IMPURITY STATES IN SOLID NEON

BY

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ABSTRACT

A formalism for the treatment of optical absorption by an isolated substitutional impurity center is given. The tight-binding approximation is used and the method of constructing one-electron trial functions for the system is outlined. The first-order absorption energies, oscillator strengths, and integrated absorption coefficients are computed in an approximation which includes spin-orbit interaction and the overlapping of heterocentric atomic wave functions through terms of order S^2 . The first-order energies are corrected for van der Waals interactions using a variational formalism. A phenomenological method for computing the emission energies of the system is given. The specific example of an argon impurity atom in solid neon is treated numerically. The computation predicts absorption lines at 11.7 and 11.6 eV due, respectively to the 1P_1 and 3P_1 states of the argon impurity, with an uncertainty of 1.3 eV. The oscillator strengths for these transitions are calculated to be 0.164 and 0.017 respectively, giving rise to integrated absorption coefficients of 0.84×10^6 N_0 and 0.09×10^6 N_0 eV cm $^{-1}$ for the two states, where N_0 is the (small) fractional concentration of impurities in the host lattice.

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VITA

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I. INTRODUCTION

The computation of the optical properties of an isolated substitutional impurity in an otherwise undisturbed infinite crystal lattice has been an object of extensive theoretical interest for some twenty years. The goal of this work has been the achievement of a quantitative understanding of the influence of the atoms of the crystal and of lattice vibration on the absorption and emission spectra of a foreign atom introduced into a solid in small concentration. These studies attempt to explain the shifting of the absorption energies from their atomic positions, the transfer of energy to lattice vibrations resulting in the Stokes shift, the broadening of sharp atomic lines into bands, and the quantum efficiency of the luminescence process. The pressure and temperature dependence of all of these phenomena have been investigated. A large literature has accumulated in the field.⁽¹⁾

There is an analogy to the history of atomic spectra, but it is incomplete. Atoms in a dilute gas may be treated as independent, non-interacting systems to a very good first-approximation, whereas in a solid or liquid the interactions are known to be large. Indeed, one of the most successful approaches in the theory of impurities in solids is the effective mass approximation in which the center's electronic wave functions are computed using an effective mass and a dielectric constant κ appropriate to the non-metallic

crystal. In this extreme the impurity itself is treated as a point charge Ze/κ , where Z is the difference of the valences of the impurity and the host atoms. Thus the details of the impurity center are completely ignored.

We shall adopt the viewpoint of the opposite extreme according to which the electronic properties are predominantly determined by the impurity atom itself, the interactions with the lattice being treated as relatively weak. A modified form of the Heitler-London scheme, accordingly, seems appropriate, in contrast to the generalization of the Bloch approach mentioned above. We deal briefly in the following paragraphs with the historical development of the "tight-binding" approximation as applied to impurities in solids.

Most of the workers in the field have concentrated their efforts on the experimentally convenient case of heavy metal impurities in alkali-halides. The classic model of such a center was proposed by Seitz⁽²⁾ in 1938 for the system KCl:Tl. The first attempt at a detailed numerical computation for such a system was made on a semi-classical basis for KCl:Tl using the Seitz model.⁽³⁾ In this case and in a later computation by Potenkhina for NaCl:Ag⁽⁴⁾ reasonable agreement with experiment has been obtained. However, certain quite serious questions have arisen in connection with the methods of computation used.⁽⁵⁾

Lax and others^{(6),(7)} have made studies on the interactions

of such centers with the local lattice modes to which they give rise and have discussed the temperature dependence of the spectra. Recently Kristoffel has made a significant contribution to the understanding of the electronic-vibrational coupling.⁽⁸⁾

During the past few years considerable interest has developed in both pure crystalline rare-gases and in solid rare-gases containing impurities, and several optical studies of their properties have been undertaken.^{(9),(10),(11)} Magnetic resonance studies of impurity centers in these materials have also been performed.^{(12),(13)}

Löwdin has reviewed the advances which have been made in treating the ground-states of pure alkali-halide crystals from first principles.⁽¹⁴⁾ Recently Knox^{(15),(16),(17)} has performed the first detailed quantum-mechanical and numerical computation on the optically preparable states of a pure insulating crystal, specifically the lowest-lying exciton bands in solid argon using the Heitler-London model. Thus far, however, no attempt has been made to predict the optical properties of an impurity center from first-quantum-mechanical principles.

We here undertake the computation of the wave functions and absorption energies of the system composed of an isolated argon impurity in solid neon in the Heitler-London approximation using the symmetrical orthogonalization method⁽¹⁸⁾ of Löwdin as developed by Knox.^{(15),(16)} The overlapping of heterocentric atomic wave

functions is explicitly taken into account through terms of second order in S (an overlap parameter to be defined). An exact diagonalization is made in the first order of perturbation theory, taking into account the effects of spin-orbit interaction and the crystal field for absorptions involving transitions to the 1P and 3P terms of the $3p^5 4s$ configuration of the argon impurity.

The absorption energies so obtained are then corrected for the dipole-dipole (van der Waals) interactions between the center and its neighbors using the variational method of Buckingham⁽¹⁹⁾ for computing the van der Waals constants appropriate to the excited-states.

The oscillator strengths for the transitions are computed to first-order, and the method of Dexter is used to obtain the integrated absorption coefficients.⁽²⁰⁾

The emission energies of the system are calculated on a phenomenological, classical basis. As is customary, we (crudely) represent neighboring lattice distortion by a single "breathing mode" and the equilibrium configuration for the ground-state is estimated from empirical data using a Lennard-Jones (12,6) potential. The equilibria for the excited-states, and subsequently the emission energies, are calculated by fitting (12,6) potentials using the computed van der Waals and excitation energies.

Sections I through VII treat the formalism of the problem, discussing successively the model and Hamiltonian, the symmetrically

orthogonalized wave functions of Löwdin, the first-order energy matrix, the dipole-dipole interaction, the oscillator strengths, and the construction of the configuration coordinates. Section VIII is a general review of the method of numerical computation and sections IX through XI present, respectively, numerical results for the first-order energy parameters, the van der Waals computation and emission energies, and the oscillator strengths and related quantities. The results of the calculation are discussed in section XII and comparison with available, related experimental data is made.

II. THE MODEL AND THE HAMILTONIAN

The model which we choose to represent an impurity center in a rare-gas crystal consists of an impurity atom of atomic number Z_A surrounded by a lattice of $N - 1$ (identical) atoms of the host material having atomic number Z_I . The host atoms contained in the first shell of the impurity's neighbors are allowed to relax radially so as to minimize the energy of the system in its ground-state. These assumptions correspond to a concentration of impurities so low that interactions among impurity atoms may be neglected, and to the commonly made approximation that only the "breathing mode"⁽²¹⁾ (the synchronous radial motion of all of the center's nearest neighbors) has an appreciable effect on the energy of the system. The Heitler-London or tight-binding approximation⁽²²⁾ is assumed valid; that is, the wave functions which serve as trial solutions are taken as orthonormalized, antisymmetrized products of one-electron functions of the free atomic constituents. In particular, the excited-states of the system to be considered are those wherein the impurity is in a state of localized excitation corresponding to one of its low-lying atomic levels. These levels are taken to be of sufficiently low energy that excitations of the host crystal will not be significantly coupled to them and that the resulting absorption bands will not be lost under the fundamental absorption of the host lattice.

For convenience we shall adopt a double subscript notation for electronic coordinates; this will consist of a pair of indices Jj where J runs over nuclear sites and j runs from 1 to Z_J .⁽²³⁾ In some instances it will be expedient to denote the impurity's electronic coordinates explicitly; in that event the indices Aa will be reserved for the center and the convention will be adopted that all running sums and products on J exclude A . In this notation the Hamiltonian for the system of $Z_J(N-1)$ host electrons and Z_A electrons centered on the impurity in a static equilibrium lattice may be written as:

$$H = -\frac{\hbar^2}{2m} \sum_I \sum_i \nabla_{\mathbf{r}_{Ii}}^2 + \frac{1}{2} \sum_{I \neq J} \sum_J \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_I \sum_i \sum_J \sum_j \frac{e^2}{|\mathbf{r}_{Ii} - \mathbf{r}_{Jj}|} - \sum_I \sum_i \sum_J \frac{Z_J e^2}{|\mathbf{r}_{Ii} - \mathbf{R}_J|} + \frac{i\hbar}{2mc^2} \sum_I \sum_i \nabla_{\mathbf{r}_{Ii}} \cdot \nabla V(\mathbf{r}_{Ii}) \times \nabla_{\mathbf{r}_{Ii}} \quad (2.1)$$

The five terms are, respectively, the kinetic energy of the electrons, the potential energy of the nuclei, the potential energy of the system of electrons, the potential energy of the electrons interacting with the nuclei, and finally the spin-orbit interaction. In equation (2.1) the symbols e , $\hbar$, c , and m have their usual meanings and $\nabla_{\mathbf{r}_{Ii}}$ is the gradient operator for the coordinate $\mathbf{r}_{Ii}$. The notation $I \neq J$ means that every term for which $I = J$ and $i = j$

is excluded from the summation over I and i . The positions of the nuclei are denoted by $\underline{R}_I$. $V(\underline{r}_{Ii})$ is the potential due to all electrons and nuclei except electron Ii . S_{Ii} is the spin operator for electron Ii . We shall assume that the lattice maintains cubic point symmetry about the impurity A.* Nuclear kinetic energies are missing from (2.1). We assume the lattice to be static at its equilibrium configuration.

*In particular we shall concern ourselves with a substitutional impurity in a face-centered cubic lattice.

III. TRIAL WAVE FUNCTIONS

In treating the first-order problem we wish to find the eigenvalues and eigenfunctions of the Schrödinger equation

$$H\psi_{\alpha} = E_{\alpha} \psi_{\alpha} , \quad (3.1)$$

where H is given by (2.1). The method is straightforward. It consists of finding the eigenvalues and eigenvectors of the matrix H whose elements are formed using a suitable complete set of trial functions chosen for convenience, and with the Heitler-London model in mind.

(a) Ground-state

An unnormalized zero-order ground-state crystal wave function may be written

$$\chi_0(r_m, \sigma_m) = A_M \prod_a \phi_{Aa}(r_{ma}, \sigma_{ma}) \prod_I \prod_i \phi_{Ii}(r_{mi}, \sigma_{mi}) . \quad (3.2)$$

Here A_M is the usual antisymmetrization operator operating on all M electrons of the system and is defined as

$$A_M = (M!)^{-\frac{1}{2}} \sum_{\nu} (-1)^{P_{\nu}} P_{\nu} , \quad (3.3)$$

where P_{ν} is one of the $M!$ permutations of M objects, $(-1)^{P_{\nu}}$ is the parity of P_{ν} , and the sum runs over all $M!$ permutations of electronic coordinates. The ϕ_j are taken to be the normalized one-electron functions of an atom in its ground-state centered at nucleus J , and j denotes the set of central field quantum numbers,

$\chi_{\mathbf{I}, \mathbf{m}_s}$, describing each function. The vector $(\mathbf{r}, \sigma)$ stands for the entire set of electron space and spin coordinates and will often be omitted for brevity. The products over $\mathbf{I}$ and $\mathbf{i}$ run from 1 to $(N-1)$ and 1 to $Z_{\mathbf{I}}$ respectively and the product over $\mathbf{a}$ runs from 1 to $Z_{\mathbf{A}}$.

In order to normalize χ_0 we adopt the well-known symmetrical orthogonalization technique introduced by Löwdin.^{(14), (18)} In computing $\int |\chi_0|^2 d\tau$ the following overlap integrals are encountered:

$$S_{\mathbf{I}, \mathbf{J}} = \int \phi_{\mathbf{I}, \mathbf{i}}(\mathbf{r}, \sigma)^* \phi_{\mathbf{J}, \mathbf{j}}(\mathbf{r}, \sigma) d\tau = \delta_{\mathbf{I}, \mathbf{J}} \delta_{\mathbf{i}, \mathbf{j}}. \quad (3.4)$$

The deltas are the usual Kronecker symbols. Löwdin showed that an appropriate normalization constant compensating for the non-orthogonality of $\phi_{\mathbf{I}, \mathbf{i}}$ centered on different nuclei is automatically introduced into χ_0 if one replaces each function $\phi_{\mathbf{I}, \mathbf{i}}$ by the following linear combination of functions:

$$\phi_{\mathbf{J}, \mathbf{j}}(\mathbf{r}, \sigma) = \sum_{\mathbf{K}=1}^N \sum_{\mathbf{k}=1}^{Z_{\mathbf{K}}} \left(\underline{\mathbb{1}} + \underline{\underline{S}} \right)^{-\frac{1}{2}}_{\mathbf{J}, \mathbf{j}, \mathbf{K}, \mathbf{k}} \phi_{\mathbf{K}, \mathbf{k}}(\mathbf{r}, \sigma). \quad (3.5)$$

Here $\underline{\mathbb{1}}$ and $\underline{\underline{S}}$ are the unit and overlap matrices respectively. Conditions for convergence and divergence of a power series expansion of the matrix elements encountered in (3.4) are discussed in detail in Löwdin's review.⁽¹⁴⁾ We shall assume such an expansion converges and write $\phi_{\mathbf{J}, \mathbf{j}}$ explicitly to second-order in $\underline{\underline{S}}$ as

$$\phi_{J_j} = \phi_{J_j} - \frac{1}{2} \sum_K \sum_k S_{Kk, J_j} \phi_{Kk} + \frac{3}{8} \sum_K \sum_k \sum_L \sum_R S_{Kk, Lk} S_{Lk, J_j} \phi_{Kk}. \quad (3.6)$$

Retention of higher order terms would lead to formidable formal complications and an impractically large quantity of numerical work.

The following function is a simple multiple of χ_0 and is normalized:

$$\Psi_0(r, \sigma) = A_M \prod_a \phi_{A_a}(r_{A_a}, \sigma_{A_a}) \prod_I \prod_i \phi_{I_i}(r_{I_i}, \sigma_{I_i}). \quad (3.7)$$

The ground-state energy of the system is then given by

$$E_0 = \int \Psi_0^* H \Psi_0 d\tau. \quad (3.8)$$

We shall consider its evaluation in detail later.

(b) States of localized excitation

A normalized state in which the impurity atom has been raised to an excited-state λ is built in a manner completely analogous to that used in constructing the ground-state. It is given by

$$f_A(\lambda; r, \sigma) = A \prod_a \phi_{Aa}^\lambda(r_{Aa}, \sigma_{Aa}) \prod_I \prod_i \phi_{Ii(A\lambda)}(r_{Ii}, \sigma_{Ii}). \quad (3.9)$$

The symmetrically orthogonalized functions ϕ_{Aa}^λ and $\phi_{Ii(A\lambda)}$ are defined exactly as in (3.6) with the exception that wherever an atomic function ϕ_{Aa} at site A appears, a function ϕ_{Aa}^λ belonging to the atomic excited state λ is to be used. The notation $\phi_{Ii(A\lambda)}$ is used only for $I \neq A$.

Although we have built the state $f_A(\lambda)$ from single determinants of one-electron functions it is feasible and desirable to use linear combinations of the zero-order functions which will diagonalize all or part of the atomic Hamiltonian. Thus, the localized excitation states actually used in the computation may be of the form

$$\Phi_A(\mu) = \sum_\lambda (\mu/\lambda) f_A(\lambda). \quad (3.10)$$

where the coefficients (μ/λ) are exactly those obtained from constructing linear combinations of zero-order determinants in the related atomic problem.⁽²⁴⁾ The states λ and coefficients most convenient to use in treating the p^5 configuration at sites of cubic symmetry use the Cartesian form of the p function as given by Knox⁽²⁵⁾ and will be used throughout the present paper.

We shall assume that excited states of the host crystal atoms

are sufficiently energetically separated from those of the p^5s configuration of the impurity that they need not be mixed with the localized excitation here. If, for example, we consider an argon impurity in solid neon we have excitation energies of the order of 11.6 eV for the impurity compared with 16.7 eV for the host.^{(26),(27)} Host crystal absorption as treated in the work of Dexter⁽²⁰⁾ will not be considered in the present calculation.

IV. MATRIX ELEMENTS

Since the Franck-Condon principle states that excitations will take place between Born-Oppenheimer states having the same nuclear configuration, we may proceed to compute the first-order absorption energy using a static array of nuclei in positions corresponding to those giving a minimum total energy for the ground-state of the system, E_0 . Using this ground state energy as a reference we shall calculate

$$E_1(\mu, \mu') = (\mu | H | \mu') - E_0 \delta_{\mu\mu'} , \quad (4.1)$$

where

$$(\mu | H | \mu') = \int \Psi_A^*(\mu) H \Psi_A(\mu') d\tau \quad (4.2)$$

We shall explicitly treat the case of an excited impurity in a p^5 configuration. Its normal configuration is taken to be p^6 and it is assumed to rest substitutionally in an otherwise perfect monatomic lattice whose constituents are in p^6 normal states. It will be further assumed that the spin-orbit term of H [equation (2.1)] is "atomic" in nature, i.e., that the expectation value of $\nabla V \times \nabla$ contributes to $(\mu | H | \mu')$ only in the vicinity of the nucleus of excited atom A. This assumption removes the necessity of considering spin-induced splitting by the crystal field, and is quite reasonable, since the atomic spin-orbit interaction is associated with the tightly bound p^5 hole rather than with the spatially ex-

tended s electron. These assumptions are discussed by Knox in reference 15. As Knox has pointed out, great care must be taken in applying them to excited states where the atomic p function involved in the spin-orbit interaction is not tightly bound to its lattice site. (16), (28) Thus, we replace the last term of (2.1) by

$$H_s = \sum_I \sum_i \xi_I(r_{\underline{r}_{Ii}}) \underline{L}_{\underline{r}_{Ii}} \cdot \underline{S}_{\underline{r}_{Ii}} , \quad (4.3)$$

where $\underline{L}_{\underline{r}_{Ii}}$ is the orbital angular momentum operator $i\hbar \underline{r}_{Ii} \times \underline{r}_{Ii}^{\nabla}$ and ξ_I is defined by

$$\xi_I(r) = (2m^2c^2 r_I)^{-1} \partial V(r_I) / \partial r_I , \quad (4.4)$$

in which $\underline{r}_I = |\underline{r} - \underline{R}_I|$.

The matrix $\underline{E}_1(\mu, \mu')$ connecting the twelve p^5 s states discussed in section III and in reference 16 is found to have the following form

$$\underline{E}_1 = \begin{pmatrix} \underline{A}_1 & \underline{O} & \underline{O} \\ \underline{O} & \underline{A}_2 & \underline{O} \\ \underline{O} & \underline{O} & \underline{A}_3 \end{pmatrix} \quad (4.5)$$

where

$$\underline{\underline{A_1}} = \begin{matrix} & \begin{matrix} X & Y & Z & X' & Y' & Z' \end{matrix} \\ \begin{matrix} X \\ Y \\ Z \\ X' \\ Y' \\ Z' \end{matrix} & \begin{pmatrix} 'E & 0 & 0 & -\lambda^p/\sqrt{2} & 0 & 0 \\ 0 & 'E & 0 & 0 & -\lambda^p/\sqrt{2} & 0 \\ 0 & 0 & 'E & 0 & 0 & -\lambda^p/\sqrt{2} \\ -\lambda^p/\sqrt{2} & 0 & 0 & {}^3E + \frac{1}{2}\lambda^p & 0 & 0 \\ 0 & -\lambda^p/\sqrt{2} & 0 & 0 & {}^3E + \frac{1}{2}\lambda^p & 0 \\ 0 & 0 & -\lambda^p/\sqrt{2} & 0 & 0 & {}^3E + \frac{1}{2}\lambda^p \end{pmatrix} \end{matrix} \quad (4.6)$$

$$\underline{\underline{A_2}} = \begin{matrix} & \begin{matrix} XY & YZ & ZX & ZR & YY \end{matrix} \\ \begin{matrix} XY \\ YZ \\ ZX \\ ZR \\ YY \end{matrix} & \begin{pmatrix} {}^3E - \frac{1}{2}\lambda^p & 0 & 0 & 0 & 0 \\ 0 & {}^3E - \frac{1}{2}\lambda^p & 0 & 0 & 0 \\ 0 & 0 & {}^3E - \frac{1}{2}\lambda^p & 0 & 0 \\ 0 & 0 & 0 & {}^3E - \frac{1}{2}\lambda^p & 0 \\ 0 & 0 & 0 & 0 & {}^3E - \frac{1}{2}\lambda^p \end{pmatrix} \end{matrix} \quad (4.7)$$

$$\underline{\underline{A_3}} = \begin{matrix} & R \\ R & ({}^3E + \lambda^p) \end{matrix} \quad (4.8)$$

The submatrices $\underline{\underline{0}}$ denote appropriate blocks of zeros and the abbreviations " $\underline{\underline{XR}} = 3X^2 - R^2$ " and " $\underline{\underline{YY}} = Y^2 - Z^2$ " have been used in labeling the rows and columns of $\underline{\underline{A_2}}$. The various quantities appearing in the matrix elements are defined as follows

$${}^1E = \int \Psi_A(x)^* (H - H_s) \Psi_A(x) d\tau - E_0, \quad (4.9)$$

$${}^3E = \int \Psi_A(x')^* (H - H_s) \Psi_A(x') d\tau - E_0, \quad (4.10)$$

$$\xi = 2 \int \Psi_A(x')^* H_s \Psi_A(x') d\tau, \quad (4.11)$$

$$\lambda \xi = -\sqrt{2} \int \Psi_A(x)^* H_s \Psi_A(x') d\tau. \quad (4.12)$$

Although the non-zero matrix elements themselves are considerably more complicated, E_1 is seen to have exactly the same form as the corresponding atomic p^5 matrix.⁽²⁴⁾ Bethe has shown that terms of different J will not mix regardless of the nature of the interactions in H , so long as H has cubic symmetry.⁽²⁹⁾ This accounts for the null submatrices in (4.5). One further expects the states X, Y, Z to be degenerate and uncoupled from one another; the same statement applies to X', Y', Z' . Thus we need concern ourselves only with optically preparable $J=1$ states. We further notice that (4.6) is diagonal with respect to the Cartesian components of the P states reducing the secular problem to a two-by-two diagonalization involving, say, Y and Y' states. This is completely analogous to the secular problem encountered in work on phosphors like KCl:Tl.⁽⁵⁾

The quantities (4.9) through (4.12) have been computed in the

S^2 approximation. This means that any quantity which involves more than two products of orthogonal or heterocentric wave functions is dropped. In the case of 1E and 3E one first writes the total energy of the crystal in the form introduced by Löwdin⁽¹⁸⁾ with the exception that the Ψ_A wave functions associated with atom A belong to appropriate zero-order excited-states of the atom. Then the original expression for E_0 is subtracted analytically from $\langle \mu | H | \mu \rangle$ of the excited-state μ . A straightforward but extremely lengthy algebraic computation produces the result

$$^3E = \mathcal{E}_A + \mathcal{E}_c + \mathcal{E}_x + \mathcal{E}_L + \mathcal{E}_T, \quad (4.13)$$

where $\mathcal{E}_A$ is the difference between the energies of the pure-triplet and ground-states of the free atom, and the "Coulomb", "exchange", "Löwdin", and "three-center" terms are defined, respectively, as

$$\begin{aligned} \mathcal{E}_c = & \sum_a \left[1 + \sum_k \sum_k (\bar{S}_{kk, Aa})^2 \right] \int |\bar{\Phi}_{Aa}|^2 C^A d\tau \\ & + \sum_a \left[1 + \sum_k \sum_k (S_{kk, Aa})^2 \right] \int |\bar{\Phi}_{Aa}|^2 C^A d\tau \\ & + \sum_a \sum_k \sum_h \left[(\bar{S}_{kk, Aa})^2 \int |\phi_{kk}|^2 (C^{Ak} + \bar{C}_A) d\tau \right. \\ & \quad \left. - (S_{kk, Aa})^2 \int |\phi_{kk}|^2 (C^{Ak} + C_A) d\tau \right] \\ & + \sum_k \sum_k \sum_{j \neq k} \sum_j (S_{kk, j})^2 \int |\phi_{kk}|^2 (\bar{C}_A - C_A) d\tau, \end{aligned} \quad (4.14)$$

$$\mathcal{E}_x = - \sum_a \sum_k \sum_k \left[(kk, \bar{A}_a | g | \bar{A}_a, kk) - (kk, A_a | g | A_a, kk) \right], \quad (4.15)$$

$$\begin{aligned} \mathcal{E}_L = - \sum_a \sum_K \sum_k [(\bar{S}_{Kk, Aa})^2 (Kk, \bar{Aa} | g | Kk, \bar{Aa}) \\ - (S_{Kk, Aa})^2 (Kk, Aa | g | Kk, Aa)] , \end{aligned} \quad (4.16)$$

$$\begin{aligned} \mathcal{E}_T = - \sum_a \sum_K \sum_k [\bar{S}_{Kk, Aa} \int \bar{\phi}_{Aa} (2C^{KA} + C_K^k + \bar{C}_A^a) \phi_{Kk} d\tau \\ - S_{Kk, Aa} \int \phi_{Aa} (2C^{KA} + C_K^k + C_A^a) \phi_{Kk} d\tau] \end{aligned} \quad (4.17)$$

$$- 2 \sum_K \sum_k \sum_{J \neq K} \sum_{J'} S_{Kk, J'} \int \phi_{Kk} (\bar{C}_A - C_A) \phi_{J'} d\tau .$$

In equations (4.14) through (4.17) a bar over any symbol means that wave functions from the excited (triplet) configuration are to be used when atom A is involved. Elsewhere, ground-state functions are used. The following additional abbreviations have been made

$$C_L(r_m) = \sum_{\mathcal{L}} \int |\phi_{\mathcal{L}e}(r'_m, \sigma'_m)|^2 e^{-Z_L r'_m} r'_m d\tau' = Z_L e^{-Z_L r_m} , \quad (4.18)$$

$$C^{L, M, \dots, T} = \sum_{K \neq L, M, \dots, T} C_K(r_m) , \quad (4.19)$$

$$(I_i, J_j | g | Kk, Le) = \int \phi_{I_i}(1) \phi_{J_j}^*(2) \frac{e^2}{r_{12}} \phi_{Kk}(1) \phi_{Le}(2) d\tau_1 d\tau_2 . \quad (4.20)$$

Thus, C_L is the classical Coulomb potential due to the entire atom L when its electrons are in states labeled $l=1, 2, \dots, Z_L$, and $C^{L,M,\dots,T}$ is the combined potential due to all atoms in the lattice except L, M, ..., T. When the k-th electron is to be excluded from the sum in $C_L(r)$, we write $C_L^k(r)$.

The summations over a in (4.14) through (4.17) run over the configuration $1s^2 \dots np^6$ in the ground state and over $1s^2 \dots np^5 n'$'s when the center is excited. In the latter case the np functions may be chosen as $npx+$, $npx-$, $npz+$, $npz-$, $npz+$. It has been shown⁽¹⁵⁾ that in the S^2 approximation 1E differs from 3E only in that appropriate (singlet) radial wave functions are used in the computation and $\mathcal{E}_A$ is to be taken as the energy difference between the pure-singlet and ground-state energies of the free atom.

It should be pointed out that the last terms of both (4.14) and (4.17) were omitted by Knox in each of his corresponding equations.^{(15),(16)} However, they are both small in magnitude and probably give rise to no serious numerical errors in his work.

The atomic wave functions used in computations from (4.14) through (4.17) must be solutions of the atomic Hartree-Fock equations. If they are not, additional exchange correction as given by Löwdin⁽¹⁴⁾ is necessary.

Knox has given many helpful formulae for the evaluation of $\mathcal{E}_e$, $\mathcal{E}_L$, $\mathcal{E}_x$, and $\mathcal{E}_T$,⁽¹⁵⁾ and we have developed others which are particularly convenient for performing sums in a distorted lattice. All

of these terms are of importance when computed numerically for the case of an argon impurity in solid neon. The first three give rise to appreciable depressions of the excitation energy. The three-center term provides a very large positive contribution.

After a tedious derivation, we find the spin-orbit parameters and are given to order S^2 by the relationships

$$\begin{aligned} \zeta_p = & \left[1 + \frac{3}{4} \sum_K \sum_k (\bar{S}_{Kk, npz+})^2 \right] \zeta_p \\ & + \frac{1}{4} \sum_K \sum_k \sum_{k' \neq k} \bar{S}_{Kk, npz+} \bar{S}_{Kk', npz+} \int \phi_{Kk} H_S \phi_{Kk'} d\tau \\ & - \sum_K \sum_k \bar{S}_{Kk, npz+} \int \phi_{Kk} H_S \phi_{npz+} d\tau, \end{aligned} \quad (4.21)$$

$$\begin{aligned} \lambda \zeta_p = & \left\{ 1 + \frac{3}{8} \sum_K \sum_k [(\bar{S}'_{Kk, npz+})^2 + (\bar{S}_{Kk, npz+})^2] \right\} \lambda_p \zeta_p \\ & + \frac{1}{4} \sum_K \sum_k \sum_{k'} \bar{S}'_{Kk, npz+} \bar{S}_{Kk', npz+} \int \phi_{Kk} H_S \phi_{Kk'} d\tau \\ & - \frac{1}{2} \sum_K \sum_k (\bar{S}'_{Kk, npz+} \int \phi_{Kk} H_S \bar{\phi}_{npz+} d\tau \\ & + \bar{S}_{Kk, npz+} \int \bar{\phi}_{npz+} H_S \phi_{Kk} d\tau). \end{aligned} \quad (4.22)$$

Here ζ_p and λ_p are the atomic spin-orbit parameters and primed quantities with a bar over them are to be evaluated using functions belonging to the atomic pure-singlet. Equation (4.22) is identical with the similar expression given in the appendix of reference 28. Equation (4.21) is derived in an entirely analogous manner. In the argon-in-neon computation only those terms con-

taining ζ_p and $\lambda_p \zeta_p$ contribute appreciably to the spin-orbit parameters of the system. The remainder are listed here for the sake of completeness.

It must be pointed out that the simplicity of the first-order expressions for the excitation energy presented above is a result of taking energy differences with the nuclear positions held fixed. If one wished to perform a complete calculation for a configuration coordinate model this analytic procedure could not be used because of the presence of many terms dependent parametrically on nuclear positions. However, if one were able to construct a suitable ground-state configuration coordinate in some appropriate and simple manner (perhaps semi-empirically) the first-order excited state curve could be constructed, in principle, by repeated point by point application of the results of the present section.

V. VAN DER WAALS INTERACTIONS

Since the bonding of a molecular crystal is entirely due to van der Waals forces it seems necessary to take them into account in a computation of excitation energies. In the usual treatment of such problems it is customary to expand the electrostatic interaction between pairs of atoms in a multipole series and then to treat the dipole-dipole (and perhaps the dipole-quadrupole) interactions explicitly. These are written in the form $-(c_1 R_{12}^{-6} + c_2 R_{12}^{-8} + \dots)$ where R_{12} is the internuclear separation and c_1 and c_2 are constants. The validity of such a procedure in cases where the charge distributions involved are overlapping has been discussed in detail by Brooks.⁽³⁰⁾ He concludes that though the procedure is, of course, not rigorously justified, it nonetheless may be expected to give reasonable results if only the lower order terms of the expansion are considered at small internuclear separations.

In solids it is usually assumed that only two-body interactions are of importance and the van der Waals energy is evaluated using the simple lattice sums given by Lennard-Jones and Ingham.⁽³¹⁾ Three-body interactions in solid argon have been examined by Axelrod and have been shown to be negligibly small.⁽³²⁾

Theoretical study of dipole-dipole interactions has been conducted along two principal lines. The first is the use of second-

order perturbation theory. A rigorous pursuit of the treatment would require the knowledge of all of the excited-state wave functions of the constituents of the system and is therefore so difficult as to be out-of-the-question. Eisenschitz and London introduced certain simplifying assumptions into the theory which permit the computation of van der Waals constants to be made from an empirical knowledge of the polarizabilities and first ionization potentials of the atoms involved.⁽³³⁾ Margenau has given a thorough review of progress made in its application.⁽³⁴⁾ The second approach is the use of the Ritz-Rydberg variational principle. Earliest work with this method was carried out by Slater⁽³⁵⁾ and Kirkwood⁽³⁶⁾ and it was further developed by Buckingham.⁽¹⁹⁾ Here knowledge of the wave functions of the constituent atoms in the state of immediate interest is sufficient to perform the computation.

There are two objections to the use of the Eisenschitz-London method in the present computations. First, the polarizabilities of rare-gas atoms in excited-states are not experimentally known. Second, the use of such a procedure would seem contrary to the spirit of computing the excitation energies from first principles. Thus, we adopt the method of Buckingham to compute van der Waals constants for the ground-and excited-states of our system. The energy differences thus encountered will be added to the first-order excitation energies derived from the results of section IV.

A calculation of van der Waals interactions formally similar to ours has been made by Potekhina in considering the system NaCl:Ag.⁽⁴⁾

Buckingham computes the dipole-dipole interaction between two atoms assuming that the wave function for the system is represented by a simple product of the two (antisymmetrized) atomic wave functions. The details of the computation will not be repeated here.* The result for the dipole-dipole interaction is as follows

$$E_{d-d} = -C(1,2)/R^6, \quad (5.1)$$

$$C(1,2) = \frac{4}{9} \sum_i \sum_j (R^2)_{ii}^2 (R^2)_{jj}^2 / [(R^2)_{ii} + (R^2)_{jj}], \quad (5.2)$$

where

$$(R^2)_{kk} = (kk|r^2|kk) - \sum_{k' \neq k} [(kk|x|kk')^2 - (kk|y|kk')^2 + (kk|z|kk')^2], \quad (5.3)$$

In the matrix elements of (5.3) the symbols r,x,y,z retain their

*Though we have verified Buckingham's final results we note that several of the evaluation theorems concerning integrals containing products of minors of Slater determinants are incorrect. However, the errors made seem to be compensatory.

usual meaning as coordinates measured from the nucleus of atom K. The summations on i and j in (5.2) run only over quantum numbers occupied by electrons in the atomic state considered. We include this last statement to emphasize the fact that electronic wave functions belonging to higher excited states are unnecessary in Buckingham's formalism.

Only the dipole-dipole interaction will be taken into account in the present computation. Dobbs and Jones have discussed the validity of neglecting higher order terms for the ground state of rare-gases and conclude that satisfactory fits to elastic and thermodynamic data may be made using a simple Lennard-Jones (6,12) potential.⁽³⁷⁾ It would seem inconsistent to include higher multipole effects for the excited-states without also including second-order exchange interactions between pairs of atoms; the use of a simple product of atomic wave functions as encountered in Buckingham's work excludes these.

VI. OSCILLATOR STRENGTHS AND INTEGRATED ABSORPTION COEFFICIENTS

Using the customary procedure⁽²⁴⁾ for the exact diagonalization of the two-by-two matrix connecting the $J=1$ singlet and triplet states of the same n the following expressions are obtained for the dipole matrix elements for electric dipole transitions to the optically preparable first-order states of the p^5 configuration

$${}^1M = \int \Psi({}^1S_0)^* \sum_i e r_i \Psi({}^1P_1) d\tau = (1 + \zeta^2 \bar{F}^2)^{-\frac{1}{2}} \underline{d}_0, \quad (6.1)$$

$${}^3M = \int \bar{\Psi}({}^1S_0)^* \sum_i e r_i \bar{\Psi}({}^3P_1) d\tau = (1 + \bar{F}^2 \zeta^2)^{-\frac{1}{2}} \underline{d}_0. \quad (6.2)$$

Here $\underline{d}_0$ is the dipole matrix element obtained evaluating the integral

$$\int \Psi({}^1S_0)^* \sum_i e r_i \bar{\Psi}({}^1P) d\tau$$

using wave functions belonging to the pure singlet state of the system. The spin-orbit parameters ζ and λ are defined in section IV,

$$\frac{1}{\sqrt{2}} \bar{F} = \frac{1}{2} \Delta - \frac{1}{4} \zeta + \left[\left(\frac{1}{2} \Delta - \frac{1}{4} \zeta \right)^2 + \frac{1}{2} \lambda^2 \zeta^2 \right]^{-\frac{1}{2}}, \quad (6.3)$$

and $\Delta \equiv {}^1E - {}^3E$. Corrected to second-order in overlap $\underline{d}_0$ is given by

$$d_o = M_o + \rho_m, \quad (6.4)$$

where

$$M_o = e \int \bar{\phi}_{A4s}(r_m) r_m \phi_{A3p\chi_m} dr_m, \quad (6.5)$$

and

$$\begin{aligned} \rho_m = & \left\{ \delta + \sum_I \sum_i \left[(S_{Ii,3p\chi_m})^2 + (\bar{S}_{Ii,4s})^2 \right] \right\} M_o \\ & - \sum_I \sum_i S_{Ii,3p\chi_m} \int \bar{\phi}_{4s} e r_m \phi_{Ii} dr_m \\ & - \sum_I \sum_i \bar{S}_{Ii,4s} \int \phi_{3p\chi_m} e r_m \phi_{Ii} dr_m \\ & + \sum_I \sum_i S_{Ii,3p\chi_m} \bar{S}_{Ii,4s} \int e r_m |\phi_{Ii}|^2 dr_m. \end{aligned} \quad (6.6)$$

The quantity δ is a correction term which accounts for the fact that the expressions $\int \bar{\phi}_\mu \phi_\nu dr_m - \delta_{\mu\nu}$ do not in general vanish. It is defined and computed in Appendix A of reference 15.

In complete analogy to the free atomic case^{(27),(28)} the oscillator strengths for the singlet and triplet transitions are given, respectively, by

$${}^1f = \frac{8\pi^2\nu({}^1P_1, {}^1S_0)}{he^2} \frac{(|d_o|^2 - |\rho|^2)}{(1 + \zeta^2 \mathcal{F}^{-2})}, \quad (6.7)$$

$${}^3f = \frac{8\pi^2\nu({}^3P_1, {}^1S_0)}{he^2} \frac{(|d_o|^2 - |\rho|^2)}{(1 + \mathcal{F}^2 \zeta^{-2})}. \quad (6.8)$$

where the quantities $\nu(\lambda, {}^1S_0)$ are the first order transition frequencies. The quantity $|d_o|^2 - |\rho|^2$ instead of $|d_o|^2$ is used in the numerators of (6.7) and (6.8) in order to eliminate terms of fourth-

order in overlap.

Following Dexter⁽²⁰⁾ we write the integrated absorption coefficient as

$$\int \mu_{\lambda}(\epsilon) d\epsilon = \frac{1}{n} \left(\frac{2 \pi e^2 \hbar}{m c} \right) \left(\frac{n^2 + 2}{3} \right)^2 N_0 f, \quad (6.9)$$

where f is the oscillator strength for the transition as given above, N_0 is the concentration of impurities, and n is the index of refraction of the host crystal at the energy of the transition. The errors, uncertainties, and implications of equation (6.9) are discussed in reference 20.

VII CONSTRUCTION OF CONFIGURATION COORDINATES

In order to compute the energies at which impurity-induced absorptions and emissions will occur it is necessary to have a knowledge of the energy of the system as a function of all nuclear coordinates. Since this is obviously an impractical task using all 10^{23} nuclear coordinates involved, it has become customary to reduce the number which are taken into account to a tractable few, in particular, one. The coordinate customarily retained is the so called "breathing mode" which involves only the synchronous radial motion of the impurity's nearest neighbors.^{(1),(3),(4)}

In addition to being the local mode which intuitively seems most effective in determining the energy of the system, it possesses, in a cubic lattice, the further virtue of preserving the simple symmetry properties of the system. We shall adopt its use without further ado, noting only that a justification can be given for the formal procedure of treating only one mode, even when many modes of oscillation are known to be important.^{(6),(7a)}

The ground-state configuration for a dilute rare-gas alloy could, in principle, be computed by repeated application of Löwdin's method for the determination of binding energies. However, in the absence of ionic (Madelung) contributions encountered in computations involving, for example, alkali-halides, this task becomes exceedingly difficult, involving poorly known small differ-

ences between large numbers and the inaccuracies attendant to strong dependence on the tails of Hartree-Fock atomic wave functions. For excited-states involving highly overlapping wave functions the situation is even worse and the labor involved multiplied. Thus, in the present paper, we resort to a semi-empirical treatment. The ground state configuration coordinate is constructed using a Lennard-Jones (12,6) potential and the data on rare-gas crystals compiled by Dobbs and Jones.⁽³⁷⁾ The excited-state configuration coordinates are constructed from a (12,6) potential using a van der Waals constant computed by the method of section V and a repulsive coefficient determined by the energy difference between the ground-state minimum and the excited state calculated using the formalisms of sections IV and V, at the ground-state equilibrium lattice distance. Thus, emission energies may be computed on a classical, phenomenological basis, in analogy to the method which has been used in heavy-metal sensitized alkali-halide phosphors.^{(3),(4)} These results should not be taken to represent a theoretical determination of luminescence spectra from first principles. At best the emission predictions are of a semi-quantitative or qualitative nature.

(a) Ground state equilibrium

The interaction energy of a pair of rare-gas atoms may be written empirically as

$$E(R_{AB}) = 4\epsilon_{AB} \left[(\sigma_{AB}/R_{AB})^{12} - (\sigma_{AB}/R_{AB})^6 \right], \quad (7.1)$$

where R_{AB} is the internuclear distance between atoms A and B, ϵ_{AB} is the depth of the potential well between them and σ_{AB} is the intercept of the potential on the R_{AB} axis. Using the results of Lennard-Jones and Ingham⁽³¹⁾ we may write the interaction of a single atom of type A with the rest of an undistorted face-centered cubic lattice composed of atoms of type B as

$$E(a_{AB}) = 4\epsilon_{AB} \left[12.13 (\sigma_{AB}/a_{AB})^{12} - 14.45 (\sigma_{AB}/a_{AB})^6 \right], \quad (7.2)$$

where a_{AB} is the nearest neighbor distance for the host lattice. To account for the relaxation of the nearest neighbors of the center in determining the ground-state equilibrium position we correct (7.2) to read

$$E(a_{AB} + \xi) = E(a_{AB}) + \Delta E_1(\xi) + \Delta E_2(\xi), \quad (7.3)$$

where in a face centered cubic lattice

$$\Delta E_1(\xi) = 48\epsilon_{AB} \left[(\sigma_{AB}/a_{AB})^{12} - (\sigma_{AB}/a_{AB})^6 - (\sigma_{AB}/[a_{AB} + \xi])^{12} + (\sigma_{AB}/[a_{AB} + \xi])^6 \right], \quad (7.4)$$

$$\Delta E_2(\xi) = 48\epsilon_{BB} \left[(\sigma_{BB}/a_{AB})^{12} - (\sigma_{BB}/a_{AB})^6 - (\sigma_{BB}/[a_{AB} + \xi])^{12} + (\sigma_{BB}/[a_{AB} + \xi])^6 \right]. \quad (7.5)$$

Here q is the deviation from the host crystal nearest neighbor distance in the separation of the atoms in the breathing shell from the center. $\Delta E_1(q)$ represents the change of the interaction between the impurity and its neighbors; $\Delta E_2(q)$ is the change in energy among the host atoms. The equilibrium distance for the ground-state is found simply by inserting the empirically determined nearest neighbor distance for the host as a_{AB} and differentiating (7.3) with respect to q .

In deriving the equilibrium position from the data given by Dobbs and Jones⁽³⁷⁾ it is necessary to use the following well-known semi-empirical "combining relationships" for the constants ϵ_{AB} and σ_{AB} .⁽³⁸⁾ Given that $\epsilon_{AA}, \epsilon_{BB}, \sigma_{AA}, \sigma_{BB}$ are the constants appropriate to pairs of atoms of the same species we have

$$\epsilon_{AB} \sigma_{AB}^6 = \sigma_{AA}^3 \sigma_{BB}^3 (\epsilon_{AA} \epsilon_{BB})^{1/2}, \quad (7.6)$$

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{1/2}. \quad (7.7)$$

(b) Luminescence spectra

It is convenient for our present purposes to rewrite (7.1) in the form

$$E(R_{AB}) = \frac{A_{AB}}{R_{AB}^{12}} - \frac{C(AB)}{R_{AB}^6}. \quad (7.8)$$

Here $C(AB)$ is the same as the van der Waals constant encountered in section V and A_{AB} is the appropriate constant for the repulsion. Then for the system as a whole in an excited state we write, (ne-

glecting small changes in host-host interactions),

$$\mu E_{abs} - \mu E_{atomic} = \sum_B \left\{ \frac{(\mu A_{AB} - {}^0 A_{AB})}{{}^0 R_{AB}^{12}} - \frac{[\mu C(AB) - {}^0 C(AB)]}{{}^0 R_{AB}^6} \right\}, \quad (7.9)$$

$$\mu E_{lum} - \mu E_{atomic} = \sum_B \left\{ \frac{(\mu A_{AB} - {}^0 A_{AB})}{\mu R_{AB}^{12}} - \frac{[\mu C(AB) - {}^0 C(AB)]}{{}^0 R_{AB}^6} \right\}. \quad (7.10)$$

In (7.9) and (7.10) the prescript zero refers to the ground state, the prescript μ on the various symbols indicates the excited-state to which absorption and from which emission takes place, μE_{abs} is the absorption energy at the ground-state equilibrium as computed from sections IV and V, μE_{atomic} is the excitation energy of the corresponding atomic state, and the μR_{AB} are the equilibrium separations for the states in question; μE_{lum} is the energy of the emission from the minimum of the excited state curve. Knowing μE_{abs} , μE_{atomic} , ${}^0 R_{AB}$, ${}^0 A_{AB}$ and the various van der Waals constants we may proceed to calculate μA_{AB} , μR_{AB} , and hence μE_{lum} . Again we emphasize that such a procedure is no better than semi-quantitative.

VIII. GENERAL REMARKS ON THE COMPUTATION FOR THE SYSTEM Ne:A

Though several computations of a semi-quantitative nature have been carried out for impurity states in ionic crystals, no detailed quantitative account of them has been made in the tight-binding approximation. Knox has carried out the first complete numerical calculation of optical absorption by a pure crystal based on the present first-order formalism.^{(15),(16),(17)} The most ambitious attempts at treating the impurity problem have been made by Williams⁽³⁾ and Potekhina⁽⁴⁾ who did not explicitly account for overlap. This is wholly understandable in terms of the amount of labor encountered in the numerical evaluation of energies through terms of order S^2 .

We have chosen to consider the system Ne:A in detail for several reasons. The lattice, in its ground-state, is a cubic array of neutral atoms in closed-shell configurations and the absence of strong ionic or covalent bonds leads to relatively large interatomic spacings. Thus, we would expect the tight-binding approximation to hold best in such a simple molecular crystal. Neon is the rare-gas of lowest atomic number which crystalizes in a cubic lattice, and argon is the lightest rare-gas which has a lower absorption than this host and will thus be expected to lead to minimum lattice distortion; finally, necessary Hartree-Fock atomic wave functions are available for both species in the states to be considered.⁽²⁶⁾

(39), (40)

Only states built from the $3p^5 4s$ configuration of the argon impurity will be considered. Hartree-Fock functions for the higher excited-states of the argon atom are not known and, in any event, their inclusion would force explicit consideration of configuration interactions both between the atomic argon states and with the excited states of the host lattice, vastly increasing the complexity of the problem.

The two- and three- center integrals involving atomic wave functions are evaluated using the alpha-function method of Löwdin⁽¹⁴⁾ which was used in a somewhat different notation by Kunimune.⁽⁴¹⁾ As the lattice constant representative of a real neon crystal we choose $5.9 a_0$ (nearest neighbor distance) in accordance with the recent measurements of Henshaw.⁽⁴²⁾ Using the method of section VII the equilibrium separation of the impurity from its nearest neighbors is found to be $6.3 a_0$. Ground-state and excited-state argon functions were interpolated and tabulated at constant intervals of $0.05 a_0$ for use in computing the necessary alpha-functions. Ground-state neon functions were similarly treated. The interval $0.05 a_0$ was chosen because it was small enough to yield a reasonable picture of the wave functions as they varied rapidly near the nuclei, but large enough to restrict the functions to a reasonable number of tabular entries. (It was also small enough to ensure the accuracy of the necessary "Simpson's rule" integrations). Because

of the large spatial extent of the singlet and triplet $4s$ functions it was necessary in many instances to extend the computations through third neighbors and through $1s$ functions on the neighbors.

The numerical work described herein was carried out at the University of Rochester Computing Center, using an IBM type-650 Magnetic Drum Data Processing Machine. Three machine-language programs by Rimmer and Knox were used for the major tasks of evaluating α -functions and double and single integrals.⁽⁴³⁾ The computation required about one-hundred and thirty hours of machine running time. Analytic reduction of the integrals to explicit form for machine evaluation, organization of the material and preparations for machine operation consumed something over twice this amount of time and about one-hundred and twenty thousand punched cards.

IX. COMPUTATION OF FIRST-ORDER ENERGY PARAMETERS

Our first task will be the computation of the "electrostatic" energy change, ^{2s+1}E , of (4.13), giving the first-order energy change of the system when the impurity is raised from its normal configuration to a state of definite multiplicity $2S + 1$ in the $3p^5 4s$ configuration. Equations (4.14) through (4.17) are used in obtaining ^{2s+1}E from Hartree-Fock functions. The quantities λ and ζ are computed from equations (4.21) and (4.22). The lattice sums encountered in these computations are straightforward and most have been treated in reference 15. Only the essential features of the numerical work will be presented here.

Table 1 summarizes the first-order electrostatic contributions as listed in equation (4.13) for the singlet and triplet terms. The quantities ϵ_A are the pure-singlet and pure-triplet energies computed for the free atom in reference 26, with a probable error of ± 0.5 eV given there for both quantities.

The various difficulties and errors encountered in the evaluation of ϵ_L , ϵ_x , and all but the last terms of ϵ_c and ϵ_T have been discussed previously. (17)

The principal source of error in ϵ_c is the necessity for computing the small differences between the large electron-electron and electron-nucleus interactions. The exchange interactions, ϵ_x , present an entirely different problem. The alpha-function expan-

sions encountered converge so slowly that extrapolation methods must be used to sum them in many instances. The three-center term, $\mathcal{E}_T$, combines, to some extent, the problems encountered in computing both $\mathcal{E}_c$ and $\mathcal{E}_x$. $\mathcal{E}_c$ presents no particular difficulties and has a high numerical accuracy.

The last term in $\mathcal{E}_c$ is found to be negligibly small, depending as it does on the squares of overlaps of ground-state neon functions and yields a contribution smaller than the numerical accuracy to which it can be computed. In any event, $\mathcal{E}_c$ is completely dominated by the terms involving the excited 4s electron.

The last term of $\mathcal{E}_T$, which was omitted by Knox,⁽¹⁶⁾ may be written as a sum over terms of the form

$$e^2 S_{I_i, I_i'} \int \phi_{I_i} \phi_{I_i'} \sum_{a=1}^{Z_A} \left(\frac{|\phi_{I_a}|^2}{r_{i2}} - \frac{1}{|R_A - r_i|} \right) d\tau. \quad (9.1)$$

$I_i, I_i' \neq A$
 $I_i' \neq I_i$

We may think of $\phi_{I_i} \phi_{I_i'}$ as a fictitious "overlap charge distribution" of magnitude $S_{I_i, I_i'}$. For $a \neq 4s$ we find that the contributions to the nuclear and electronic parts of (9.1) are nearly cancelling and give rise to contributions of the order of $e^2 (S_{I_i, I_i'})^2 / R$ where R is the distance of the "center of gravity" of the fictitious overlap charge distribution from the nucleus of the impurity and is in general no less than the smaller of R_I and $R_{I'}$. In the case $a=4s$ we find that the deviation from $e^2 (S_{I_i, I_i'})^2 / R$ for the electronic part of the coulomb interactions is of the order of 6 to 7%. The

largest overlap integrals encountered among ground-state neon functions are as follows: (all are for first neighbors)

$$S(2p_x, 2p_x)_{6.3a_0} = -0.00609; S(2p_x, 2s)_{6.3a_0} = -0.00203; S(2s, 2s)_{6.3a_0} = 0.00023.$$

Of these only the last will fail to suffer large cancellations during the performance of the lattice sums over I and I' . Because

$\phi_{I, I'}$ does not overlap appreciably with nucleus A , we find that the $4s$ term is a sum of terms of the order of

$$(0.07)e^2(S_{I, I'})^4/R - e^2(S_{I, I'})^2/R.$$

The resulting contributions of order $(0.07)e^2(S_{I, I'})^2/R$, where $R \geq 6.3 a_0$, (the largest single contribution is of the order of $4 \times 10^{-6} e^2/a_0$) are well below the limit of our computational error in computing the individual integrals of the form (9.1), not to speak of the overall computational error in E_r . Thus, these terms will be neglected in the present calculation.

It should be noted at this point that the so-called "three-on-one" terms give the largest contribution to E_r . These are the terms formally included in (4.17) which involve only two centers. In the case of the singlet they amount to 6.960 eV and for the triplet to 6.526 eV. Again, as in all of the other parts of (4.13), the excited $4s$ electron terms are vastly dominant.

Using an overall estimate of ten per-cent for the computational error resulting from the computational difficulties previously discussed we write,

$$\begin{aligned} {}^1E &= 12.1 \pm 1.2 \text{ eV} \\ {}^3E &= 12.0 \pm 1.2 \text{ eV} \end{aligned} \quad (9.2)$$

The spin-orbit parameters ζ and λ have been computed using equations (4.21) and (4.22). It is found that the only appreciable contributions in each case come from the leading terms (the coefficients of ζ_p and $\lambda_p \zeta_p$). We obtain the results

$$\begin{aligned} \zeta &= 0.1159 \text{ eV} \\ \lambda &= 1.001. \end{aligned} \quad (9.3)$$

The value of ζ_p is 0.1157 eV for the free atom, and λ is identical with its atomic counterpart λ_p . We note the interesting fact that the values (9.3) are precisely the same as those obtained for a pure argon lattice in connection with the computation of its exciton absorption spectrum.⁽¹⁷⁾ These last results are not surprising in light of the fact that the spin-orbit interaction involves the tightly bound 3p hole which is not strongly influenced by the crystal field.

Diagonalizing the two-by-two matrix

$$\begin{pmatrix} {}^1E & -\lambda\zeta/\sqrt{2} \\ -\lambda\zeta/\sqrt{2} & {}^3E + \frac{1}{2}\zeta \end{pmatrix} \quad (9.4)$$

we arrive at the following values for the first-order excitation energies of the $3p^5 4s$ configuration:

$$\begin{aligned} {}^1W &= 12.18 \pm 1.2 \text{ eV} \\ {}^3W &= 12.01 \pm 1.2 \text{ eV} \end{aligned} \quad (9.5)$$

Here 1E and 3E are the pure-singlet and triplet excitation energies computed above, and 1W and 3W are the eigenvalues of (9.4).

X. COMPUTATION OF VAN DER WAALS ENERGIES

In an attempt to ascertain the accuracy of Buckingham's method⁽¹⁹⁾ for the evaluation of van der Waals constants we have calculated the coefficient of the R^{-6} interaction for pairs of argon and neon atoms in their ground-states as well as for argon-neon with the argon atom in various states. These results are presented in the first column of Table 2. The second column represents values computed by Buckingham using various experimental data (e.g., atomic polarizabilities, second virial coefficients, and scattering cross-sections). The values in the third column are derived from the (12,6) potential constants computed from experimental data on pure neon and argon lattices by Dobbs and Jones. The entry for $^{\circ}C(A,Ne)$ in that column is derived using the semi-empirical "combining relationships" of section V, i.e., by demanding that $C(A,B) = [C(A,A)C(B,B)]^{1/2}$. Rather than enter into a detailed (and probably fruitless) argument of the merits of the various numbers encountered we shall content ourselves with noting that the computed constants are at least semi-quantitatively correct, and are, in any event, the best one can do for the excited-states without a great deal more labor, which will be shown to be unjustified. However, one should be cautioned not to take them in too literal a fashion.

We have used calculated values for the pure-singlet and pure-triplet van der Waals constants and values derived from the empiri-

cal data of Dobbs and Jones for the ground-state van der Waals constants to compute a correction to the first-order excitation energies. Writing $E_{abs} = W + E_{vdW}$ where $E_{vdW} = E(\mu) - E_d(^1S_0)$ we have

$$\begin{aligned} {}^1E_{abs} &= 11.69 \text{ eV} \\ {}^3E_{abs} &= 11.58 \text{ eV} \end{aligned} \quad (10.1)$$

Taking the accuracy of the dipole-dipole energies to be $\pm 25\%$, the estimated errors in (10.1) are ± 1.3 eV.

Using the same values of the van der Waals constants as in the computation of the correction to the absorption energy and the value $A_{ANe} = 2.653 \times 10^{-104} \text{ erg cm}^{12}$ derived from the empirical potential for the ground-state in equations (7.9) and (7.10) we obtain the following phenomenological predictions for the emission energies: ${}^1A_{ANe} = 22.139 \times 10^{-104} \text{ erg cm}^{12}$; ${}^3A_{ANe} = 23.211 \times 10^{-104} \text{ erg cm}^{12}$; and ${}^1R_{ANe} = 7.41 a_0$; ${}^3R_{ANe} = 7.59 a_0$.

$$\begin{aligned} {}^1E_{lum} &= 11.26 \text{ eV} \\ {}^3E_{lum} &= 11.11 \text{ eV} \end{aligned} \quad (10.2)$$

In obtaining (10.2) we have used the values ${}^1E_{atomic} = 11.36 \text{ eV}$; ${}^3E_{atomic} = 11.19$ and the absorption energies (10.1). These results are to be considered no more than semi-quantitative and are included because they are simple to obtain while still being of some interest.

The values of R obtained are a clear indication of the uncertainty of the computation. They indicate that the predicted e-

missions will take place at a breathing-shell separation which is greater than the normal lattice constant ($7.1 a_0$) of a pure argon crystal. They also state that $^3R > ^1R$, a result contrary to what one would expect considering the relative extent of the singlet and triplet charge distributions.

XI. OSCILLATOR STRENGTHS AND INTEGRATED ABSORPTION COEFFICIENTS

Using the formalism of section VI and the computed values $\delta = 0.20$ (this value is taken from reference 26) and $\Delta = {}^1E - {}^3E = 0.095$ in addition to the computed first-order energies and spin-orbit parameters we obtain the following values for the dipole matrix elements encountered:

$$M_0 = 0.379 ea_0; \quad \rho = 0.078 ea_0; \quad |d_0|^2 - |\rho|^2 = 0.202 e^2 a_0^2.$$

These values give oscillator strengths

$$\begin{aligned} {}^1f &= 0.164 \\ {}^3f &= 0.017 \end{aligned} \tag{11.1}$$

These may be compared with calculated values of the free argon atom of ${}^1f = 0.185$ and ${}^3f = 0.052$.⁽²⁶⁾ Since the computed oscillator strengths have a very strong dependence on Δ , a quantity which is a poorly known small difference of large numbers, we assign a probable error of $\pm 20\%$ to the singlet value and $\pm 40\%$ to the triplet. These represent the same range of uncertainty encountered in the atomic calculation, wherein the problems encountered are much the same.

The integrated absorption coefficients obtained using the oscillator strengths (11.1) are

$$\begin{aligned} \int \mu_1(E) dE &= \frac{0.84 \times 10^6}{N_0} \text{ eV cm}^{-1} \\ \int \mu_3(E) dE &= \frac{0.09 \times 10^6}{N_0} \text{ eV cm}^{-1} \end{aligned} \tag{11.2}$$

where N_0 is the fractional concentration of the impurity. Since

we have no knowledge, experimentally, of the index of refraction of the argon host crystal at the energies of the absorptions, and since a calculation of these indices is beyond the scope of the present work, we have arbitrarily adopted a value of $n = 1$ in (6.9). Thus, the results (11.2) should be taken as being of an order-of-magnitude quality.

XII. DISCUSSION

We have presented a generalization of the Heitler-London approximation for the ground- and excited-states of a substitutional impurity in a solid rare-gas crystal. Explicit consideration has been given to the overlapping of heterocentric atomic wave functions and spin-orbit interaction in determining the first-order excitation energies and oscillator strengths. The equilibrium ground-state lattice configuration has been calculated from an empirically obtained (12,6) potential, but the remainder of the first-order absorption calculation has proceeded from first principles. Van der Waals corrections to the excitation energies have been computed using a variational procedure. Predictions of the emission energies have been made on a phenomenological basis using computed excitation energies and excited-state van der Waals constants and the empirical interatomic potential for the ground-state.

In calculating the first-order excitation energies three basic assumptions have been made. They are: (1) the assumed validity and accuracy of the atomic Hartree-Fock functions involved, (2) the neglect of perturbations on pure $3p^5 4s$ states by higher excited-states of the impurity and by host crystal excited-states, (3) the assumed convergence of the Löwdin orthonormalization series at terms of order S^2 .

The use of Hartree-Fock functions for the excited state of the

impurity probably places a lower limit of 5% on the attainable accuracy of the first-order calculation. The dipole matrix elements derived from these functions, depending as they do on the tails for the accuracy, are probably given to not much better than 20% - 30%. (26), (27)

Reference 16 discusses the neglect of configuration interactions in connection with the exciton problem in solid rare-gases. The conclusions drawn therein may be taken over bodily to the consideration of higher excited-states of the impurity itself and do, indeed, justify their neglect. The difference of almost five volts between the predicted absorption energies of the present work and the atomic absorption to the $2p^5 3s$ state of neon suggest that host crystal coupling may be neglected. Although Knox has predicted a depression of the order of two-and-a-half volts in going from the free atom to the first exciton bands of solid argon⁽¹⁷⁾ giving rise to absorptions in the neighborhood of $1380 \text{ \AA}$ (9 eV) in the crystal, his conclusions seem to be in disagreement with the experimental work of Schnepf⁽⁹⁾ wherein no absorption is observed in solid argon at wavelengths greater than $1200 \text{ \AA}$ (10.3 eV). In addition, Schnepf observed absorptions in solid xenon and solid krypton which were within 0.1 eV of their atomic positions. Thus, we conclude that there are unlikely to be any states of the neon host lattice which are appreciably coupled to the argon $3p^5 4s$ transitions.

The third assumption above is without doubt the worst made in

the present computation. Table 3, consisting of overlap integrals between an excited argon atom and a neon atom in its normal configuration, calculated for various interatomic separations, is presented for general reference. It will be noted that, in point of fact, Löwdin's⁽¹⁴⁾ condition for the divergence of the sum

$\sum_{K \neq J} S_{Jj, Kk} > 1$ (for any Jj), is met at the computed equilibrium breathing shell position of $6.3 a_0$ from the center. This is to say that $\sum_{I \neq 4s} S_{4sI2s} = 1.117 > 1$.

However, the situation may not be as dire as first appearances indicate. We note two points (other than the very weak support of present experimental evidence which indicates that absorption lines are little shifted from their atomic positions for various other impurities in solid rare-gases). First, we have computed the relevant overlap integrals at various interatomic distances and find that the series do meet Löwdin's criterion for convergence,

$\sum_{I \neq 4s} |S_{4sI}| < 1$ (all II), at breathing shell distances of 6.7 and $6.9 a_0$ for the pure-triplet and singlet states respectively, and also that the principal overlap integrals (in the sense of those most important in determining the energy parameters of the problem) suffer a change of $\lesssim 10\%$ in going from $6.3 a_0$ to their "radii of convergence". Further, the configuration coordinate curves, especially that for the ground state, are quite flat, having a total energy change of about 0.1 eV above the minima in a range $5.9 a_0$ to $7.6 a_0$. Since the phenomenologically predicted minima of the excited-state

curves lie well beyond the minimum of the ground-state, small changes in the assumed point of excitation will have a rather small effect on the predicted absorptions. Thus we may expect the results computed at $6.3 a_0$ to be physically reasonable.

The computed van der Waals constants contribute a correction of the order of 7% to the predicted absorption energies, and thus, great accuracy in their value is not essential to the present work. Those for which comparison may be made to the Dobbs and Jones values for pure solids are seen to agree with a range of 6 to 25%. This is certainly adequate for our present purposes. The use of van der Waals constants for states of pure multiplicity and with the neglect of overlap corrections is an expedient adopted in the light of the fact that additional corrections would be no more plausible than the results of the simple calculation, and the labor involved would be fruitlessly multiplied. Further, it would seem inconsistent to consider overlap explicitly in the van der Waals calculation while neglecting, as one does in the Buckingham variational formalism, interatomic exchange terms which are of order S^2 .

The use of a phenomenological potential in computing the emission energies is, as previously noted, no more than a semi-quantitative calculation. Experimental credence for this sort of procedure is gained from the work of McCarty and Robinson.⁽¹¹⁾ They have succeeded in determining empirical potential constants (in particular, excited-state polarisabilities and repulsive constants)

for various impurity species introduced into a rare-gas matrix from optical measurements. They then find that these quantities give good agreement with experiment when the impurity is introduced into a different rare-gas matrix. They use the equivalent of the so-called "combining relations" of section V in making these fits. We must note, however, that we have made no attempt to take into account such potentially important considerations as the Jahn-Teller⁽⁴⁴⁾ effect in the luminescence calculation. Throughout the computation we work in the static approximation. This is to say that we invoke the Franck-Condon principle for the excitation and compute the integrated absorption coefficient on the assumption that Born-Oppenheimer wave functions are applicable to the vibrating crystal and that the Condon⁽⁴⁵⁾ approximation is valid. We have made no attempt to compute the temperature dependence of the spectra, or to compute the first, or higher-order moments using, say, the formalism of Lax.⁽⁶⁾

There exists, at present, no experimental data with which direct comparison of the results of the present calculation may be made. However, there are some results which at least serve to verify the "spirit" of our predictions. Schnepf's previously quoted experimental work on pure solid rare-gases⁽⁹⁾ finds absorption energy shifts of the order of tenths of volts from the free atomic values. Schnepf has also investigated the optical absorption spectra of magnesium and manganese atoms in rare-gas matrices

and finds energy shifts of the same order of magnitude.⁽¹⁰⁾ These are positive or negative depending on the particular impurity and matrix involved. In some cases he finds splittings of the lines corresponding to the removal of the degeneracy of the P states. These are ascribed to the impurities finding themselves in sites of lower than cubic symmetry, e.g., in interstitial positions.

McGarty and Robinson⁽¹¹⁾ have examined the absorption spectra of Hg, NH, Na, and C₂ in argon, krypton and xenon lattices. Their results are of the same general tenor as Schnepf's. Shifts, either red or blue, of the order of tenths of volts from the corresponding atomic lines are observed. Line splitting presumably caused by a multitude of trapping sites, including surface positions, are also noted, especially in the case of the sodium impurity where extremely complex spectra are observed. Unfortunately, no measurements have yet been made of the luminescence, if any, from these centers. We present Table 4 for quick reference to calculated (blue) absorption line shifts of the present work. They seem to agree in order of magnitude with those discussed above. It is hoped that the experiments for the system Ne:A will be performed despite their technical difficulty. Such work would serve not only to test the present specific case, but would serve as an important guide in determining the validity of the Heitler-London model for impurity centers, with the S² approximation, however, serving as an important qualification.

It seems both unfortunate and apparent that both the present

calculation and Knox's work⁽¹⁷⁾ share a common failing. The powerful tool of symmetrical orthogonalization has indeed produced a formally correct procedure for performing the computation; however, the large amount of numerical work involves Hartree-Fock functions, and in particular small differences between large numbers computed with them, so that our extensive labors are rewarded with no better than ten per-cent computational accuracy.

The difficulty is that the Hartree-Fock functions are unavoidably not very accurate on the tails, and it is the tails that are responsible for the difference between electronic and nuclear electrostatic interactions between neighbors. Further, we have considered only terms up to second-order in overlap and have entirely neglected the possibility of large contributions from the quartic and higher terms. Finally, in the computation of exchange and three-center energies we have been forced to terminate alpha-function expansions of the integrals after a small number of terms and use extrapolation methods to sum the series.

Carrying out a computation to higher order in overlap, say, S^4 , would be a task of huge proportions. It is clear that just doing the lattice sums for the many, complex multi-center terms that would arise would require years of algebraic manipulation. The necessary numerical work would be increased by at least an order of magnitude. With all this, however, the use of Hartree-Fock functions would lead to results no more numerically precise or plausible

than those of this work.

At first it would seem that the use of a crude method for estimating the electrostatic forces which bind the crystal together is inconsistent with the use of an extension of Knox's elaborate formalism for the localized excitation energy. However, the large numerical uncertainties incurred in the first-order calculation do, indeed, make the use of the simple van der Waals formalism as good as the remainder of the calculation. It seems clear that an approach outside of the simple Heitler-London approximation will be necessary to gain a deeper quantitative insight into processes involving the excitation of atoms to spatially extended states in even the most "tightly-bound" of solid-state systems. A fundamental limitation is placed on computations of the present type by the use of the best available (Hartree-Fock) atomic wave functions. It would seem that the course of future research must be directed to the development of more satisfactory zero-order wave functions to represent the excited-states of the system. Generalizations of the method of linear combinations of atomic orbitals or the adaptation of the Hock scheme may be of value in this pursuit.

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Interaction	Singlet		Triplet	
	Contribution	Running Total	Contribution	Running Total
$\mathcal{E}_c$	- 2.876	- 2.876	- 2.169	- 2.169
$\mathcal{E}_L$	- 0.555	- 3.431	- 0.495	- 3.114
$\mathcal{E}_X$	- 3.899	-7.330	- 3.725	- 6.839
$\mathcal{E}_T$	+ 8.083	+ 0.753	+ 7.666	+ 0.827
$\mathcal{E}_A$	+11.357	+12.110	+11.188	+12.015

Table 1. Contributions to 1E and 3E , the first-order electrostatic energy of the pure-singlet and triplet crystal states relative to the ground state. A discussion of the calculation is given in the text. All energies are measured in electron volts.

Constant	Present Calc.	Buckingham (expt.)	Dobbs and Jones (expt.)
$^{\circ}C(\text{Ne}, \text{Ne})$	6.77	4.69 to 7.48	8.51
$^{\circ}C(\text{A}, \text{A})$	129.02	55.5 to 107	104.78
$^{\circ}C(\text{A}, \text{Ne})$	27.85	—	29.88
$^1C(\text{A}, \text{Ne})$	101.66	—	—
$^3C(\text{A}, \text{Ne})$	92.81	—	—

Table 2. Van der Waals constants computed for various pairs of rare-gas atoms from wave functions using Buckingham's variational method compared to various experimental determination. The values in the second column represent the range found by Buckingham using various experimental data. Those in the third column are computed from the work of Dobbs and Jones fitting the constants for a (12,6) potential with data on pure solid rare-gases. Symbols are defined in the text. All constants are in units of 10^{-60} erg cm⁶.

	$R = 6.3 a_0$	$R = 8.3 a_0$	$R = 10.2 a_0$
$S(4s, 2p\sigma)$	0.03985	0.02691	0.01461
$S(4s', 2p\sigma)$	0.04202	0.02682	0.01399
$S(4s, 2s)$	0.09514	0.04883	0.02361
$S(4s', 2s)$	0.09305	0.04557	0.02106
$S(4s, 1s)$	-0.00834	-0.00441	-0.00209
$S(4s', 1s)$	-0.00871	-0.00409	-0.00186
$S(3p\sigma, 2p\sigma)$	0.01385	0.00171	0.00020
$S(3p\pi, 2p\pi)$	-0.00210	-0.00018	-0.00001

Table 3. Several representative overlap integrals (computed with the wave functions of references 26 and 40). All $4s$ functions belong to the singlet term of the argon atom except those which are primed and taken from its triplet term. The second term of each argument belongs to the normal configuration of the neon atom. These quantities are dimensionless and are functions of the interatomic separation R which heads the columns with values corresponding to the equilibrium distances for the system in its ground state. Standard nomenclature for p functions in a diatomic configuration is used.

State	E_{atomic} (eV)	E_{abs} (eV)	E_{lum} (eV)	Absorption blue shift (eV)
$1P_1$	11.36	11.69	11.26	0.33
$3P_1$	11.19	11.58	11.11	0.37

Table 4. Comparison of calculated absorption and emission energies with those computed for the free argon atom.