above rectangle. Tinkham<sup>5</sup> has found that with a  $\text{Mn}^{++}$  ion at the  $\text{Zn}^{++}$  ion lattice site, the experimental values of  $A_F^I$  and  $A_F^{II}$  for the two inequivalent sets of  $\text{F}^-$  ions are  $19 \pm 1$  oersteds and  $16 \pm 1$  oersteds, respectively.

Fermi's formula<sup>8</sup> for the contact interaction between a nucleus with spin  $\mathbf{I}_N$  and a set of electrons is given by

$$\mathcal{H}_C = (16\pi/3)\gamma\beta\beta_N \langle \Phi | \sum_i \delta(\mathbf{r}_i - \mathbf{r}_N) \mathbf{I}_N \cdot \mathbf{s}_i | \Phi \rangle, \quad (1)$$

where  $\mathbf{s}_i$  is the spin of the  $i$ th electron and the summation over  $i$  extends over all the electrons.  $\Phi$  is the determinantal wave function including all the electrons.  $\gamma$  is the gyromagnetic ratio for the  $\text{F}^{19}$  nucleus, while  $\beta$  and  $\beta_N$  are the Bohr and nuclear magnetons, respectively. As pointed out in the Introduction, following Gourary and Adrian we have to take account of the Pauli correlation between the  $\text{Mn}^{++}$   $d$  electrons and the electrons on the nearest-neighbor  $\text{F}^-$  ions. For this

purpose, we have to take the determinantal function  $\Phi$  as

$$\Phi = \frac{1}{(5!)^{\frac{1}{2}} P} \sum (-)^P P \phi_{d2}(1) \phi_{d1}(2) \phi_{d0}(3) \phi_{d-1}(4) \phi_{d-2}(5), \quad (2)$$

where

$$\phi_{di} = N_i^{-\frac{1}{2}} [\psi_{di} - \sum_{Mm} a_{Mmi} \psi_{Mm}]. \quad (3)$$

$\psi_{di}$  is an unorthogonalized  $3d$  function of  $\text{Mn}^{++}$  ( $i = \pm 2, \pm 1, 0$ ), and  $\psi_{Mm}$  is the  $m$ th wave function ( $1s, 2s$ , or  $2p$ ) on the  $M$ th nearest-neighbor  $\text{F}^-$  ion.

$$a_{Mmi} = \langle \psi_{di} | \psi_{Mm} \rangle \quad (4)$$

is the overlap of the  $\text{Mn}^{++}$   $d_i$  orbital and the  $\text{F}^-$ -electron orbital  $\psi_{Mm}$ .

$$N_i = 1 - \sum_{Mm} a_{Mmi}^2 \quad (5)$$

is a normalization factor. The  $\phi_{di}$ 's are now orthogonal to the orbitals of the nearest-neighbor  $\text{F}^-$  ions. It then follows from Eqs. (1), (2), and (3) that in units of field (oersteds)

$$A_F = (16\pi/15) \beta_N \mu_F N_0^{-1} [a_{M2s0}^2 \langle \psi_{M2s} | \delta(\mathbf{r}_F) | \psi_{M2s} \rangle - 2a_{M2s0} \langle \psi_{d0} | \delta(\mathbf{r}_F) | \psi_{M2s} \rangle], \quad (6)$$

where  $\mu_F$  is the magnetic moment of  $\text{F}^{19}$  in nuclear magnetons ( $\beta_N$ ). The  $\text{Mn}^{++}$ - $\text{F}^-$  line is chosen as the  $z$  axis. In deriving Eq. (6) we have made the following assumptions:

(i) We have neglected the direct terms of the type  $\langle \psi_{di} | \delta(\mathbf{r}_F) | \psi_{di} \rangle$ , which were found to be extremely small in comparison to the other terms included in the square brackets in Eq. (6) (about  $10^{-3}$  of the first term and  $10^{-2}$  of the second).

(ii) We have ignored the overlaps between the  $\text{F}^-$  ions themselves.

(iii) We have also neglected the overlaps of the  $\text{Mn}^{++}$   $d_0$  electron with the inner shell  $1s$  electrons of the  $\text{F}^-$  ions.

For a preliminary orientation, Slater nodeless orbitals were used for both  $\text{Mn}^{++}$   $d_0$  electron ( $Z-s=5.6$ ) and  $\text{F}^-$   $2s$  electrons ( $Z-s=4.85$ ) in the calculation of the overlap  $a_{I2s0}$ . It is found that  $a_{I2s0}=0.17$  for  $\text{F}^-$  ions of type I.

For calculating  $\langle \psi_{I2s} | \delta(\mathbf{r}_F) | \psi_{I2s} \rangle$  and  $\langle \psi_{I2s} | \delta(\mathbf{r}_F) | \psi_{d0} \rangle$ , we used for the  $\text{F}^-$  orbital Tubis<sup>9</sup> recently calculated variation function, while for  $\text{Mn}^{++}$ , Slater orbitals were still used. We then get  $A_F^I=72$  oersteds. The first term in (6) contributes the major portion in the value of  $A_F^I$ .

If we had ignored the nonorthogonality of  $\psi_{d0}$  and  $\psi_{I2s}$ , we would have got only the term  $\langle \psi_{d0} | \delta(\mathbf{r}_F) | \psi_{d0} \rangle$  in the brackets of (6). This would give a value of 0.02 oersteds only for  $A_F^I$ . The results of this section thus emphasize the importance of considering the overlap between  $\text{Mn}^{++}$   $3d$  orbitals and the  $\text{F}^-$   $2s$  orbitals.

<sup>8</sup> E. Fermi, *Z. Physik* **60**, 320 (1930).

<sup>9</sup> A. Tubis, *Phys. Rev.* **102**, 1049 (1956).

However, the quantitative agreement with the experimental value of 19 oersteds is not good.

It will be seen from the discussion of the next paragraph that this overestimation is to be expected with Slater functions. The calculations were therefore repeated with currently available self-consistent field (S.C.F.) functions (with exchange)<sup>10,11</sup> for Mn<sup>++</sup> 3*d* and F<sup>-</sup> 2*s* orbitals.

It is seen from Figs. 2 and 3 that in the peripheral regions, the Slater orbitals for both the Mn<sup>++</sup> 3*d* state and the F<sup>-</sup> 2*s* state lie markedly above the S.C.F. orbitals. In particular, at a value of  $r=3.8$  a.u. from the Mn<sup>++</sup> ion, where the nucleus F<sup>19</sup> is situated, the Slater wave function is nearly a factor of 20 bigger than the Hartree-Fock function. This explains qualitatively the very large value of  $A_F^I$  obtained in Sec. I.

In recalculating the overlaps and other integrals in Eq. (6) using S.C.F. orbitals for Mn<sup>++</sup> 3*d* and F<sup>-</sup> 2*s* states, analytic fits are needed for the numerically tabulated wave functions. In doing this we followed the procedure outlined by Löwdin<sup>12</sup> and obtained

$$\psi_{Mn^{++}(3d_0)} = r^2 \sum_k A_k e^{-a_k r} Y_2^0(\theta, \phi), \quad (7)$$

$$\psi_{F^-(2s)} = (r_0' - r) \sum_k B_k e^{-b_k r} Y_0^0(\theta, \phi), \quad (8)$$

where

$$\begin{aligned} A_1 &= 0.11148, & A_2 &= 8.74253, & A_3 &= 68.28978, \\ a_1 &= 1.47111, & a_2 &= 2.68324, & a_3 &= 5.62181, \\ B_1 &= 0.12254, & B_2 &= 5.30446, & B_3 &= 30.0, & B_4 &= 12.4, \\ b_1 &= 1.26746, & b_2 &= 2.12980, & b_3 &= 3.97955, & b_4 &= 8.61754, \\ r_0' &= 0.24410. \end{aligned}$$

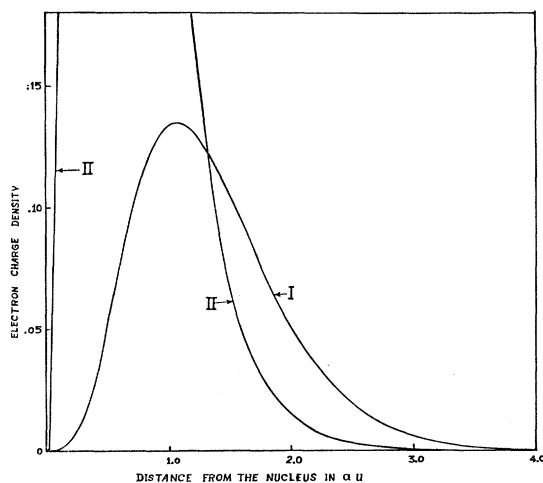


FIG. 2. Comparison of the radial dependences of the electronic charge density  $|\psi_{3d_0}|^2$  in the Mn<sup>++</sup> ion along the  $\theta=0$  direction for Slater and Hartree-Fock wave functions. Curves I and II give the charge densities obtained using Slater's nodeless orbital and Hartree-Fock orbital, respectively.

<sup>10</sup> D. R. Hartree, *Calculation of Atomic Structures* (John Wiley and Sons, Inc., New York, 1957), p. 173.

<sup>11</sup> C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

<sup>12</sup> P. Löwdin and K. Appel, Phys. Rev. **103**, 1746 (1956).

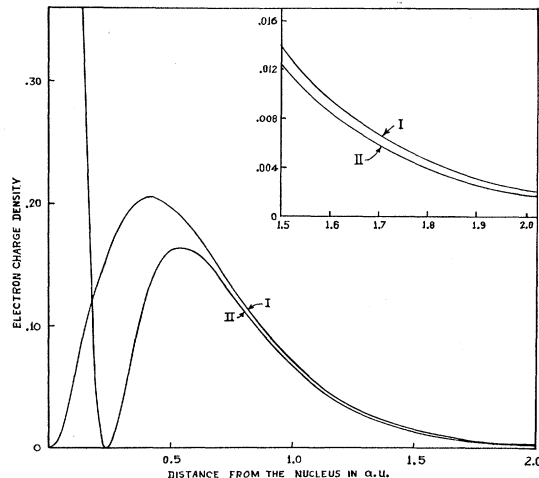


FIG. 3. Comparison of the radial dependences of the electronic charge density  $|\psi_{2s}|^2$  in the F<sup>-</sup> ion for Slater and Hartree-Fock wave functions. Curve I represents the charge density for Slater's nodeless orbital and Curve II shows that obtained using the Hartree-Fock orbital.

For the Mn<sup>++</sup> 3*d* orbitals, the fit of the analytic function to the numerical table is within 10% from large distances down to about 0.2 a.u. from the nucleus. For a good fit in the inner regions an additional exponential term would be necessary in Eq. (7). However this inner region of the Mn<sup>++</sup> ion contributes nothing significant to the F<sup>19</sup> hf interaction. For F<sup>-</sup> 2*s* orbitals, the analytic fit with the numerically tabulated function is within 1% over the whole range of  $r$ .

With these wave functions, the values of  $A_F^I$  and  $A_F^{II}$  were calculated to be 10.3 oersteds and 9.8 oersteds, respectively. We thus see that the use of Hartree-Fock wave functions improves the agreement with experiment considerably. The calculated values are still about a factor of 2 less than the experimental results. The possible causes which could produce this discrepancy are discussed in Sec. III. It is gratifying that the treatment of this section explains a fairly substantial portion (about 16%) of the observed difference between  $A_F^I$  and  $A_F^{II}$  and what is more important, in the right direction.

## II. EFFECT OF VARIOUS SOURCES OF CORRECTION ON $A_F$

In this section the effects on  $A_F$  of a number of factors not taken into account in Sec. I shall be considered. We first discuss the correction factors within the free Mn<sup>++</sup> ion and next those due to the surroundings.

While calculating the Pauli distortion effects on the Mn<sup>++</sup> *d* electrons by the F<sup>-</sup> electrons, we have taken for the free-ion orbitals in both cases the S.C.F. Hartree-Fock wave functions. The Hartree-Fock calculation takes into account only the isotropic part of the inter-electronic potential energy in the form of an additional central potential. But it disregards the statistical corre-

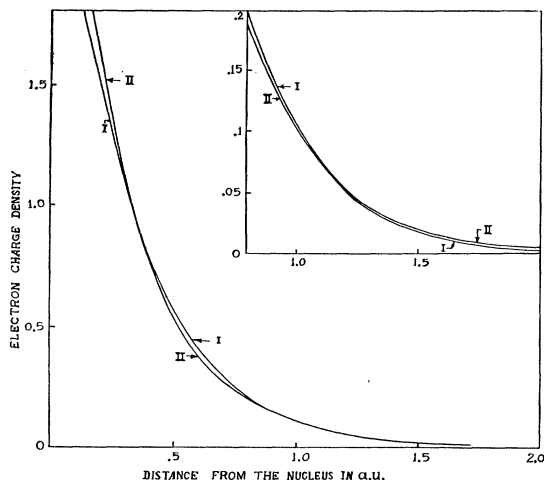


FIG. 4. Comparison of the radial dependences of the electronic charge density  $|\psi_{1s}|^2$  in the normal He atom using two different wave functions. Curve I refers to the Morse-Young-Horowitz wave function neglecting electronic correlation. Curve II refers to the Hylleraas three-parameter function which takes correlation into account.

lation between the positions of the electrons themselves. From physical considerations it is expected that this correlation effect will tend to reduce the electron density in the central region and push the electron cloud both towards the periphery as well as towards the nucleus. This is demonstrated in Fig. 4 where we compare the charge densities for the helium atom obtained by a S.C.F. procedure with those obtained from a Hylleraas 3-parameter wave function. The correlation effects within the  $Mn^{++}$  and  $F^-$  ions will thus increase the overlap terms  $a_{Mmi}$  in Eq. (4) and also the  $\delta$ -function integrals in Eq. (6). These corrections will tend to increase the calculated value of  $A_F$  and bring it closer to experiment.

We shall now discuss the correction factors due to sources external to the ions. The orbitals of each ion (aside from Pauli distortion effects) will be deformed by electrostatic interactions with the nuclei and electrons of other ions. We can divide these corrections up into two parts, (a) the electrostatic interactions with the nuclei and electrons of the nearest-neighbor ions and (b) that with other than nearest-neighbor ions, to be termed distant ions henceforth.

Effect (b) can be estimated by considering the distant ions as point charges and calculating the crystalline field due to them. We have analyzed the effects of the quadrupolar component of this crystalline field on the  $Mn^{++}$   $d$  orbitals. It is seen to lead to a deformation of the orbitals which produces a change in  $A_F$  less than

$10^{-3}$  of its value.<sup>13</sup> There is no reason to suppose that higher multipole components will contribute anything more significant.

Finally we consider the electrostatic interaction of the  $Mn^{++}$   $3d$  electrons with the nearest neighbor ions. We have the following: (a) direct electrostatic interactions with the  $F^-$  electrons and nuclei, and (b) exchange interactions with  $F^-$  electrons of parallel spin.

The effect (a) will alter the  $Mn^{++}$  orbitals as well as the  $F^-$  orbitals leading to change in the overlaps  $a_{Mmi}$  involved in Eq. (6) for  $A_F$ . However, the direction of this change cannot be predicted without actual calculations which involve the difficulties emphasized in the introduction.

Thus the exchange interaction (b) will cause the  $2s$  orbitals of  $F^-$  ions with spins parallel to the  $Mn^{++}$   $d$  electrons to be different from those with spins antiparallel. This will produce a net unbalance in the spin density of the  $F^-$   $2s$  electrons at each  $F^{19}$  nucleus leading to an additional contribution to  $A_F$ . This effect is analogous to that discussed by Heine<sup>14</sup> and by Wood and Pratt<sup>15</sup> for the nuclear hyperfine interaction within the free  $Mn^{++}$  ion itself.

## CONCLUSION

It is clear that the simple theoretical approach of Sec. II starting from an undistorted  $Mn^{++}$  ion placed within an environment of surrounding  $F^-$  ions does give satisfactory semiquantitative agreement with experimental results. The various sources of correction to this simple calculation which are discussed in Sec. II will possibly improve the agreement with experiment.

It is interesting to note that a determinant built out of the orthogonalized orbitals  $\phi_{di}$  in (2) will now include some  $L=2$  part and  $L=4$  part in addition to the predominant  $L=0$  part that was present in the free ion. This would contribute to a small shift in the spectroscopic splitting factor  $g$  from the value for the free ion.

## ACKNOWLEDGMENTS

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<sup>13</sup> The crystalline field due to distant ions was estimated using the procedure enumerated by Kanamori, Moriya, Motizuki, and Nagamiya, *J. Phys. Soc. Japan* **10**, 93 (1955). The deformation of the wave functions of the  $Mn^{++}$  ion was calculated using the variational procedure outlined by T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 734 (1956).

<sup>14</sup> V. Heine, *Phys. Rev.* **107**, 1002 (1957).

<sup>15</sup> J. H. Wood and G. W. Pratt, Jr., *Phys. Rev.* **107**, 995 (1957).