

they are responsible for a trapping level about 0.25 ev above the valence band. The behavior in *p*-type germanium which previously was not explained can be accounted for quite reasonably on the basis that a high concentration of trapping centers initially present in the material is effective in the room-temperature range. Differences in the recombination behavior among types of irradiation can be explained on the basis that particles which impart higher energy to the germanium atom produce larger numbers of isolated vacancies as compared with the number of vacancy-interstitial pairs. There is

apparently a small shift in the position of the energy level for the free vacancy in the case of neutron irradiation. This is probably due to the heavy, localized damage produced by neutron irradiation.

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### Calculation of Excitation Energies in "Tightly-Bound" Solids\*

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An approximate method of computing the energy of a localized excitation in a solid described by the Heitler-London scheme is presented. The overlap of the excited electron with wave functions centered on neighboring atoms is explicitly taken into account through terms of second order. The use of a Schmidt orthogonalization process avoids questions of convergence of the overlap series expansions found in other methods. Some further simplifying assumptions which are of possible use in ionic crystals are subsequently introduced. The formalism is applied to the system  $\text{Ne} : \text{Ar}$ . In this case it is found that the electrostatic excitation energy predicted for the  $3p^6 1S - 3p^5 4s 1P$  transition using the approximation identical to the symmetric orthogonalization method is appreciably smaller than that given by an "exact" application of the present theory. Questions concerning the reliability of some previous calculations are thus raised.

#### I. INTRODUCTION

**T**HOUGH rather exhaustive investigations of the ground state and band structure of various specific crystals have been made in the past, interest in detailed, *ab initio*, calculations for nonconducting excited states of solid systems (e.g., excitons, impurity states) has flourished only recently.<sup>1-4</sup>

The systems considered in the work just cited are either rare-gas or alkali-halide crystals, and the calculations proceed to make use of the tight-binding (Heitler-London) scheme, which is known to be a good description of the ground states. The problem of the nonorthogonality of heterocentric atomic wave functions, which arises even in calculation of the ground-state energy of the systems, becomes much more formidable when spatially diffuse atomic functions are introduced in the description of an excited state.

Thus far, all of the computations have adopted the method of symmetric orthogonalization (introduced by Löwdin<sup>5</sup> in the calculation of alkali-halide cohesive

energies) to account for the overlapping of atomic functions in both the ground and excited states. The resulting expressions for the energy are then expanded in a power series which is terminated at terms of the second order in the overlap integrals. This procedure is known to be very useful for the ground state,<sup>5</sup> but in excitation energy calculations very serious questions of the convergence of the expansion arise.<sup>1,4</sup>

However, in practice it is found that the only overlaps which contribute appreciably to the energy of the optical excitations are those involving the spatially diffuse excited electron. Thus, it seems natural to develop a formalism for such states using a Schmidt orthogonalization procedure, neglecting all other overlaps from the outset.<sup>6</sup> The convergence difficulties of the symmetric orthogonalization scheme are thereby avoided completely.

We shall, for simplicity, consider only transitions which may be described in terms of a single excited atomic state, neglecting "configuration interactions." We shall generally use the word "atom" to describe the constituent units of the crystal, whether they be ions or neutral atoms.

<sup>6</sup> The Schmidt procedure has been used previously in a limited, approximate treatment of the *F* center in ionic crystals. See the review by B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10.

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<sup>1</sup> R. S. Knox, *J. Phys. Chem. Solids* **9**, 238, 265 (1959).

<sup>2</sup> N. N. Kristoffel, *Optika i Spektroskopiya* **7**, 45 (1959) and references to earlier papers, therein.

<sup>3</sup> N. D. Potekhina, *Optika i Spektroskopiya* **8**, 437 (1960).

<sup>4</sup> A. Gold, *J. Phys. Chem. Solids* **18**, 218 (1961).

<sup>5</sup> P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

## II. WAVE FUNCTIONS AND ENERGY

Henceforth we shall assume that the Born-Oppenheimer approximation has been made and that we are discussing a lattice which is static with its atoms lying in their positions of equilibrium for the initial state of interest (which will in general depend on whether we wish to compute an absorption or emission energy). Only electrostatic interactions will be discussed, although spin-orbit terms may, of course, be treated in the same manner. We shall consider only localized excitations appropriate, say, to an impurity center, but excitations may be built from these in the manner of reference 1.

A double subscript notation will be used throughout. Thus,  $Jj$  refers to the electron which is described by quantum numbers  $j$  and is centered on nucleus  $J$ . The indices  $Aa$  are reserved for the electron which makes the transition under consideration.

The ground- and excited-state wave functions for the system are given, respectively, by

$$\Psi_0 = \alpha \psi_{Aa}(\mathbf{r}_{Aa}, \sigma_{Aa}) \prod_I \prod_{i \neq a} \psi_{Ii}(\mathbf{r}_{Ii}, \sigma_{Ii}), \quad (1a)$$

$$\bar{\Psi} = \alpha \bar{\psi}_{Aa}(\mathbf{r}_{Aa}, \sigma_{Aa}) \prod_I \prod_{i \neq a} \bar{\psi}_{Ii}(\mathbf{r}_{Ii}, \sigma_{Ii}). \quad (1b)$$

$\alpha$  is the usual antisymmetrization operator acting on all electronic coordinates,  $\mathbf{r}_{Jj}$  and  $\sigma_{Jj}$ , which are, respectively, the space and spin coordinates of electron  $Jj$ , and the  $\psi$ 's are a set of localized wave functions assumed to form an orthonormal set for each state. Based on the experience of previous calculation,<sup>1-4</sup> we shall assume that we may make the following approximations to the  $\psi$ 's:

$$\bar{\psi}_{Ii} = \psi_{Ii} = \phi_{Ii}, \quad (Ii \neq Aa) \quad (2a)$$

$$\psi_{Aa} = \phi_{Aa}, \quad (2b)$$

$$\begin{aligned} \bar{\psi}_{Aa} &= (\bar{\phi}_{Aa} - \sum_{Ii} S_{Aa, Ii} \phi_{Ii}) (1 - \sum_{Ii} (S_{Aa, Ii})^2)^{-\frac{1}{2}}, \\ &= (\bar{\phi}_{Aa} - \sum_{Ii} S_{Aa, Ii} \phi_{Ii}) N^{-\frac{1}{2}}. \end{aligned} \quad (2c)$$

Here the  $\phi_{Ii}$ 's are the solutions of the Hartree-Fock

equations for atom  $I$  in its ground state, and  $\bar{\phi}_{Aa}$  is a solution for the appropriate excited state of atom  $A$ . The overlap integral is given by

$$S_{Aa, Ii} = \int \bar{\phi}_{Aa} \phi_{Ii} d\tau - \delta_{AI} \delta_{ai}. \quad (3)$$

All other overlaps are assumed to vanish. Given these assumptions, the function, Eqs. (1a), (1b), are properly normalized.

The total energy of the system (in any state) may be written in the form

$$E = E_{\text{Nuc}} + \sum_{Ii} [Ii|H|Ii] + \frac{1}{2} \sum_{Ii} \sum_{Jj \neq Ii} \{ [IiJj|g|IiJj] - [IiJj|g|JjIi] \}. \quad (4)$$

In Eq. (4),  $E_{\text{Nuc}}$  is the energy of the nuclei having charges  $Z_I e$  at sites  $\mathbf{R}_I$ ,

$$E_{\text{Nuc}} = \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (5)$$

The second term is the kinetic energy of the electrons plus their potential energy due to the presence of the nuclei:

$$[Ii|H|Ii] = \int \psi_{Ii}^*(\mathbf{r}, \sigma) H \psi_{Ii}(\mathbf{r}, \sigma) d\tau, \quad (6)$$

where

$$H = -(\hbar^2/2m) \nabla^2 - \sum_J Z_J e^2 / |\mathbf{R}_J - \mathbf{r}|. \quad (7)$$

The last two terms of Eq. (4) are the Coulomb and exchange interactions of the electrons, and the notation should be read

$$[IiJj|g|KkLl] = \int \psi_{Ii}^*(1) \psi_{Jj}^*(2) r_{12}^{-1} \times \psi_{Kk}(1) \psi_{Ll}(2) d\tau_1 d\tau_2. \quad (8)$$

The integral over  $d\tau$  is always taken to include summation over spin coordinates. Substituting the functions of Eqs. (2) into (4), we obtain the energy of the excited state:

$$\begin{aligned} \bar{E} = E_{\text{Nuc}} &+ \sum_{Ii \neq Aa} \{ (Ii|H|Ii) + \frac{1}{2} \sum_{\substack{Jj \neq Ii \\ Jj \neq Aa}} [IiJj|g|IiJj] - (IiJj|g|JjIi) \} + \frac{1}{N} \{ (\bar{Aa}|H|\bar{Aa}) \\ &+ \sum_{Ii \neq Aa} [(\bar{Aa}Ii|g|\bar{Aa}Ii) - (\bar{Aa}Ii|g|Ii\bar{Aa})] \} - \frac{2}{N} \sum_{Ii \neq Aa} [S_{Aa, Ii} (\bar{Aa}|H|Ii) + \sum_{\substack{Kk \neq Ii \\ Kk \neq Aa}} S_{Aa, Kk} (\bar{Aa}Ii|g|KkIi)] \\ &+ \frac{1}{N} \sum_{Ii \neq Aa} [(S_{Aa, Ii})^2 (Ii|H|Ii) + \sum_{\substack{Kk \neq Ii \\ Kk \neq Aa}} (S_{Aa, Kk})^2 (KkIi|g|KkIi)]. \end{aligned} \quad (9)$$

Here the matrix elements with the parentheses are to be evaluated using atomic wave functions. The bars remind us to use the excited state function for electron  $Aa$ . The notation  $Ii \neq Jj$  on a summation instructs us to

omit the term for which  $I=J$  and  $i=j$ . Terms of third and fourth order in overlap have been dropped; this is to say that no term containing more than two products of heterocentric or orthogonal wave functions

has been retained. [Orthogonal functions centered on the same atom are included in this definition of  $O(S^2)$  not because each of the  $O(S^3)$  terms which contains them is expected to be small, but because all such terms occur in a manner giving no contribution to the calculated energy. For example, sums over terms of the form  $S_{Aa, Ii}(IiIj|g|Ij\bar{A}a)$ ,  $i \neq j$ , are omitted from both Eqs. (9) and (10a). As is easily seen, their inclusion would leave Eqs. (13) unaltered. Other rather complicated looking combinations of terms which are  $O(S^3)$  in the present sense are also omitted from Eq. (9). These combinations vanish identically in consequence of the fact that the wave functions involved are the (orthogonal) solutions of the Hartree-Fock equations for the atoms in question.] In the foregoing sense an exchange integral is said to be of second order in overlap.

From the fact that all of the wave functions appearing in Eq. (9) are solutions of the Hartree-Fock equations of the free atoms it follows that [to  $O(S^2)$ ]

$$\sum_{Ii \neq Aa} [S_{Aa, Ii}(\bar{A}a|H_I|Ii) + \sum_{Ij \neq Ii} S_{Aa, Ii}(\bar{A}aIj|g|IiIj)] \\ = \sum_{Ii \neq Aa} (S_{Aa, Ii})^2 E_{Ii}, \quad (10a)$$

$$\sum_{Ii \neq Aa} [(S_{Aa, Ii})^2(Ii|H_I|Ii) + \sum_{Ij \neq Ii} (S_{Aa, Ii})^2(IiIj|g|IiIj)] \\ = \sum_{Ii \neq Aa} (S_{Aa, Ii})^2 E_{Ii}. \quad (10b)$$

In Eqs. (10),  $E_{Ii}$  is the eigenvalue of the atomic Hartree-Fock equation for electron  $Ii$  and

$$H_I = (-\hbar^2/2m)\nabla^2 - Z_I e^2/|\mathbf{R}_I - \mathbf{r}|. \quad (11)$$

Combining Eqs. (9) and (10) with the ground-state energy of the system given by

$$E_0 = E_{\text{Nuc}} + \sum_{Ii \neq Aa} \{ (Ii|H|Ii) + \frac{1}{2} \sum_{\substack{Jj \neq Ii \\ Jj \neq Aa}} [(IiJj|g|IiJj) - (IiJj|g|JjIi)] \} + (Aa|H|Aa) \\ + \sum_{Ii \neq Aa} [(AaIi|g|AaIi) - (AaIi|g|IiAa)]. \quad (12)$$

gives the excitation energy as

$$\Delta E \equiv \bar{E} - E_0 = E_{\text{at}} + E_C + E_X + E_T. \quad (13a)$$

Here

$$E_{\text{at}} = \frac{1}{N} \bar{E}_{Aa} - E_{Aa} - \frac{1}{N} \sum_{I \neq A} \sum_i (S_{Aa, Ii})^2 E_{Ii}, \quad (13b)$$

$$E_C = \frac{1}{N} \left\{ \int |\bar{\phi}_{Aa}|^2 C^A d\tau + \sum_{Ii \neq Aa} (S_{Aa, Ii})^2 \int |\phi_{Ii}|^2 \right. \\ \left. \times (C^{AI} + C_A^a) d\tau \right\} - \int |\phi_{Aa}|^2 C^A d\tau, \quad (13c)$$

$$E_X = - \sum_{I \neq A} \sum_i \left[ \frac{1}{N} (\bar{A}aIi|g|Ii\bar{A}a) - (AaIi|g|IiAa) \right], \quad (13d)$$

$$E_T = - \frac{2}{N} \sum_{I \neq A} \sum_i S_{Aa, Ii} \int \bar{\phi}_{Aa} (C^{AI} + C_A^a) \phi_{Ii} d\tau. \quad (13e)$$

The new notations introduced in Eqs. (13) are defined as follows.  $\bar{E}_{Aa}$  and  $E_{Aa}$  are, respectively, the excited and ground state atomic Hartree-Fock energies for electron  $Aa$ .  $C_J$  is the classical electrostatic potential due to atom  $J$ :

$$C_J(\mathbf{r}) = \sum_i \int |\phi_{Ji}(\mathbf{r}', \sigma')|^2 e^2 |\mathbf{r} - \mathbf{r}'|^{-1} d\tau' \\ - Z_J e^2 |\mathbf{R}_J - \mathbf{r}|^{-1}, \quad (14a)$$

$$C_J^k(\mathbf{r}) = \sum_{j \neq k} \int |\phi_{Jj}(\mathbf{r}', \sigma')|^2 e^2 |\mathbf{r} - \mathbf{r}'|^{-1} d\tau' \\ - Z_J e^2 |\mathbf{R}_J - \mathbf{r}|^{-1}, \quad (14b)$$

$$C^{K, L, \dots} = \sum_{J \neq K, L, \dots} C_J(\mathbf{r}). \quad (14c)$$

The contributions to  $\Delta E$  are seen to have simple "physical" interpretations.  $E_{\text{at}}$  is the atomic excitation energy for the transition plus corrections due to overlap which have the somewhat surprising feature of involving the atomic energies of the unexcited electrons.  $E_C$  is in the form of a "Coulomb overlap" energy.  $E_X$  is a contribution due to the interatomic exchange.  $E_T$  is formally a "three-center" term of the sort common to computations taking overlap explicitly into account.

It should be noted that no question of convergence of an expansion enters into the derivation of Eqs. (13). They may be expected to hold with reasonable validity so long as the overlap corrections of third and fourth order are small compared to the excitation energy.

### III. COMPARISON TO PREVIOUS FORMALISMS AND SOME SIMPLIFICATIONS

To facilitate comparison with previous results, we expand  $N^{-1}$  in a power series and, once more retaining only terms of  $O(S^2)$ , obtain

$$E_{\text{at}} \approx \bar{E}_{Aa} - E_{Aa} + \sum_{Ii \neq Aa} (S_{Aa, Ii})^2 (\bar{E}_{Aa} - E_{Ii}), \quad (15a)$$

$$E_C \approx [1 + \sum_{Ii \neq Aa} (S_{Aa, Ii})^2] \left[ \int |\bar{\phi}_{Aa}|^2 C^A d\tau + \int |\phi_{Ii}|^2 (C^{AI} + C_A^a) d\tau \right] - \int |\phi_{Aa}|^2 C^A d\tau, \quad (15b)$$

$$E_X \approx - \sum_{I \neq A} \sum_i [(\bar{A}aIi|g|Ii\bar{A}a) - (AaIi|g|IiAa)], \quad (15c)$$

$$E_T \approx - 2 \sum_{I \neq A} \sum_i S_{Aa, Ii} \int \bar{\phi}_{Aa} (C^{AI} + C_A^a) \phi_{Ii} d\tau. \quad (15d)$$

Of course, this expansion is possible only if

$$\sum_{Ii} (S_{AaIi})^2 < 1.$$

For the present case of only one nonvanishing overlap, we may write the excitation energy calculated by a symmetric orthogonalization process and subsequent power series expansion as<sup>4</sup>

$$\Delta E' = E_{at}' + E_C + E_X + E_T', \quad (16a)$$

where

$$E_{at}' = \bar{E}_{Aa} - E_{Aa}, \quad (16b)$$

$$E_T' = - \sum_{Ii \neq Aa} S_{Aa, Ii} \int \bar{\phi}_{Aa} (2C^{AI} + C_I^i + C_A^a) \phi_{Ii} d\tau. \quad (16c)$$

In Eq. (16a),  $E_C$  and  $E_X$  are to be taken in the approximate form, Eqs. (15b,d), not from Eqs. (13). It should be noted that the expansion required to obtain Eqs. (16) are convergent if  $\sum_{Ii} |S_{Aa, Ii}| < 1$  and divergent if  $\sum_{Ii} S_{Aa, Ii} > 1$ . To  $O(S^2)$  the atomic Hartree-Fock equations tell us that

$$\begin{aligned} \sum_{Ii \neq Aa} [S_{Aa, Ii} (Ii | H_A | \bar{A}a) + \sum_{j \neq a} (Ii A j | g | \bar{A}a A j)] \\ = \bar{E}_{Aa} \sum_{Ii \neq Aa} (S_{Aa, Ii})^2. \end{aligned} \quad (17)$$

Combining this result with Eq. (10a) shows that

$$E_{at} + E_T = E_{at}' + E_T'. \quad (18)$$

Thus, under appropriate conditions, the two methods yield identical results. However, Eqs. (13) remain useful even in the event that the expanded symmetric orthogonalization procedure is divergent.

On the basis of our assumptions concerning the negligible overlapping of core functions, we can make some further simplifications in  $E_T$  of particular usefulness in ionic systems where the large Coulomb interactions are likely to outweigh small corrections due to small deviations from zero "core" overlaps.

If  $\phi_{Aj}$  ( $j \neq a$ ) and  $\phi_{Ii}$  are nonoverlapping, the region where  $\bar{\phi}_{Aa} \phi_{Ii} \neq 0$  does not overlap  $\phi_{Aj}$  and

$$\int \bar{\phi}_{Aa} C_A^a \phi_{Ii} d\tau = -e^2 (Z_A - N_A + 1) S_{Aa, Ii} R_{eff}^{-1}, \quad (19)$$

where  $Z_A$  and  $N_A$  are, respectively, the nuclear charge and number of electrons on atom  $A$ , and  $R_{eff}$  is the distance from the "center of gravity" of the overlap charge distribution,  $\bar{\phi}_{Aa} \phi_{Ii}$ , from nucleus  $A$ . Hence,

$$\begin{aligned} \int \bar{\phi}_{Aa} C_A^a \phi_{Ii} d\tau \\ = -e^2 (Z_A - N_A + 1) (S_{Aa, Ii})^2 |\mathbf{M}_{Aa, Ii}|^{-1}, \end{aligned} \quad (20a)$$

where

$$\mathbf{M}_{Aa, Ii} = \int \bar{\phi}_{Aa} \phi_{Ii} (\mathbf{r} - \mathbf{R}_A) d\tau. \quad (20b)$$

TABLE I. Contributions to the  $3p^6 {}^1S - 3p^5 4s {}^1P$  electrostatic excitation energy in Ne:Ar. The column headed "Exact" is the result of using Eqs. (13). The values headed "Expanded" are from Eqs. (15). All energies are in ev.

Contribution	"Exact"	"Expanded"
$E_{at}$	22.16	20.53
$E_C$	-3.36	-3.27
$E_X$	-4.63	-3.90
$E_T$	2.72	2.27
$\Delta E$	16.89	15.63
Shift from atomic value ( $\Delta E - \bar{E}_{Aa} + E_{Aa}$ )	4.47	3.27

This leaves only terms really involving three centers in  $E_T$  and may be a reasonable approximation to make even in systems of neutral atoms.

Similarly, the remaining term of  $E_T$  may be thought of as the Coulomb interaction of a charge distribution  $\bar{\phi}_{Aa} \phi_{Ii}$  and the lattice with atoms  $A$  and  $I$  removed. Thus, we may write

$$\begin{aligned} \int \bar{\phi}_{Aa} C^{AI} \phi_{Ii} d\tau = -e^2 \sum_{\substack{J \neq I \\ J \neq A}} (Z_J - N_J) S_{Aa, Ii} \\ \times |\mathbf{R}_A + (\mathbf{M}_{Aa, Ii} / S_{Aa, Ii}) - \mathbf{R}_J|^{-1}. \end{aligned} \quad (21)$$

Equation (21) is likely to be of value only in ionic crystals. The interaction has been found to be quite different from zero in simple molecular crystals.<sup>1,4</sup>

#### IV. APPLICATION TO Ne:Ar AND DISCUSSION

The method of the last section has been applied to the calculation of the electrostatic energy of the  $3p^6 {}^1S - 3p^5 4s {}^1P$  transition of the argon impurity in a solid neon lattice. The computation has been made using both the "exact" form, Eqs. (13), and the "expanded" form of Eqs. (15), recalling that the latter is equivalent to the symmetric orthogonalization results. The atomic energies appearing are taken from the appropriate wave function calculations.<sup>7-9</sup> Terms in  $E_T$  not really involving three centers were computed using the approximation of Eq. (20). All other numbers are taken from the computations of reference 4. A comparison of the results in the two cases is given in Table I.

It will be noted that  $\Delta E$  (exact)  $-\Delta E$  (expanded) = 1.26 ev. The source of the difference is apparent. For the system in question  $N=0.834$ . Comparing Eqs. (13) and (15), we see that the latter altogether neglects the deviation of  $N^{-1}$  from unity in  $E_T$  and approximates it with appreciable error in  $E_{at}$ . These two are the positive terms which are decisive in determining the excitation energy. The predicted shifts from the free atomic absorption differ by 30%.

<sup>7</sup> For excited argon: R. S. Knox, Phys. Rev. **110**, 375 (1958).

<sup>8</sup> For argon in the ground state: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 45 (1938).

<sup>9</sup> For neon: B. H. Worsley, Can. J. Phys. **36**, 289 (1958).

It should be noted that the results of reference 4 and the expanded results do not fulfill the condition  $E_{at} + E_T = E_{at}' + E_T'$ . Using  $E_{A4s} - E_{A3p}$  as the atomic excitation energy in both for consistency, still leaves the present calculation 2.36 eV above the other. The discrepancy probably arises from the computation of  $E_T'$  in the older work. The complicated integrals appearing there must be approximated in the summing of poorly convergent expansions which are used in their evaluation. In the present form most of the difficulty is "transformed away" into the simple form of  $E_{at}$ . Thus, the present results are probably more reliable. It should be pointed out that the use of  $\bar{E}_{Aa} - E_{Aa}$  as the atomic energy difference in this computation neglects some intra-atomic effects which lower the energy about 1 eV. However, these corrections are omitted for simplicity's sake alone and can be taken into account in a straightforward way. They have little effect on the predicted blue shift, which should be taken as the most significant number.

The most important insight gained from the present application is the realization of the errors encountered in the calculations using the symmetric orthogonalization procedure. The elaborate framework of that formalism has hidden a severe normalization error which arises in practical calculations of excited states. This becomes apparent in the simple Schmidt scheme.

There are two further, specific points of particular interest. Knox's predictions<sup>1</sup> for the lowest exciton states in solid argon are in severe disagreement with the experimental results of Schnepf and Dressler.<sup>10</sup> Whereas the symmetric orthogonalization theory predicts a red shift of about 2 eV, the experiments seem to indicate that the absorption lies very close to its atomic position. We conjecture that the large positive contributions to  $E_T$  and  $E_{at}$  neglected in the theory may account for the difference. Potekhina's recent calculation<sup>3</sup> finds good agreement between the observed

absorption in NaCl:Ag and the predicted energy of the Ag ion's  $4d^{10} - 4d^9 5p$  transition. However, Martienssen<sup>11</sup> has presented strong experimental evidence that the band is due to the  $4d^{10} - 4d^9 5s$  transition. The spurious coincidence of the calculated level with the observed absorption may be another manifestation of the normalization error in the symmetric orthogonalization scheme.

The present work presents a method for avoiding the question of series convergence in performing practical calculations of excitation energies explicitly involving overlap. It is based on the results of earlier work which shows that the excited electron's overlap makes the dominant contribution to the predicted energy difference. It remains valid when the usual expanded symmetric orthogonalization results are not. The results point out the possibility of making large normalization errors in symmetric orthogonalization calculations thereby engendering errors in the predicted excitation energies. Some further simplifications are suggested in the computation of the three-center contribution. If one makes additional simplifications such as representing an ionic crystal as a set of point ions surrounding the excited atom and estimating the exchange energy, then a crystal excitation energy may be quickly estimated from atomic wave functions by the comparatively simple computation of overlap and two-center-dipole matrix elements. However, more accurate computations still require the extremely lengthy task of evaluating the more complicated integrals which appear.

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<sup>10</sup> O. Schnepf and K. Dressler, J. Chem. Phys. **33**, 49 (1960).

<sup>11</sup> W. Martienssen, in the Proceedings of the 1960 Semiconductor Conference, Prague [Czech. J. Phys. (to be published)].