PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 1, NO. 1 1 JANUARY 1970

Optical Properties of Substitutional H- and Li-Atom Impurities in Solid Argon and Neon[*]

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(Received 22 July 1969)

A tight-binding formalism is presented for the calculation of the excitation energies and oscillator strengths for low-lying excitations, and of the ground-state polarizabilities, of substitutional impurities in rare-gas solids. The formalism is applied to hydrogen- and lithium-atom impurities in solid neon and in solid argon at 0°K, and numerical results are presented.

I. INTRODUCTION

EARLY theoretical studies[1,2] of the optical spectra of nonmetallic solids concerned tightly bound excited states which were approximated by the use of zero-order atomic wave functions, assumed not to overlap with the surrounding electronic charge clouds of neighbors. This picture proved to be valuable in interpreting qualitative features of observed absorption spectra of pure solids. Similarly, experience with the absorption spectra and luminescence in impure solids indicated that many luminescent centers could be qualitatively understood in terms of the atomic states of the impurity[3] and an attempt was made, in the spirit of the tight-binding approximation, to include some of the impurity-neighbor interactions for the Tl$^+$ impurity in KCl.[4,5]

During this period the technique of symmetric orthogonalization was developed[6–9] in connection with the calculation of cohesive energies of ionic crystals. This is a technique for introducing corrections to the zero-order (atomic or ionic) wave functions due to nonzero overlaps with charge clouds on neighboring atoms; it accounts in a systematic way for the changes in normalization of the pseudoatomic functions. The corrections are expressed in terms of overlap integrals S_{ab} between wave functions φ_a and φ_b centered on neighboring atoms (or ions). A sufficient condition for convergence is $\sum_b |S_{ab}| \leqslant q < 1$ for all a. The method uses a series expansion in powers of S, and the series is convergent only if the overlap integrals are small.[10] In most applications to crystal theory, the overlap integrals are, unfortunately, not small, and one has to include higher than first-order (in S) terms in a realistic calculation (if indeed the series is convergent at all) of properties of condensed systems. An S^2 calculation (that is, a calculation in which terms involving overlap up to second order are retained) is feasible, but an S^4 calculation seems beyond human capabilities, simply because of the number of such terms which must be developed algebraically. Early studies concerning impurity absorption and luminescence were at best semiquantitative. The technique of symmetric orthogonalization provided a method for including interactions between neighbors in a computation of properties of condensed systems starting from first principles. Early work[11–13] along these lines from this laboratory extended the technique to include excited states of pure solid argon and of substitutional argon impurities in solid neon in the hope that

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[*] Research supported in part by a grant from USAF Office of Scientific Research.

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the tight-binding approximation might provide a quantitative description of these systems in both ground and excited states. Excited-state overlaps were large, however, and the convergence was questionable. It was suggested[14] that Schmidt orthogonalization would solve difficulties with convergence, and the Ne:Ar problem was reworked by this means with a considerably different $3p^6\,{}^1S$-$3p^5 4s\,{}^1P$ excitation energy of a substitutional argon-atom impurity in solid neon, i.e., 16.89 eV rather than the earlier value 12.11 eV.

These methods have also been applied to the calculation of ESR properties of the Ar:H system,[15,16] the excitation energies of substitutional hydrogen impurities in solid argon,[17,18] of H_2^+ in solid helium,[19] and, with the addition of charge-transfer states, in solid neon.[20] At the same time, both pure crystalline rare gases and solid–rare-gas impurity systems were studied for their optical[21–23] and magnetic[24–26] properties. For a light-impurity atom, such as hydrogen,[27] agreement was excellent wherever the comparison could be made. In all these theoretical studies for impurity states, all host-host overlaps were neglected at the outset. As a first approximation, in some cases, the overlap of the impurity atom, in its ground state, with neighbors was also regarded as negligible.

Transition matrix elements frequently are more sensitive to details of wave functions than are energies. The present work was undertaken to provide a quantitative calculation of the $ns \longrightarrow n'p$ transition matrix elements, oscillator strengths, and ground-state polarizabilities of impurity atoms in otherwise pure solids.

In these calculations we have included the overlap of the ground-state wave function, as well as that of the excited state, of the impurity atom with neighbors, correct to second order in S. For the calculation of excitation energies, for example, inclusion of the overlap of the ground state of the impurity atom does not lead to significant corrections. In contrast, in a calculation of the optical properties, the ground-state overlaps lead to contributions comparable to those arising from the excited-state overlaps, and must not be neglected.

In Sec. II we discuss the model, in Sec. III the formalism, and in Sec. IV the results and conclusions.

II. PHYSICAL DESCRIPTION OF SYSTEM

Argon and neon crystallize in a fcc system with one atom per lattice point. Recent excellent x-ray measurements of lattice constants give the nearest-neighbor separations (extrapolated to 0°K) for pure solid argon[28] and neon[29] as $7.0970a_0$ and $5.9646a_0$, respectively. (Here $a_0 = \hbar^2/me^2$ is the Bohr radius.) Atomic hydrogen is believed to enter solid argon both substitutionally and interstitially[24,25]; in the case of hydrogen in neon, only one trapping site has been reported and a substitutional site was favored[25]; lithium also is believed to enter solid argon substitutionally.[30] We shall concern ourselves with the substitutional form only.

For a lighter (than host atoms) impurity atom at a substitutional site, the nearest neighbors would be expected to relax inwards, and in an earlier calculation[17] on the substitutional Ar:H system the twelve nearest-neighbor argon atoms were assumed to reside at a separation of $7.0a_0$. However, the inward relaxation of nearest neighbors around a vacancy in solid argon is computed[31] to be only 0.017 Å, and since an impurity atom would resist even this small inward relaxation, the relaxation magnitudes would presumably be even smaller. Furthermore, overlap integrals and two-center matrix elements are not expected to vary appreciably for such small changes in atomic separations. (See Sec. III.) Accordingly, we have carried out our calculations for all neighbors at their normal positions. We ignore thermal and zero-point vibrations, and presumably some slight error is introduced thereby. That is, the computed oscillator strength is not constant, nor does it vary linearly with separation; but over the range of thermal oscillation at 4°K, the variation in excitation energy in S and in two-center matrix elements is less than 2% in a typical case, and errors implicit in the Condon approximation should be negligible.

In constructing the crystal wave functions, all spin effects are ignored and no excited states of the host atoms are admixed. Thus, possible effects of resonance between the $1s \longrightarrow 2p$ transition of hydrogen[27] at 10.6 eV and the first discrete transition of the argon host[23] at ~12.2 eV are neglected. A gap of ~1.5 eV should make the effects of configuration interaction small in comparison to the errors inherent in the S^2 approximation.

We are not concerned here with the relaxation occurring after the absorption of a photon. We would anticipate some Stokes' shift[32] accompanying the relaxation,

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as well as Jahn-Teller effects,[32–34] but, presumably, not nearly as pronounced as in ionic crystals. We would also expect deviations[35] from the Einstein A-B relation to be small.

Finally, we stipulate that the concentration of impurity atoms is so low that impurity-impurity interactions are negligible, and for convenience we treat a large host crystal with a single substitutional impurity.

III. FORMALISM

1. Hamiltonian

Starting with a static lattice picture, we write the Hamiltonian for a system of an impurity atom with atomic number Z_I and host atoms with atomic number Z_A as

$$\begin{aligned}H=&\sum_A H_{\text{at}}+\tfrac{1}{2}\sum_A\sum_{\substack{B\\A\neq B}}\frac{z_Az_Be^2}{|\mathbf{R}_A-\mathbf{R}_B|}+\sum_A\frac{z_Iz_Ae^2}{|\mathbf{R}_I-\mathbf{R}_A|}\\&+\tfrac{1}{2}\sum_A\sum_a\sum_{\substack{B\\A\neq B}}\sum_b\frac{e^2}{|\mathbf{r}_{Aa}-\mathbf{r}_{Bb}|}+\sum_A\sum_a\sum_i\frac{e^2}{|\mathbf{r}_{Aa}-\mathbf{r}_{Ii}|}\\&-\sum_A\sum_i\frac{z_Ae^2}{|\mathbf{r}_{Ii}-\mathbf{R}_A|}-\sum_A\sum_{\substack{B\\A\neq B}}\sum_b\frac{z_Ae^2}{|\mathbf{r}_{Bb}-\mathbf{R}_A|}.\end{aligned}\tag{1}$$

We have adopted a double subscript notation. Pair Aa always refers to an electron on a host atom and the pair Ii always refers to an impurity atom electron. Lowercase indices label the electrons and the upper-case ones label the nuclei. Aa refers to an electron with position vector $\mathbf{r}_{Aa}$, localized around the Ath nuclear site at $\mathbf{R}_A$. The first term is a sum over *all* atoms for their atomic Hamiltonians H_{at}. The second and third terms are the Coulomb interaction energies between all nuclei. The fourth and fifth terms, the Coulomb interaction energies between all pairs of electrons localized around different atoms, will lead to two-center Coulomb and exchange terms in the expression for the total energy of the crystal. The sixth and the seventh terms represent the electron–other-nucleus Coulomb interactions and contribute to the Coulomb-overlap energies.

2. Crystal Wave Function

Starting from the one-electron atomic wave functions, we construct orthogonalized one-electron wave functions using the symmetric orthogonalization technique[9] for the host atomic functions and the Schmidt-orthogonalization technique[14] for the impurity atom wave functions. Under these transformations the properties of the basis functions are invariant.[36] We shall write uncorrected wave functions for the impurity atom as ϕ_{Ii} and for the host atoms as ϕ_{Aa}, often abbreviated as $|Ii\rangle$ and $|Aa\rangle$, respectively, for convenience. From these the orthogonalized wave functions ψ_{Ii} and ψ_{Aa} will be constructed, and often written as $|Ii)$ and $|Aa)$ for convenience. The total crystal wave function will be constructed from these wave functions.[37]

For an impurity electron in a state described by i (i stands for a set of quantum numbers n, l, m_l, σ), we write the orthogonalized wave functions ψ_{Ii} as

$$\psi_{Ii}=N_i\Big[\phi_{Ii}-\sum_A\sum_a S_{Ii,Aa}\psi_{Aa}\Big].\tag{2}$$

Here $S_{Ii,Aa}$ is an overlap integral which determines the amount of mixing of ψ_{Aa} into ϕ_{Ii}, and is given by

$$S_{Ii,Aa}=\int\phi_{Ii}(\mathbf{r})\psi_{Aa}(\mathbf{r})d\mathbf{r}-\delta_{IA}\delta_{ia}.\tag{3}$$

N_i is a normalization constant for the corrected wave function and is given by

$$N_i=\Big[1-\sum_A\sum_a(S_{Ii,Aa})^2\Big]^{-1/2}.\tag{4}$$

According to the symmetric orthogonalization technique, ψ_{Aa} is written as

$$\psi_{Aa}=\sum_B\sum_b\big[(\mathbf{1}+\mathbf{S})^{-1/2}\big]_{Aa,Bb}\phi_{Bb}.\tag{5}$$

Here $\mathbf{1}$ and $\mathbf{S}$ are, respectively, the unit and overlap matrices. The elements of the overlap matrix determine the amount of mixing of other host-atomic functions into ϕ_{Aa}, and are given by

$$S_{Aa,Bb}=\int\phi_{Aa}(\mathbf{r})\phi_{Bb}(\mathbf{r})d\mathbf{r}-\delta_{AB}\delta_{ab}.\tag{6}$$

By definition we have that $S_{Aa,Ab}=\delta_{ab}$. This simply describes the orthonormality of atomic wave functions. The right-hand side of Eq. (5) can now be expanded into a power series in terms of overlap integrals. Since all host atoms are in their ground states and do not overlap very strongly, the convergence condition[10] is easily fulfilled for both argon and neon hosts.

Carrying out the expansion we obtain

$$\begin{aligned}\psi_{Aa}=\phi_{Aa}-\tfrac{1}{2}\sum_B\sum_b S_{Aa,Bb}\phi_{Bb}\\+\tfrac{3}{8}\sum_B\sum_b\sum_C\sum_c S_{Aa,Cc}S_{Cc,Bb}\phi_{Bb}.\end{aligned}\tag{7}$$

We stop at terms in second order in overlap integrals. This is an approximation, and will be referred to as the S^2 approximation. Within this approximation, all terms

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involving overlap quantities of higher than second order will be neglected. A two-center matrix element will be treated as a quantity of order S and a two-center exchange integral will be treated as a term of order S^2.

For an excited state of the impurity atom, we have an expression similar to Eq. (2). An excited-state wave function will be denoted by a bar; hence for an excited state of the impurity atom denoted by a set of quantum numbers j, we write

$$\bar{\psi}_{Ij}=\bar{N}_j[\bar{\phi}_{Ij}-\sum_A\sum_a \bar{S}_{Ij,Aa}\psi_{Aa}], \tag{8}$$

with

$$\bar{S}_{Ij,Aa}=\int\bar{\phi}_{Ij}(\mathbf{r})\psi_{Aa}(\mathbf{r})d\mathbf{r}-\delta_{IA}\delta_{ja} \tag{9}$$

and

$$\bar{N}_j=[1-\sum_A\sum_a (\bar{S}_{jI,Aa})^2]^{-1/2}. \tag{10}$$

We shall now briefly comment on the convergence questions arising out of expanding the right-hand side of Eq. (5). As has been assumed earlier, no excited states of host atoms are admixed; the ground-state overlaps being small, the convergence criterion is met and the use of Eq. (7) is valid. If the symmetric orthogonalization technique were to be used for excited states, then because of the diffuse nature of the excited states, the overlap integrals would be so large that the convergence criterion would usually not be met.[13] Gold[14] suggested that this difficulty can be avoided by the use of the Schmidt procedure for writing corrected excited-state wave functions. The convergence difficulties are modified and alleviated by this approach, but they are not entirely eliminated. That is, in using Eq. (8) for constructing the excited-state wave function, we might find that the overlaps (of the excited-state wave function with neighboring charge clouds) are sufficiently large that $\sum_A\sum_a(\bar{S}_{Ij,Aa})^2$ approaches or even exceeds unity. [For *ns-n′s* overlap, if S were equal to $(0.25/3)^{1/2}=0.289$, the lattice sum for an fcc lattice would equal unity; for *np-n′s* overlap, S would have to be 0.5 for the lattice sum to be equal to unity.] If overlaps were large enough to create this problem (that is to make the normalization constant approach infinity), one would not be justified in assuming a tight-binding picture for that state. However, overlap of this state with second neighbors may be small. In such cases, a cluster comprising the central (impurity) atom and all nearest neighbors should be treated exactly, as one unit. The wave function of this pseudomolecule should then be Schmidt-orthogonalized to the rest of the atoms of the crystal, symmetrically orthonormalized as before. We do not encounter this difficulty with systems treated here.

Using the orthogonalized wave functions (2), (7), and (8), we now write the crystal wave functions in the absence of all external fields as

$$\Psi=\mathfrak{A}\psi_{Ii}(\mathbf{r}_{Ii},\boldsymbol{\sigma}_{Ii})\prod_A\prod_a\psi_{Aa}(\mathbf{r}_{Aa},\boldsymbol{\sigma}_{Aa}),\quad Aa\neq Ii \tag{11}$$

and

$$\bar{\Psi}=\mathfrak{A}\bar{\psi}_{Ij}(\mathbf{r}_{Ij},\boldsymbol{\sigma}_{Ij})\prod_A\prod_a\psi_{Aa}(\mathbf{r}_{Aa},\boldsymbol{\sigma}_{Aa}),\quad Aa\neq Ij \tag{12}$$

for the ground and excited states, respectively. $Aa\neq Ii$ excludes the function for which $A=I$ and $a=i$. Thus, in Eqs. (11) and (12), Aa runs over all occupied host electronic states and over all impurity electronic states except the one which is involved in the transition. $\mathfrak{A}$ is the usual antisymmetrization operator and $\mathbf{r}$ and $\boldsymbol{\sigma}$ are the usual space and spin coordinates.

In writing Eqs. (11) and (12) it has been implicitly assumed that the "core" electronic wave functions for the impurity atom are the same for both ground and excited states. For the hydrogen atom, of course, there are no core electrons; but for lithium there are two $1s$ electrons. Core electrons are usually very tightly bound and their wave functions are almost parallel (in function space) in the ground and excited states.

From Eqs. (6) and (7) we can immediately see that all ψ_{Aa} form an orthonormal set, to order S^2. Similarly, the impurity wave functions ψ_{Ii} and $\bar{\psi}_{Ij}$ are orthogonal to each other and to the core electronic wave functions to a certain approximation. That is, ψ_{Ii} and $\bar{\psi}_{Ij}$ would be exactly orthogonal to each other if the lattice sum $\sum_A\sum_a S_{Ii,Aa}\bar{S}_{Ij,Aa}$ were to vanish. This sum does vanish for a cubic lattice if the ground state is an S state and the excited state is a P state. This being the case in this work, the ground- and excited-state wave functions ψ_{Ii} and $\bar{\psi}_{Ij}$ are exactly orthogonal; similar comments apply to orthogonality of the core electronic states to the excited states (and also to the ground state). Core electrons are, however, quite tightly bound and do not overlap with neighbors appreciably. The overlap integrals are very small, leading to a negligibly small nonorthogonality of the core electronic states to the valence electronic states. We shall regard these states as exactly orthogonal to each other.

3. Energy Parameters

The total energy of the crystal is given by the expectation value of the Hamiltonian. For the ground state, the crystal energy is given by

$$E=\int\Psi^*H_0\Psi d\tau. \tag{13}$$

Here $d\tau$ denotes integration over all space and summation over all spin variables. The asterisk denotes complex conjugation. Substituting from Eqs. (1) and (11), we obtain

$$\begin{aligned}E=E_N&+\sum_A\sum_a(Aa|H|Aa)+\sum_i(Ii|H|Ii)\\&+\tfrac{1}{2}\sum_A\sum_a\sum_B\sum_b{}_{Aa\neq Bb}[(AaBb|g|AaBb)-(AaBb|g|BbAa)]\\&+\tfrac{1}{2}\sum_i\sum_j{}_{i\neq j}[(IiIj|g|IiIj)-(IiIj|g|IjIi)]\\&+\sum_A\sum_a\sum_i[(AaIi|g|AaIi)-(AaIi|g|IiAa)].\end{aligned} \tag{14}$$

Here E_N is the total nuclear repulsion energy, that is, the sum of the expectation values of the second and third term in Eq. (1). H is defined to be

$$H=-\frac{h^2}{2m}\nabla^2-\sum_A\frac{z_Ae^2}{|\mathbf{r}-\mathbf{R}_A|}-\frac{z_Ie^2}{|\mathbf{r}-\mathbf{R}_I|}, \qquad (15)$$

and g is the operator $e^2/|\mathbf{r}_1-\mathbf{r}_2|$. Here the matrix elements in parentheses are to be evaluated using the orthogonalized wave functions ψ, that is,

$$(Aa|H|Aa)=\int\psi_{Aa}^*(\mathbf{r})H\psi_{Aa}(\mathbf{r})d\mathbf{r}$$

and

$$(AaBb|g|AaBb)=\int\psi_{Aa}^*(\mathbf{r}_1)\psi_{Bb}^*(\mathbf{r}_2)\times\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{Aa}(\mathbf{r}_1)\psi_{Bb}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \qquad (16)$$

We now wish to express the elements in Eq. (14) in terms of the atomic wave functions. The details are presented elsewhere.[36] Since no host excited states are allowed and since core electronic states are the same for both ground and excited states, some labor can be saved by writing all such elements, which cancel out when a difference is taken of the ground- and excited-state crystal energies, collectively as E_0, that is,

$$\begin{aligned}E_0=E_N&+\sum_A\sum_a(Aa|H|Aa)+\sum_{k\neq i}(Ik|H|Ik)\\&+\tfrac{1}{2}\sum_{\substack{A\\Aa\neq Bb}}\sum_a\sum_B\sum_b[(AaBb|g|AaBb)-(AaBb|g|BbAa)]\\&+\tfrac{1}{2}\sum_{\substack{k\\k,l\neq i}}\sum_l[(IkIl|g|IkIl)-(IkIl|g|IlIk)]\\&+\sum_{k\neq i}\sum_A\sum_a[(IkAa|g|IkAa)-(IkAa|g|AaIk)]. \qquad (17)\end{aligned}$$

Hence the ground-state crystal energy can be written as

$$\begin{aligned}E=E_0&+(Ii|H|Ii)\\&+\sum_{k\neq i}[(IiIk|g|IiIk)-(IiIk|g|IkIi)]\\&+\sum_A\sum_a[(IiAa|g|IiAa)-(IiAa|g|AaIi)]. \qquad (18)\end{aligned}$$

Similarly, for the excited state the crystal energy is

$$\begin{aligned}\bar{E}=E_0&+(\bar{I}j|H|\bar{I}j)\\&+\sum_{k\neq j}[(\bar{I}jIk|g|\bar{I}jIk)-(\bar{I}jIk|g|Ik\bar{I}j)]\\&+\sum_A\sum_a[(\bar{I}jAa|g|\bar{I}jAa)-(\bar{I}jAa|g|Aa\bar{I}j)]. \qquad (19)\end{aligned}$$

The elements in Eqs. (18) and (19) can be expressed in terms of atomic wave functions. Using atomic Hartree-Fock equations, the ground-state crystal energy can be written as

$$E=E_0+E_{\text{at}}+E_C+E_{\text{ex}}+E_T+E_S, \qquad (20)$$

with

$$E_{\text{at}}=N_i^2[E_{Ii}-\sum_A\sum_a(S_{Ii,Aa})^2E_{Aa}], \qquad (21\text{a})$$

$$E_{\text{C}}=N_i^2[\langle Ii|C^I|Ii\rangle+\sum_A\sum_a(S_{Ii,Aa})^2\langle Aa|C^{I,A}+C_I^i|Aa\rangle], \qquad (21\text{b})$$

$$E_{\text{ex}}=-N_i^2\sum_{Aa}\langle IiAa|g|AaIi\rangle, \qquad (21\text{c})$$

$$\begin{aligned}E_{\text{T}}=&-2N_i^2\sum_A\sum_aS_{Ii,Aa}\langle Ii|C^{I,A}+C_I^i|Aa\rangle\\&+N_i^2\sum_{k\neq i}\sum_A\sum_a(S_{Ik,Aa})^2[\langle IiIk|g|IiIk\rangle\\&\qquad-\langle IiIk|g|IkIi\rangle], \qquad (21\text{d})\end{aligned}$$

$$\begin{aligned}E_S=&N_i^2\sum_{k\neq i}N_k^2\sum_A\sum_a(S_{Ik,Aa})^2\langle IiAa|g|IiAa\rangle\\&-2N_i^2\sum_{k\neq i}N_k^2\sum_A\sum_aS_{Ik,Aa}\langle IiIk|g|IiAa\rangle\\&+N_i^2\sum_A\sum_a\sum_B\sum_b(S_{Aa,Bb})^2\langle IiAa|g|IiAa\rangle\\&-N_i^2\sum_A\sum_a\sum_B\sum_bS_{Aa,Bb}\langle IiAa|g|IiBb\rangle. \qquad (21\text{e})\end{aligned}$$

Here we have used the notation

$$C_A=\sum_a\langle Aa|g|Aa\rangle-\frac{z_Ae^2}{|\mathbf{r}-\mathbf{R}_A|}, \qquad (22\text{a})$$

$$C^{I,J,\cdots}=\sum_{M\neq I,J,\cdots}C_M, \qquad (22\text{b})$$

$$C_I^i=\sum_{k\neq i}\langle Ik|g|Ik\rangle-\frac{z_Ie^2}{|\mathbf{r}-\mathbf{R}_I|}. \qquad (22\text{c})$$

In Eqs. (21) and (22) the matrix elements are evaluated using atomic wave functions ϕ, that is,

$$\langle Aa|g|Aa\rangle=\int\phi_{Aa}^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_{Aa}(\mathbf{r}')d\mathbf{r}'-\frac{z_Ae^2}{|\mathbf{r}-\mathbf{R}_A|}, \qquad (23\text{a})$$

$$\langle AaBb|g|AaBb\rangle=\int\phi_{Aa}^*(\mathbf{r}_1)\phi_{Bb}^*(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\times\phi_{Aa}(\mathbf{r}_1)\phi_{Bb}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \qquad (23\text{b})$$

In Eq. (21a) E_{Ii} and E_{Aa} are the atomic Hartree-Fock energies for the respective electronic states. C^I is simply the classical Coulomb potential at the Ith atom due to all other atoms in the solid.

The excited-state crystal energy can be similarly calculated. The total energy is given by

$$\bar{E}=E_0+\bar{E}_{\mathrm{at}}+\bar{E}_{\mathrm{ex}}+\bar{E}_C+\bar{E}_T+\bar{E}_S. \qquad (24)$$

All quantities in Eq. (24) are defined by equations similar to those for corresponding ground-state quantities and can be obtained from Eqs. (21) and (22) by the transcription

$$Ii\rightarrow\bar{I}_j$$

and

$$N_i\rightarrow\bar{N}_j. \qquad (25)$$

The excitation energy for the ground → excited-state transition of the impurity atom is given by $\bar{E}-E$ plus corrections arising out of the van der Waals energy differences for the ground and excited states and other higher-order corrections, and can be written as

$$\Delta E=\Delta E_{\mathrm{at}}+\Delta E_C+\Delta E_{\mathrm{ex}}+\Delta E_T+\Delta E_S+\Delta E_{d\text{-}d}. \qquad (26)$$

The contributions to ΔE are seen to have simple physical meaning. ΔE_{at} is the atomic excitation energy plus corrections (due to overlap) involving the atomic Hartree-Fock energies for the host atoms. ΔE_C is the change in Coulomb-overlap energy. ΔE_{ex} is the contribution from the exchange energy terms. ΔE_T and ΔE_S are correction terms due to nonzero overlaps. $\Delta E_{d\text{-}d}$ is the contribution due to van der Waals energy differences between the ground and excited states.

For the computation of $\Delta E_{d\text{-}d}$ we follow the approach due to Buckingham,[38] where the small effects of nonzero overlaps are neglected. This contribution $\Delta E_{d\text{-}d}$ to the total excitation energy ΔE is small, and hence the over-all error in ΔE from neglect of overlap in $\Delta E_{d\text{-}d}$ is insignificant. We use the formula

$$C_{lm}=\frac{4}{9}\sum_{Ai}\sum_{Bj}\frac{[(R^2)_{Ai}]^2[(R^2)_{Bj}]^2}{(R^2)_{Ai}+(R^2)_{Bj}}\,\frac{E_l+E_m}{2}, \qquad (27)$$

with

$$(R^2)_{Ai}=\langle Ai|r^2|Ai\rangle-\sum_{j\neq i}\sum_{\mu=x,y,z}\langle Ai|x_\mu|Aj\rangle^2. \qquad (28)$$

Here the summation over μ runs over the Cartesian coordinates x, y, and z measured from the nucleus of atom A. The sum over i and j run over all occupied electronic states. The l and m refer to the "configuration" of the atoms A and B, respectively. The van der Waals energy between the atoms A and B is given by $-C_{lm}/R_{AB}{}^6$. This is summed over all neighbors in the crystal. $(E_l+E_m)/2$ is a mean excitation energy.

4. Oscillator Strength

The oscillator strength tensor $\mathbf{f}_{ij}{}^{lm}$ is defined as

$$\mathbf{f}_{ij}{}^{lm}=\frac{2m_0E_{ij}}{\hbar^2}\langle i|\rho_l|j\rangle\langle j|\rho_m|i\rangle. \qquad (29)$$

Here E_{ij} is the excitation energy between states characterized by quantum numbers i and j; $\langle i|\rho_l|j\rangle$ is the transition matrix element of the l component of operator ρ between the initial and final states; $\hat{l}$, $\hat{m}$, and $\hat{n}$ are unit vectors along the Cartesian axes; the vector operator $\boldsymbol{\rho}$ is defined to be the sum of all electronic coordinates. For an $s\rightarrow p$ transition in a cubic lattice (or for a free atom), the tensor reduces to a scalar and we have

$$f_{ij}=\frac{2m_0E_{ij}}{\hbar^2}|\langle i|\rho_z|j\rangle|^2. \qquad (30)$$

Overlap effects change the value of the oscillator strength from the free-atom value, both in the excitation energy E_{ij} (treated above) and in the transition matrix element:

$$M=\int\bar{\Psi}^*\rho_z\Psi d\tau. \qquad (31)$$

Rewriting the crystal wave functions $\bar{\Psi}$ and Ψ in terms of the atomic Hartree-Fock functions ϕ and simplifying within the S^2 approximation, we obtain

$$\begin{aligned}M_{i\rightarrow j}=N_i\bar{N}_j\Big[\langle\bar{I}j|z|Ii\rangle&-\sum_A\sum_a\bar{S}_{Ij,Aa}\langle Aa|z|Ii\rangle\\&-\sum_A\sum_a S_{Ii,Aa}\langle Aa|z|\bar{I}j\rangle\\&+\sum_A\sum_a\sum_{b\neq a}S_{Ii,Aa}\bar{S}_{Ij,Ab}\langle Aa|z|Ab\rangle\\&+\sum_A\sum_a S_{Ii,Aa}\bar{S}_{Ij,Aa}R_{IA}\cos\Theta_{IA}\Big]. \qquad (32)\end{aligned}$$

Here R_{IA} is the distance of the Ath host atom from the impurity atom, which will be taken as the origin of the coordinate system. Θ_{IA} is the angle between the Z axis and the vector pointing toward the site of the Ath atom from the origin, and

$$\langle\alpha|z|\beta\rangle=\int\phi_\alpha(\mathbf{r})z\phi_\beta(\mathbf{r})d\mathbf{r}. \qquad (33)$$

The first term within the square bracket in Eq. (32) is the free-atom dipole matrix element between the initial and final states. The second term involves the overlap of the excited state of the impurity atom with the host neighbors and the two-center dipole matrix element connecting the ground state of the impurity atom with the host neighbors. The third term describes the contribution from the overlap of the ground state of the impurity atom with the medium and the two-center matrix element connecting the excited state of the impurity atom with the host neighbors. The fourth and fifth terms describe the contributions from the dipole matrix elements (and orthonormality) on the host neighbors, coupled by an impurity atom ground-state and an excited-state overlap. Contributions involving host-host overlaps arise only in third order (in S). Since we

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[38] R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 (1937); **A160**, 113 (1937).

retain terms up to second order only, these do not appear in the expression for the transition matrix element.

Corrections to the dipole matrix element [second to fifth terms in square bracket in Eq. (32)] tend to decrease their values. The normalization factors N_i and $\bar{N}_j$ are always greater than unity and act to increase the values of the dipole matrix elements.

It should be emphasized here that the third, fourth, and fifth terms involve overlap of the ground state of the impurity atom with the host atoms. These overlaps may be small (so that the ground-state normalization factor N_i does not differ from unity appreciably), but they lead to contributions which are comparable to or larger (see below) than those coming from the second term, which would be the only correction term if the excited-state impurity atom function were orthogonalized to the host atoms. Since both ground- and excited-state wave functions of the impurity atom appear implicitly in each term, it is essential to orthogonalize the ground-state wave function of the impurity atom, as well as that of the excited state, to the neighbors. In contrast, note that for calculations of energy differences, the ground-state overlaps might well be neglected with no appreciable error. This is an important difference, and serves to emphasize the assertion that oscillator strength calculations are more sensitive to wave functions than are energies.

5. Polarizability

For convenience in this section, a host crystal of $N-1$ host atoms at their normal sites and a single vacancy will be called a vacancy crystal; one containing $N-1$ host atoms and an impurity atom will be called an impurity crystal. We shall adopt a variational approach. Crystal wave functions for the vacancy and the impurity crystals in the presence of an external electric field $\boldsymbol{\mathcal{E}}$ are constructed from the orthogonalized one-electron wave functions. We shall use two variational parameters. One parameter describes the effect of the medium and the other describes effects due to interactions between the impurity atom and the host solid. Ideally, one should like to include as many variational parameters for the impurity atoms as the number of occupied shells of the impurity atom, because all electronic states of the impurity atom have different interactions (for example, overlap) with the host atoms. However, such an approach does not seem computationally feasible when overlap effects are taken into account, and we use only one parameter to describe the impurity-host interactions. We should not expect the one-parameter formalism to yield an accurate value even for the polarizability of a free atom. However, the *change* in the value of polarizability of the impurity atom, from the free-atom value, due to the host-impurity interactions would be an important quantity. The formalism would also give the polarizability of a host atom in the pure-host solid and also that of a free-host atom. Again these quantities are not expected to be accurate, and only the change in the value of polarizability is expected to be significant.

We define the crystal wave functions for the vacancy and impurity crystals, respectively, as

$$\Psi_v{}^0=\mathcal{A}_v\Phi\prod_{A\neq I}\prod_a\psi_{Aa}(\mathbf{r}_{Aa},\boldsymbol{\sigma}_{Aa}) \tag{34}$$

and

$$\Psi_I{}^0=\mathcal{A}_I\prod_i\psi_{Ii}(\mathbf{r}_{Ii},\boldsymbol{\sigma}_{Ii})\prod_{A\neq I}\prod_a\psi_{Aa}(\mathbf{r}_{Aa},\boldsymbol{\sigma}_{Aa})\,, \tag{35}$$

in the absence of an externally applied electric field (indicated by the superscript 0). Here $\mathcal{A}_v$ and $\mathcal{A}_I$ are the proper antisymmetrization operators. $A\neq I$ disallows the occupation of the vacant site at the origin by a host atom; the impurity atom goes in substitutionally at this site in the impurity crystal. We denote the crystal Hamiltonians for the vacancy and the impurity crystals by H_v and H_I, respectively, in the absence of an external field. When an external electric field $\boldsymbol{\mathcal{E}}$ is applied along the Z direction of the crystal frame of reference, there is an accompanying change in the potential energy. The perturbation Hamiltonian for the vacancy crystal is

$$v_1=-e\mathcal{E}\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)\,, \tag{36}$$

and that for the impurity crystal is

$$v_1+v_2=-e\mathcal{E}\Big[\sum_i(z_{Ii}-Z_I)+\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)\Big]. \tag{37}$$

v_2 is the perturbation Hamiltonian for the impurity atom only. Due to these perturbations, the crystal wave functions are expected to change from their unperturbed (zero field) values. Following the variational approach, we write the crystal wave functions as

$$\Psi_v=\Psi_v{}^0(1+\lambda_1v_1) \tag{38}$$

and

$$\Psi_I=\Psi_I{}^0(1+\lambda_1v_1+\lambda_2v_2) \tag{39}$$

for the vacancy and impurity crystals, respectively. λ_1 and λ_2 are the two variational parameters and must be determined in a consistent manner. λ_1 describes the changes in the vacancy crystal wave function due to the external field (assumed uniform over the extent of the crystal), and λ_2 describes the changes in the impurity crystal wave function due to changes at the impurity site when the electric field is turned on. λ_1 and λ_2 are determined by minimizing the expectation values of H_v+v_1 in state Ψ_v and of $H_I+v_1+v_2$ in state Ψ_I, respectively. Let E_v denote the energy of the vacancy crystal

$$E_v=\langle\Psi_v|(H_v+v_1)|\Psi_v\rangle/\langle\Psi_v|\Psi_v\rangle\,. \tag{40}$$

Here, we use the notation

$$\langle\Psi_v|H_v+v_1|\Psi_v\rangle=\int\Psi_v{}^*(H_v+v_1)\Psi_v d\tau\,. \tag{41}$$

Substituting for Ψ_v, we obtain

$$E_v=\frac{\langle\Psi_v{}^0|(1+\lambda_1 v_1)(H_v+v_1)(1+\lambda_1 v_1)|\Psi_v{}^0\rangle}{\langle\Psi_v{}^0|(1+\lambda_1 v_1)(1+\lambda_1 v_1)|\Psi_v{}^0\rangle}. \tag{42}$$

Using the fact that v_1 is an odd operator and H is an even operator, some terms in Eq. (42) are seen to vanish, and we obtain

$$E_v=\frac{\langle\Psi_v{}^0|H_v+2\lambda_1 v_1{}^2+\lambda_1{}^2 v_1 H_v v_1|\Psi_v{}^0\rangle}{\langle\Psi_v{}^0|1+\lambda_1{}^2 v_1{}^2|\Psi_v{}^0\rangle}. \tag{43}$$

The parameter λ_1 is now determined by minimizing E_v with respect to λ_1. After dropping terms proportional to $\mathcal{E}^4$ (which lead to nonlinear polarizability), we obtain

$$\lambda_1=-\frac{\langle\Psi_v{}^0|v_1{}^2|\Psi_v{}^0\rangle}{\langle\Psi_v{}^0|v_1 H_v v_1|\Psi_v{}^0\rangle-\langle\Psi_v{}^0|H_v|\Psi_v{}^0\rangle\langle\Psi_v{}^0|v_1{}^2|\Psi_v{}^0\rangle}. \tag{44}$$

The denominator can be simplified by using the fact that v_1 commutes with everything in H_v except the kinetic energy terms, and we obtain

$$\lambda_1=-\frac{\langle\Psi_v{}^0|v_1{}^2|\Psi_v{}^0\rangle}{(\hbar^2/2m)\langle\Psi_v{}^0|\sum_{A\neq I}\sum_a(\nabla_{Aa}v_1)^2|\Psi_v{}^0\rangle+\Delta}, \tag{45}$$

with

$$\Delta=\langle\Psi_v{}^0|v_1{}^2 H_v v_1{}^2|\Psi_v{}^0\rangle-\langle\Psi_v{}^0|v_1{}^2|\Psi_v{}^0\rangle\langle\Psi_v{}^0|H_v|\Psi_v{}^0\rangle. \tag{46}$$

The quantity Δ as defined by Eq. (46) would vanish if $\Psi_v{}^0$ were an exact eigenfunction of the Hamiltonian H_v. Since $\Psi_v{}^0$ is only an approximate eigenfunction of H_v, because of electron-electron correlations, Δ is not identically zero, but is expected to be very small. In our calculations we shall set $\Delta=0$. More will be said about this approximation in Sec. IV. The denominator of Eq. (45) can be simplified by the use of Eq. (36), and λ_1 is found to be

$$\lambda_1=-\frac{2m\langle\Psi_v{}^0|v_1{}^2|\Psi_v{}^0\rangle}{\hbar^2(N-1)Z_A e^2\mathcal{E}^2}. \tag{47}$$

The parameter λ_2 is determined in a similar manner. When an impurity atom is introduced at the vacant site, the crystal energy is changed. Since λ_2 describes the effect of such changes, we determine λ_2 by requiring that the total energy of the impurity crystal be a minimum with respect to λ_2 (with λ_1 as determined earlier). Hence, we set equal to zero the partial derivative with respect to λ_2 of the expectation value of $H_I+v_1+v_2$ in state Ψ_I. Again we neglect terms proportional to $\mathcal{E}^4$ since we are interested in the linear polarizability only. After considerable simplifications we may write λ_2 in the form

$$\begin{aligned}\lambda_2=-[&2\langle\Psi_I{}^0|v_2(v_1+v_2)|\Psi_I{}^0\rangle\\&+\lambda_1(\langle\Psi_I{}^0|v_1 H_I v_2+v_2 H_I v_1|\Psi_I{}^0\rangle\\&-2\langle\Psi_I{}^0|H_I|\Psi_I{}^0\rangle\langle\Psi_I{}^0|v_1 v_2|\Psi_I{}^0\rangle)]\\&\times(2\langle\Psi_I{}^0|v_2 H_I v_2|\Psi_I{}^0\rangle\\&\qquad-2\langle\Psi_I{}^0|H_I|\Psi_I{}^0\rangle\langle\Psi_I{}^0|v_2{}^2|\Psi_I{}^0\rangle)^{-1}.\end{aligned} \tag{48}$$

Again, the numerator and the denominator can be simplified by using the fact that v_1 and v_2 commute with everything in H_I except the kinetic energy operators, and λ_2 can be written as

$$\lambda_2=-\frac{2\langle\Psi_I{}^0|v_2(v_1+v_2)|\Psi_I{}^0\rangle+\lambda_1\Delta_1}{(\hbar^2/m)\langle\Psi_I{}^0|\sum_i(\nabla_{Ii}v_2)^2|\Psi_I{}^0\rangle+\Delta_2}, \tag{49}$$

with

$$\Delta_1=\langle\Psi_I{}^0|v_1 v_2 H_I|\Psi_I{}^0\rangle-\langle\Psi_I{}^0|v_1 v_2|\Psi_I{}^0\rangle\langle\Psi_I{}^0|H_I|\Psi_I{}^0\rangle \tag{50}$$

and

$$\Delta_2=\langle\Psi_I{}^0|H_I v_2{}^2|\Psi_I{}^0\rangle-\langle\Psi_I{}^0|H_I|\Psi_I{}^0\rangle\langle\Psi_I{}^0|v_2{}^2|\Psi_I{}^0\rangle. \tag{51}$$

As in the case of Δ above, Δ_1 and Δ_2 do not vanish, and contribute to λ_2 formally. However, both Δ_1 and Δ_2 depend on four-electron operators, and we neglect them as in the case of Δ above. The expression for λ_2 can be simplified by using Eq. (37), and λ_2 is found to be

$$\lambda_2=-\frac{2m\langle\Psi_I{}^0|v_2(v_1+v_2)|\Psi_I{}^0\rangle}{\hbar^2 z_I e^2\mathcal{E}^2}. \tag{52}$$

We now calculate the crystal dipole moments for the vacancy and impurity crystals. The total dipole moment of the vacancy crystal is given by

$$\mathbf{P}_v=e\langle\Psi_v|\sum_{A\neq I}\sum_a(\mathbf{r}_{Aa}-\mathbf{R}_A)|\Psi_v\rangle. \tag{53}$$

When an impurity atom is residing at the previously vacant site, its charges are displaced by the applied electric field. The total dipole moment of the impurity crystal is

$$\mathbf{P}_I=e\langle\Psi_I|\sum_i(\mathbf{r}_{Ii}-\mathbf{R}_I)+\sum_{A\neq I}\sum_a(\mathbf{r}_{Aa}-\mathbf{R}_A)|\Psi_I\rangle. \tag{54}$$

The change in the total dipole moment of the crystal due to introduction of the impurity atom is P_I-P_v and points in the direction of $\boldsymbol{\varepsilon}$, the applied electric field. The ratio of P_I-P_v and $\mathcal{E}$, a scalar in this case, is the polarizability of the impurity atom in the crystal,

$$\alpha_I=(|\mathbf{P}_I-\mathbf{P}_v|)/|\boldsymbol{\varepsilon}|. \tag{55}$$

From Eqs. (53) and (54) and the definitions of the crystal wave functions in terms of the atomic functions.

P_I and P_v can be expressed in terms of simple one-electron quantities and correction terms involving overlap integrals and multicenter matrix elements. After considerable simplification, α_I is obtained in terms of dimensionless quantities μ_1, μ_2, and β:

$$\alpha_I=4[\mu_2{}^2/Z_I-(\mu_1/Z_A)(\mu_2-\beta)]a_0{}^3, \tag{56}$$

with

$$\mu_1=(N-1)^{-1}\langle\Psi_v{}^0|[\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)]^2|\Psi_v{}^0\rangle, \tag{57a}$$

$$\mu_2=\langle\Psi_I{}^0|\sum_i(z_{Ii}-Z_I)[(z_{Ii}-Z_I)+\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)]|\Psi_I{}^0\rangle, \tag{57b}$$

$$\beta=\langle\Psi_I{}^0|[\sum_i(z_{Ii}-Z_I)+\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)]^2|\Psi_I{}^0\rangle-\langle\Psi_v{}^0|[\sum_{A\neq I}\sum_a(z_{Aa}-Z_A)]^2|\Psi_v{}^0\rangle. \tag{57c}$$

Detailed expressions for μ_1, μ_2, and $\mu_2-\beta$ in terms of the atomic functions ϕ are presented below:

$$\begin{aligned}\mu_1=&\sum_a\langle Aa|z^2|Aa\rangle-\sum_{\substack{b\\ b\neq a}}\sum_a\langle Aa|Z|Ab\rangle^2-\sum_a\sum_B\sum_b S_{Aa,Bb}\langle Bb|Z^2|Aa\rangle-\sum_a\sum_{\substack{B\\ B\neq A}}\sum_b\langle Aa|z|Bb\rangle^2\\
&+\sum_a\sum_B\sum_b\sum_c S_{Aa,Bb}S_{Bb,Ac}\langle Ac|z^2|Aa\rangle+4\sum_a\sum_B\sum_b\sum_c S_{Ac,Bb}\langle Aa|z|Ac\rangle\langle Aa|z|Bb\rangle\\
&+\sum_a\sum_B\sum_b S_{Aa,Bb}\langle Aa|z|Bb\rangle R_{AB}\cos\Theta_{AB}-2\sum_a\sum_B\sum_b\sum_c\sum_d S_{Ac,Bb}S_{Bb,Ad}\langle Aa|z|Ad\rangle\langle Aa|z|Ac\rangle\\
&-\sum_a\sum_B\sum_b\sum_c\sum_d S_{Aa,Bc}S_{Bb,Ad}\langle Aa|z|Ad\rangle\langle Bc|z|Bb\rangle\\
&-\sum_a\sum_B\sum_b\sum_c S_{Aa,Bb}S_{Bb,Ac}\langle Ac|z|Aa\rangle R_{AB}\cos\Theta_{AB},\end{aligned} \tag{58a}$$

$$\begin{aligned}\mu_2=&\sum_i N_i{}^2[\langle Ii|z^2|Ii\rangle-\sum_{j\neq i}\langle Ii|z|Ij\rangle^2-2\sum_A\sum_a S_{Ii,Aa}\langle Aa|z^2|Ii\rangle\\
&-\sum_A\sum_a\langle Ii|z|Aa\rangle^2+\sum_A\sum_a\sum_b S_{Aa,Ii}S_{Ab,Ii}\langle Aa|z^2|Ab\rangle-\sum_A\sum_a\sum_b\sum_c S_{Ii,Ab}S_{Ii,Ac}\langle Aa|z|Ab\rangle\langle Aa|z|Ac\rangle\\
&+2\sum_A\sum_a\sum_b S_{Ii,Ab}\langle Ab|z|Aa\rangle\langle Aa|z|Ii\rangle+2\sum_A\sum_a S_{Ii,Aa}\langle Ii|z|Aa\rangle R_{IA}\cos\Theta_{IA}],\end{aligned} \tag{58b}$$

and

$$\begin{aligned}\mu_2-\beta=&\sum_i N_i{}^2[\sum_A\sum_a\langle Ii|z|Aa\rangle^2+\sum_A\sum_a\sum_b\sum_c S_{Ii,Ab}S_{Ii,Ac}\langle Aa|z|Ab\rangle\langle Aa|z|Ac\rangle\\
&+\sum_A\sum_a(S_{Ii,Aa})^2R_{IA}{}^2\cos^2\Theta_{IA}-2\sum_A\sum_a\sum_b S_{Ii,Ab}\langle Ab|z|Aa\rangle\langle Ii|z|Aa\rangle\\
&-2\sum_A\sum_a S_{Ii,Aa}\langle Ii|z|Aa\rangle R_{IA}\cos\Theta_{IA}+2\sum_A\sum_a\sum_b S_{Ii,Aa}S_{Ii,Ab}\langle Aa|z|Aa\rangle R_{IA}\cos\Theta_{IA}].\end{aligned} \tag{58c}$$

The sums over i and j run over all occupied electronic states of the impurity atom, N_i is the normalization constant [as defined by Eq. (4)] for the state i; sums over A and B run over all host atoms in the crystal, and sums over a, b, c, and d run over all occupied electronic states of the host atoms. R_{AB} is the distance between two host atoms A and B; and Θ_{AB} is the angle between vectors R_A and R_B.

The first two terms in the expression for μ_1 are single-center (atomic) terms and will be defined as $\mu_1{}^0$, that is,

$$\mu_1{}^0=\sum_a[\langle Aa|z^2|Aa\rangle-\sum_{b\neq a}\langle Aa|Z|Ab\rangle^2]. \tag{59}$$

$\mu_1{}^0$ is related to the polarizability of a free-host atom by the relation

$$\alpha_A{}^0=(4/Z_A)(\mu_1{}^0)^2a_0{}^3. \tag{60}$$

μ_1 is related to the polarizability of a host atom in the pure solid by

$$\alpha_A=(4/Z_A)(\mu_1)^2a_0{}^3. \tag{61}$$

Similarly, the first two terms in (58b) are atomic terms. We define

$$\mu_2{}^0=\sum_i[\langle Ii|z^2|Ii\rangle-\sum_{j\neq i}\langle Ii|z|Ij\rangle^2]. \tag{62}$$

$\mu_2{}^0$ can be used to evaluate the polarizability of a free impurity atom by using

$$\alpha_I{}^0=(4/Z_I)(\mu_2{}^0)^2a_0{}^3. \tag{63}$$

Eqs. (60) and (62) can be easily derived for a free atom by the use of the variational technique using only one parameter. Similarly, Eq. (61) can be derived for the polarizability of an atom in the pure solid. In our case, they are obtained simply as limiting cases.

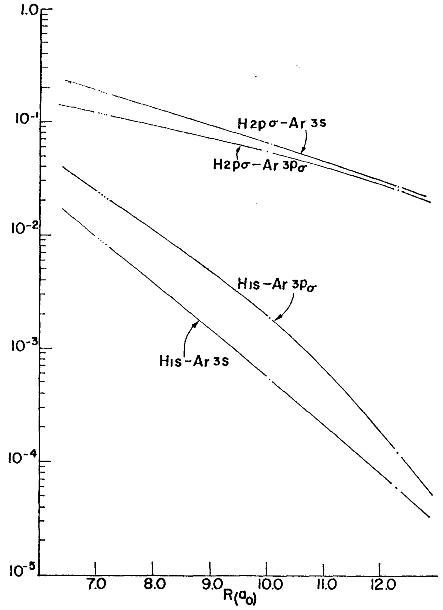

FIG. 1. Variation of some Ar-H overlap integrals with interatomic separation.

We shall now say a few words about the calculation of the polarizability of a free atom. Above we have presented a one-parameter formalism. This procedure is not expected to give good results, because the inner-shell electrons are not influenced by the external field as much as the outer-shell electrons, as a result of the effective shielding. If one uses a different variational parameter for each shell, one finds the polarizability of the free atom to be given by[38]

$$\alpha_I{}^0(\textstyle\sum\lambda_i)=4\sum_i\left[\langle i|Z^2|i\rangle-\sum_{j\neq i}\langle i|Z|j\rangle^2\right]^2a_0{}^3. \quad (64)$$

It is generally true in applications of the variational method with a given form for the perturbed wave function that, as more parameters are introduced, the calculated energy approaches the exact value as a lower limit. The energy of polarization being negative, we should expect the magnitude of the calculated polarizability to increase as the number of variational parameters is increased. Thus Eq. (64) is expected to give a higher value for the free-atom polarizability than that obtained by using (59) and (60), leading to better agreement. However, such a calculation does not seem computationally feasible for an atom in a solid.

TABLE I. Variation of hydrogen-argon overlap integrals with the interatomic separation R. The interatomic axis is taken as the Z axis. R is measured in units of a_0. In $\langle\phi_1|\phi_2\rangle$ for two-center integrals the function ϕ_1 is at the origin and the function ϕ_2 is centered at R.

R	7.05	7.07	7.10	7.15
$\langle \mathrm{H}1s\|\mathrm{Ar}3s\rangle$	0.0093	0.0091	0.0089	0.0085
$\langle \mathrm{H}1s\|\mathrm{Ar}3p_z\rangle$	0.0233	0.0230	0.0224	0.0216
$\langle \mathrm{H}2p_z\|\mathrm{Ar}3s\rangle$	0.1882	0.1871	0.1851	0.1824
$\langle \mathrm{H}2p_z\|\mathrm{Ar}3p_z\rangle$	0.1202	0.1198	0.1192	0.1181

TABLE II. Contributions from successive terms in the infinite series for two argon-hydrogen exchange integrals. All numbers are given in units of 27.21 eV. Argon functions are at the origin and the hydrogen $2p_z$ function is centered at $R=7.10a_0$ along the Z axis.

$l=$	0	1	2	3
$\langle \mathrm{Ar}3s\ \mathrm{H}2p_z\|g\|\mathrm{H}2p_z\ \mathrm{Ar}3s\rangle$	0.014574	0.000490	0.000018	0.000001
$\langle \mathrm{Ar}3p_z\ \mathrm{H}2p_z\|g\|\mathrm{H}2p_z\ \mathrm{Ar}3p_z\rangle$	0.008966	0.001580	0.000098	0.000002

IV. NUMERICAL RESULTS AND DISCUSSION

1. General Remarks on Computations

Nearest-neighbor separations for solid argon and neon were taken to be $7.10a_0$ and $5.96a_0$, respectively. Accurate self-consistent Hartree-Fock wave functions[39–41] for argon, neon, and lithium were available in analytic form. All overlap integrals, two-center matrix elements, and atomic matrix elements were evaluated using a program written for the University of Rochester Computing Center IBM 360-50 computer. All Coulomb and exchange integrals were evaluated numerically using two programs ALPHA and DICE (double integral Coulomb and exchange). All input functions were in an analytical form. For numerical evaluation, a uniform interval of $0.01a_0$ was chosen and all integrals were evaluated between $r=0.0$ and $20.0a_0$. This range was large enough to include all nonzero contributions, and the interval $(0.01a_0)$ was small enough to keep all errors arising from approximations inherent in the use of Simpson's rule to a minimum. As a check on accuracy, we computed several integrals first with one center at the origin and the other at a distance R, and then by exchanging the positions. For all overlap integrals and

TABLE III. Contributions from various shells of neighbors to the excitation energy in eV for the $1s\rightarrow 2p$ transition of a substitutional hydrogen-atom impurity in solid argon. The last column shows the variation of the excitation energy as successive terms are added. The last row shows contributions to $\Delta E'=\Delta E_C+\Delta E_{\mathrm{ex}}+\Delta E_T$ from successive shells. Free-atom excitation energy is 10.204 eV.

	1st nbrs	2nd nbrs	3rd nbrs	Distant nbrs	Total	Cumulative total
ΔE_{at}					20.533	
ΔE_C	−4.314	−0.237	−0.155		−4.706	15.827
ΔE_{ex}	−7.001	−0.458	−0.316		−7.775	8.052
ΔE_T	2.730	0.141	0.083		2.954	11.006
$\Delta E_{d\text{-}d}$					−0.386	10.620
ΔE_S					0.030	10.650
$\Delta E'$	−8.585	−0.554	−0.388	−0.048	−9.575	10.602

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[39] P. S. Bagus, Argonne National Laboratory Report No. ANL-6959, 1964 (unpublished).

[40] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

[41] A. W. Weiss, Astrophys. J. **138**, 1262 (1963).

TABLE IV. Contributions from various shells of neighbors to the excitation energy in eV for the $1s \rightarrow 2p$ transition of a substitutional hydrogen impurity in solid neon. The last column shows the variation of the excitation energy as successive terms are added. The last row shows contributions to $\Delta E' = \Delta E_C + \Delta E_{\text{ex}} + \Delta E_T$ from successive shells. Free-atom excitation energy is 10.204 eV.

	1st nbrs	2nd nbrs	3rd nbrs	Distant nbrs	Total	Cumulative total
ΔE_{at}					18.862	
ΔE_C	−2.878	−0.247	−0.220		−3.345	15.517
ΔE_{ex}	−5.121	−0.496	−0.470		−6.087	9.430
ΔE_T	1.500	0.112	0.088		1.700	11.130
$\Delta E_{d\text{-}d}$					−0.150	10.980
ΔE_S					0.020	11.000
$\Delta E'$	−6.499	−0.631	−0.602	−0.112	−7.844	10.888

two-center matrix elements, agreement was obtained to at least the seventh significant figure. Thus no meaningful errors were introduced in these computations. For the Coulomb and exchange integrals, the agreement was to the fourth significant figure for the larger (and dominant) integrals and to the third place for the smaller integrals.

As stated earlier, the atomic positions chosen here are those of the pure host crystals. This is not expected to lead to significant error, since the relaxation magnitudes for nearest-neighbor host atoms around vacancies in solid argon were computed to be quite small,[31] and further since overlap integrals do not vary appreciably for such small changes in the interatomic separations. This is shown in Table I and Fig. 1.

All two-center exchange integrals are given by infinite series. Each term involves a given α function (α functions are coefficients in the expansion of an atomic orbital, localized at R, around the origin in terms of spherical harmonics Y_l^m) for certain l and contributes to the exchange integral, at least formally. In actual practice it was found that the first few terms (three or four beginning with $l=0$) give all of the significant contributions. For these computations the impurity functions were localized at a distance R from the origin and their α functions computed using the program ALPHA. The host-atomic functions were kept at the origin and the exchange integrals were evaluated using DICE. This was done because for this choice the convergence of the infinite series was very good and the first three or four terms gave all the significant contributions. This is shown in Table II for two typical exchange integrals. When the centers were interchanged (that is, α functions of the host-atomic function calculated and the exchange integral evaluated with the impurity function localized at the origin) the convergence was poor. This was to be expected since the hydrogen (and lithium) $2p$ function has a long tail.

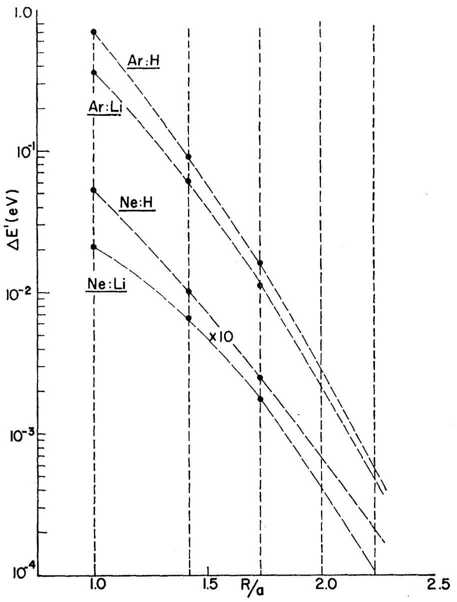

FIG. 2. The contributions, per atom, to $\Delta E' = \Delta E_{\text{ex}} + \Delta E_T + \Delta E_C$ from successive shells of neighbors. The ordinate shows $\Delta E'$ in eV. Values of neon host have been multiplied by 0.10 before plotting. The abscissa shows the radii of successive shells R in units of the nearest-neighbor separation a. The successive radii in units of a, are 1.0, $\sqrt{2}$, $\sqrt{3}$, 2, and $\sqrt{5}$.

TABLE V. Contributions from various shells of neighbors to the excitation energy for the $2s \rightarrow 2p$ transition of a substitutional lithium impurity in solid argon. The last column shows the variation of the excitation energy as successive terms are added. The last row shows contributions to $\Delta E' = \Delta E_C + \Delta E_{\text{ex}} + \Delta E_T$ from successive shells. Free-atom excitation energy is 1.848 eV.

	1st nbrs	2nd nbrs	3rd nbrs	Distant nbrs	Total	Cumulative total
ΔE_{at}					6.478	
ΔE_C	−1.699	−0.150	−0.105		−1.954	4.524
ΔE_{ex}	−3.317	−0.306	−0.227		−3.850	0.674
ΔE_T	0.679	0.080	0.056		0.815	1.489
$\Delta E_{d\text{-}d}$					0.361	1.850
ΔE_S					0.050	1.900
$\Delta E'$	−4.337	−0.376	−0.276	−0.037	−5.026	1.863

TABLE VI. Contributions from various shells of neighbors to the excitation energy in eV for the $2s \rightarrow 2p$ transition of a substitutional lithium-atom impurity in solid neon. The last column shows the variation of the excitation energy as successive terms are added. The last row shows contributions to $\Delta E' = \Delta E_C + \Delta E_{\text{ex}} + \Delta E_T$ from successive shells. Free-atom excitation energy is 1.848 eV.

	1st nbrs	2nd nbrs	3rd nbrs	Distant nbrs	Total	Cumulative total
ΔE_{at}					4.774	
ΔE_C	−0.769	−0.141	−0.149		−1.059	3.715
ΔE_{ex}	−2.019	−0.310	−0.332		−2.661	1.054
ΔE_T	0.224	0.052	0.055		0.331	1.385
$\Delta E_{d\text{-}d}$					0.159	1.544
ΔE_S					0.040	1.584
$\Delta E'$	−2.564	−0.399	−0.426	−0.074	−3.463	1.510

TABLE VII. Some typical Ar:H overlap integrals and two-center matrix elements. The a is taken to be $7.10a_0$. The interatomic axis is taken as the z axis.

	a	$\sqrt{2}a$	$\sqrt{3}a$
$\langle \mathrm{H}1s \| \mathrm{Ar}3s \rangle$	0.0089	0.0005	0.0001
$\langle \mathrm{H}1s \| \mathrm{Ar}2p_z \rangle$	−0.0003	−0.0000	−0.0000
$\langle \mathrm{H}1s \| \mathrm{Ar}3p_z \rangle$	0.0224	0.0019	0.0002
$\langle \mathrm{H}2p_z \| \mathrm{Ar}3s \rangle$	0.1853	0.0659	0.0271
$\langle \mathrm{H}2p_z \| \mathrm{Ar}2p_z \rangle$	−0.0043	−0.0016	−0.0007
$\langle \mathrm{H}2p_z \| \mathrm{Ar}3p_z \rangle$	0.1192	0.0551	0.0252
$\langle \mathrm{H}2p_x \| \mathrm{Ar}2p_x \rangle$	0.0017	0.0004	0.0001
$\langle \mathrm{H}2p_x \| \mathrm{Ar}3p_x \rangle$	−0.0569	−0.0151	−0.0052
$\langle \mathrm{H}1s \| Z \| \mathrm{Ar}3s \rangle$	0.0447	0.0042	0.0006
$\langle \mathrm{H}1s \| Z \| \mathrm{Ar}2p_z \rangle$	−0.0018	−0.0002	−0.0000
$\langle \mathrm{H}1s \| Z \| \mathrm{Ar}3p_z \rangle$	0.0736	0.0099	0.0017
$\langle \mathrm{H}1s \| x \| \mathrm{Ar}3p_x \rangle$	−0.0154	−0.0013	−0.0002
$\langle \mathrm{H}2p_z \| Z \| \mathrm{Ar}3s \rangle$	1.2032	0.6119	0.3117
$\langle \mathrm{H}2p_z \| Z \| \mathrm{Ar}2p_z \rangle$	−0.0183	−0.0119	−0.0065
$\langle \mathrm{H}2p_z \| Z \| \mathrm{Ar}3p_z \rangle$	0.4031	0.3537	0.2183
$\langle \mathrm{H}2p_x \| Z \| \mathrm{Ar}3s \rangle$	0.0516	0.0132	0.0045
$\langle \mathrm{H}2p_x \| x \| \mathrm{Ar}3p_z \rangle$	0.0686	0.0213	0.0079

2. Energy Parameters

All energy parameters E_{at}, E_C, E_{ex}, E_T, E_S, and $E_{d\text{-}d}$ for both the ground and excited states were evaluated following standard techniques for performing lattice sums. All lattice sums were generally carried through to third neighbors and through all occupied states on each atom. This is necessary since contributions from the second and third shells of neighbors are not negligible, and separately they are comparable because there are four times as many (24) third neighbors as second neighbors. The fourth and the fifth shells have 12 atoms each and, since the contribution per atom (obtained by dividing the total contribution from a shell by the number of atoms in the shell) falls off nearly exponentially, these contributions are expected to be small. The per-atom contributions to $\Delta E'(=\Delta E_C+\Delta E_{\mathrm{ex}}+\Delta E_T)$ from the first three shells of neighbors were plotted against the radius of the shell. The variation is almost exponential as shown in Fig. 2. (The numbers for Ne: impurity systems have been multiplied by 0.1 before plotting.) This variation is used to estimate the contributions from the fourth and the fifth shells of neighbors.

Tables III–VI summarize the results of computations for the excitation energies. The columns labeled nth nbrs show contributions from entire shells of nth neighbors. The columns labeled distant nbrs show the estimated contribution from the fourth and fifth neighbors. It is seen that these contributions are small. The fact that the contributions fall off in an almost exponential manner may be an indication of the validity of the tight-binding model for the systems treated here. The column labeled total shows total contribution to each term. The last column shows the variation of excitation energy as the successive terms are added. The last entry in this column gives the computed excitation energy. Errors in the predicted excitation energy are estimated to be within about 2%.

3. Oscillator Strength

The transition matrix element for an $i\rightarrow j$ transition is given by Eq. (32). All lattice sums were evaluated using standard methods. The results confirmed the expectation that the ground state of the impurity atom must be orthogonalized to the host-atomic functions. The contributions involving overlap of the ground state of the impurity atom are comparable to those involving overlap of the excited state. We list some typical overlap integrals and two-center matrix elements for Ar:H in Table VII.[42] In Table VIII we list the contributions from the individual terms in Eq. (32); they are labeled the 1st, 2nd, 3rd, 4th, and 5th terms as they appear in Eq. (32). We also list the respective normalization constants. In Table IX we list the excitation energies and oscillator strengths for free atoms and for impurity absorption in solids.

The effect of the medium on the hydrogen impurity is to increase the oscillator strength for the $1s\rightarrow 2p$ transition by about 17% for the argon host solid and by 11% for neon as host solid. On the other hand, the oscillator strengths for the $2s\rightarrow 2p$ transition of lithium atom impurity are *lowered* by about 10% in argon and by about 23% in neon. The increase in oscillator strength of the $1s\rightarrow 2p$ transition of the hydrogen impurity is caused by a blue-shifted excitation energy and an increased matrix element. The Ar:Li system shows a very small ($\sim$0.02 eV) blue-shift for the excitation energy, and the decrease in oscillator strength arises from a decreased transition matrix element. For the Ne:Li system we predict a red-shifted excitation energy and a decreased matrix element leading to a decreased oscillator strength.

4. Polarizability

The lattice sums for μ_1, μ_2, and $\mu_2-\beta$ were evaluated using standard methods. The results are summarized in Table X. The polarizability of a hydrogen atom at a substitutional site α_I is lowered in argon by about 1% and in neon by about 4% from the variational value of $\alpha_I{}^0$, $4.0a_0{}^3$, for the free hydrogen atom. (The exact value is $4.5a_0{}^3$.) Using the one-variational-parameter formalism, we obtain the polarizability of a free lithium atom as $\alpha_I{}^0=51.4a_0{}^3$. The ground-state polarizability of a lithium atom at a substitutional site in solid argon and in solid neon is computed to be $44.2a_0{}^3$ and $18.0a_0{}^3$, respectively. Thus the polarizability of a lithium atom impurity at a substitutional site is lowered by 13% in argon and by 65% in neon. Application of the many-parameter-variational formalism (one variational parameter for each shell of electrons in an atom) to the

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[42] All overlap integrals, two-center matrix elements, and Coulomb and exchange integrals are presented in Ref. 36 in detail.

TABLE VIII. Contributions from various terms to the transition matrix element. Numbers in column 3 (1st term) are the free-atom matrix elements, those in columns 4–7 give additional contributions. Columns 1 and 2 give the ground- and excited-state normalization constants. Numbers in the last column give the corrected transition matrix element. All numbers (except N_i and $\bar{N}_j$) are in units of a_0. The sign preceding the term in Eq. (32) is not included here.

System	N_i	$\bar{N}_j$	1st term	2nd term	3rd term	4th term	5th term	Matrix element
Ar:H	1.0035	1.1560	0.744936	0.098408	0.078151	−0.014982	0.126965	0.789301
Ar:Li	1.0941	1.1439	−2.377659	−0.649882	−0.636050	0.058878	−0.764395	−2.249386
Ne:H	1.0029	1.0875	0.744936	0.060797	0.057698	−0.006205	0.074969	0.758286
Ne:Li	1.0603	1.0826	−2.377659	−0.386718	−0.393841	0.018199	−0.430388	−2.306366

calculation of the polarizability of the free lithium atom $\alpha_I^0(\lambda_i)$ gave $140.0a_0^3$. This should be compared with the experimental[43] value $148.5a_0^3$. This confirms the expectation that the polarizability would increase, and approach the exact value, as the number of variational parameters is increased.

Two approximations were made for these calculations. First was the neglect of terms in quadratic and higher powers of λ_1 and λ_2. This is reasonable since such terms would necessitate inclusion of terms involving $\mathcal{E}^4$ and hence would lead to nonlinear polarizability. The second approximation concerned the terms Δ, Δ_1, and Δ_2. These were neglected completely. Each of these terms involves two types of terms: the intra-atomic terms and the interatomic terms. The intra-atomic terms will change the value of polarizability which the theory yields for a free atom. The interatomic terms contain four-electron operator terms (two coming from $1/r_{12}$ in the Hamiltonian and two coming from v^2 terms). Since these terms lead to only small additive corrections to the variational parameters λ_1 and λ_2 in a good tight-binding system, and since we are interested only in the magnitude of the change of polarizability of the impurity atom from the free-atom value, we feel that the neglect of Δ, Δ_1, and Δ_2 is a sound approximation within the S^2 approximation. Keil[44] has discussed the implications regarding such terms in his calculation of the polarizability of an argon atom in solid argon. He concludes that such terms lead to the effective field parameters.

This formalism also gives the polarizability of a free host atom, α_A^0, (e.g., a free argon atom) and that of an atom in a pure solid α_A (e.g., an argon atom in solid argon). The polarizability of an argon atom is slightly lowered by the medium (solid argon) from the free-atom value. The computed decrease is about 0.3%. This is smaller than the 1.5% lowering predicted by Smith and Pings[45] and the predicted[46] decrease of about 1.3% for the Lorentz-Lorenz function. For a neon atom in solid neon we compute a very slight decrease (about 0.2%) from the free-atom value. Thus we predict a very small dispersion in the Lorentz-Lorenz function of neon.

TABLE IX. Excitation energies, oscillator strengths, and total absorption cross sections. The quantities in columns 1 and 2 refer to a free atom and those in columns 3 and 4 refer to an impurity atom. Atomic excitation energy and oscillator strength for the $2s \rightarrow 2p$ transition of a free lithium atom are taken from Ref. 41. Energies are in eV and Σ is in units of 10^{-16} eV cm^2.

	Free atom		Impurity atom		
System	Energy	Osc strength	Energy	Osc strength	Σ
Ar:H	10.204	0.4160	10.602	0.4855	0.5322
Ar:Li	1.848	0.7680	1.863	0.6928	0.7594
Ne:H	10.204	0.4160	10.888	0.4602	0.5045
Ne:Li	1.848	0.7680	1.510	0.5904	0.6472

V. INTEGRATED ABSORPTION CROSS SECTIONS

So far we have treated a static lattice near 0°K. This allowed us to neglect the parameteric dependence of the electronic wave functions on the nuclear coordinates, and effects of line broadening were completely ignored. In real systems, however, one observes substantial line broadening. Here we are not concerned with the details of the impurity absorption bands; we shall compute only the zeroth moment (total absorption cross section) associated with the absorption line caused by the transition from the ground state to a low-lying excited state of the impurity atom.

The total (integrated) absorption cross section is given by[47]

$$\Sigma_{0\rightarrow j}=\int \sigma_{0\rightarrow j}(E)dE=\frac{2\pi^2e^2\hbar}{m_0c}\frac{1}{n_0(E_{0j})}\left(\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}}\right)^2 f_{0j}. \qquad (65)$$

TABLE X. The ground-state polarizabilities of free impurity atoms α_I^0, of free host atoms α_A^0, of impurity atoms α_I, and of atoms in pure solids α_A. All numbers except in the two columns on the right are derived using the one-parameter formalism. The numbers in column labeled $\alpha_I^0(\Sigma\lambda_i)$ give the polarizability of a free atom using one parameter for each occupied shell [see Eq. (64)]. The last column shows the experimental values for hydrogen and lithium atoms. All numbers are in units of a_0^3. The experimental value for lithium is taken from Ref. 43.

	α_I^0	α_I	α_A^0	α_A	$\alpha_I^0(\Sigma\lambda_I)$	α_I^0(expt)
Ar:H	4.00	3.96	6.65	6.63	4.0	4.5
Ne:H	4.00	3.84	1.641	1.639	4.0	4.5
Ar:Li	51.40	44.18	6.65	6.63	140.0	148.5
Ne:Li	51.40	17.98	1.641	1.639	140.0	148.5

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Here $n(E_{0j})$ is the real part of the refractive index of the host solid at the energy of the transition, $\mathcal{E}_{\text{eff}}/\mathcal{E}$ is the effective field ratio, and f_{0j} is the oscillator strength for the ground $\rightarrow j$th excited-state transition. $\sigma_{0\rightarrow j}(E)$ is the differential cross section at energy E. This result was derived by assuming that the dominant interactions of the center with the host can be represented by an effective field and that overlap and exchange effects can be neglected. In this case, if the interactions are simply dipole-dipole interactions, the effective field ratio $\mathcal{E}_{\text{eff}}/\mathcal{E}$ is given by $\frac{1}{3}[n^2(E_{0j})+2]$.

For prediction of the total cross section, the refractive index $n(E_{0j})$ must be known at the transition energy. Also the effective field ratio, if indeed it can be properly defined, must be accurately known. However, no experimental data could be found for the refractive indices of argon and neon solids at the computed transition energies of hydrogen, nor for lithium in neon. Hence for purposes of listing a theoretical value for the integrated absorption cross section Σ in Table IX, we omit the factors $n(E_{0j})$ and $(\mathcal{E}_{\text{eff}}/\mathcal{E})^2$, replacing them by unity.

In principle, Eq. (65) provides a method for determining the effective field ratio. $\Sigma_{0\rightarrow j}$ can be determined experimentally, as can the refractive index at the transition energy E_{0j}. The computed oscillator strength for the $0 \rightarrow j$ transition then allows a solution for $\mathcal{E}_{\text{eff}}/\mathcal{E}$.

VI. DISCUSSION

Numerical results confirmed the expectation that the ground-state overlaps play an important role in a computation of matrix elements; they are less important in a calculation of the excitation energies. The computed oscillator strength for the $1s \rightarrow 2p$ transition of a substitutional hydrogen-atom impurity is increased by the medium, while that for the $2s \rightarrow 2p$ transition of the lithium atom impurity is decreased. The computed polarizability of the impurity atom in each case is lowered by the medium. Since the oscillator strengths and polarizabilities are related quantities, this suggests a possible breakdown of the f-sum rule in condensed systems.[48]

Our predicted excitation energies agree well with the experimental[27] values for the Ar:H and Ne:H systems and also with the earlier[17] calculation on the Ar:H system. In the case of Ar:Li, our predicted excitation energy agrees well with the position of the peak labeled *c* by Andrews and Pimental,[30] who identify this peak with absorption by a *substitutional* lithium atom impurity. The Ne:Li system has not been studied experimentally. We predict a red shift of 0.34 eV from the atomic $2s \rightarrow 2p$ excitation energy.

In a one-electron approximation, the atomic radius of a lithium atom is somewhat larger than that of a neon atom. This may mean that our neglect of relaxation effects in Ne:Li is unjustified. A substitutional lithium atom impurity may push the nearest-neighbor neon atoms out, leading to somewhat larger nearest-neighbor separations, and hence to smaller overlaps, two-center integrals, etc. Thus, relatively large predicted shifts for the Ne:Li system may be partly due to our neglect of the relaxation effects.

ACKNOWLEDGMENTS

The authors wish to thank Professor R. S. Knox, Professor A. Gold, and Professor T. H. Keil for helpful discussions during the course of this investigation. We also thank Dr. P. S. Bagus for supplying a copy of argon and neon wave functions.

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