

(Prentice-Hall, Englewood Cliffs, N. J., 1952).

²¹In order to obtain numerical results, the summations are performed over a sufficiently large number of lattice sites so that convergence is obtained to within the desired number of significant figures; in the present calculations at least four significant figures were obtained for the

lattice summations.

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Polarizability and Two-Quantum Excitations in Alkali Halides and Deep Impurity States in Rare-Gas Solids

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The general theory of the electronic dielectric constant of crystals, developed in a previous paper in the framework of an individual-ion model, is analyzed for diatomic systems. Use is made of an effective two-state model for the individual atoms. An exception is made, however, for certain terms in the polarizability which depend very strongly on the higher excited states, whose effect is thus taken into account, in an average-excitation-energy approximation. The final result of this analysis is a simplified expression for the frequency-dependent polarizability of an individual atom in the crystal, which includes explicitly the quantum correction arising from the induced dipole-dipole interaction. In a first application of these results, we carry out a detailed study of the static polarizability of alkali halide crystals, on the basis of a reasonable assumption for the polarizability of a free ion in an excited state. The dipole-dipole correction in the polarizability is found to be positive and to vary from 2 to 8%. This effect is in good quantitative agreement with a correction which has been derived from an empirical analysis of dielectric-constant data for the alkali halides. For the effects of frequency dispersion in the polarizability, we also find reasonable agreement with similar empirical results for the alkali halide ions. As a second type of application, we consider the problem of deep impurity states in crystals. An explicit expression for the electronic frequency shift of a substitutional impurity is obtained from the study of the singularities of the polarizability. In particular, this leads to a simple expression for the van der Waals constant for an excited impurity interacting with a matrix atom in the ground state. Application of this formula to rare-gas and molecular impurities in rare-gas matrices leads to surprisingly good agreement with empirical results, as obtained from an analysis of experimental shifts in terms of 6-12 potentials. As a last application we study the oscillator strength of two-quantum excitations (double excitons), which arise as a consequence of the quantum dipole fluctuations. For the alkali halides we find that this oscillator strength ranges from 4.5 to 20% of that of the ordinary one-quantum excitations in the NaCl structure, while rising to 30% in the CsCl structure.

I. INTRODUCTION

Theoretical and experimental studies of electronic excited states of the alkali halides and rare-gas solids seem to indicate that the model of tight-binding excitons, as developed originally by Frenkel, does not provide an adequate description of the electronic states in these systems. Most of these investigations were started, in fact, after the unexpected finding that the electronic spectra of the pure rare-gas solids can be interpreted rather well in terms of the Wannier model, which describes the opposite limit of loosely bound exci-

tons of large radii.¹ This provided strong evidence, of course, for non-negligible effects associated with the overlap of the charge distributions of neighboring atoms or ions in these crystals, especially in excited states. It has led to numerous attempts to improve the extreme tight-binding approximation by taking overlap and exchange effects into account, in addition to the Coulomb interaction. In this improved form, the tight-binding approximation has been rather successful in predicting excitation energies in the pure rare gases^{2,3} as well as excitation energies of impurities in solid He, Ne,

and Ar.⁴ A more general pseudopotential formalism which is valid, in particular, in both tight-binding and weak-binding limits has been given by Hermanson and Phillips.⁵ These authors arrive at the interesting conclusion that the Wannier weak-binding approximation, while working quite well for exciton states in the pure rare gases, becomes very poor for deep impurity states (because of large central cell corrections), thereby providing a firm basis for the validity of the corrected Frenkel model in deep impurity problems.

On the other hand, from the experience provided by the papers cited above, it has been concluded⁶ that in practice it is very difficult to treat overlap and electron-exchange effects in an accurate general way in the framework of the Frenkel model. Part of the difficulties are due to the fact that a parameterization of the theory in terms of macroscopic physical properties is either impossible or does not result in an adequate description for most real systems.

In contrast to the importance of overlap effects in the detailed interpretation of optical spectra of alkali halide and rare-gas crystals, it must be recalled, however, that there are properties of these crystals which also depend to some extent on the excited states and which are quite well interpreted on the basis of a model of individual ions or atoms which do not overlap in first approximation. The most striking example is that of the electronic dielectric constant of the alkali halides. The polarizability of these crystals can be discussed surprisingly well, in fact, by using an individual-ion model as shown originally by Tessman, Kahn, and Shockley⁷ and later, more carefully, by Pirenne and Kartheuser.⁸ From the work of these authors as well as from other evidence, provided by the study of frequency dispersion of the polarizability as well as by the success of the Born theory of crystal binding, it follows that a model of individual nonoverlapping ions (or atoms) is probably a valid starting point for a theory of the dielectric constant of alkali halides (and the electronically similar rare gases). Overlap effects are certainly of some significance but it seems reasonable to expect that they will only slightly modify the effect of the electrostatic interaction between the atoms. Thus it would appear that the two effects are essentially additive and may be treated independently of each other to a good approximation.⁹ In turn, this justifies the use of a multipole expansion for the Coulomb interaction where then the dipole-dipole (and perhaps the dipole-quadrupole) term is treated explicitly. Further evidence for the validity of this procedure in cases where the charge distributions involved are overlapping has been obtained by Brooks.¹⁰ He concludes that although the

use of a multipole expansion is of course not rigorously justified in this case, it nonetheless may be expected to give reasonable results if only the lower-order terms are considered at small internuclear separations.

In a recent paper,¹¹ we have discussed a general theory of the frequency-dependent dielectric constant which is based on the model of individual nonoverlapping atoms. The most interesting feature of this theory is that, as a result of an exact treatment of the classical Lorentz field effect in a first step, it provides the framework for a systematic study of the effect of quantum dipole fluctuations on the polarizability of individual atoms by means of perturbation theory. For an individual atom A , this correction to the free polarizability has the form

$$\Delta \vec{\alpha}_A(\omega) = \sum_{B \neq A} \Delta \vec{\alpha}_{AB}(\omega),$$

where the summation extends over all neighboring atoms B and ω is the frequency. The pair-interaction term $\Delta \vec{\alpha}_{AB}(\omega)$ is proportional to the inverse six power of the distance R_{AB} which separates A and B . Since the general expression of $\Delta \vec{\alpha}_{AB}(\omega)$ is quite complicated, we were later¹² led to simplify it by introducing convenient but reasonable approximation for the effect of the real spectrum of the atoms in various terms of this expression. The approximate result was then evaluated numerically and applied in a detailed study of the effect of dipole fluctuations on the energies of long-wavelength tight-binding excitons as well as on the oscillator strength of two-quantum excitations in monatomic systems.

The nature of the approximations which were used in II and the identification of, and reason for, discarding an alternative approximation scheme for $\Delta \vec{\alpha}_{AB}(\omega)$ may be further elucidated as follows. Since the correction in the polarizability originates from a physical mechanism which is similar to that of the ordinary two-body van der Waals dispersion forces, it is useful to compare the simplest approximations which have been proposed in the two cases for purposes of detailed applications. In both cases the goal is to get rid (in some approximation) of the complicated summation over the complete set of intermediate excited states of the individual atoms which is always present in second-order perturbations. For simplicity, we discuss the problem for an isolated pair of identical spherical atoms A and B , which are characterized by their polarizability α_0 and a typical excitation energy ω_0 ($\hbar = 1$) in the bound-state spectrum of excited states. In fact, throughout this work we shall use a single excitation energy for each atom, which we roughly identify with the energy of the first allowed transition. Consider first the expression of

the van der Waals energy ΔE_{AB} of the pair. The first step is to make the so-called Lennard-Jones-Ünsöld (LJU) approximation where one replaces the free-atom excitation energies in the exact second-order perturbation formula by the constant (average) value ω_0 . If in addition, the same approximation is made in α_0 , one has

$$\alpha_0 \simeq (2/\omega_0) \langle 0, A | p_{z,A}^2 | 0, A \rangle, \quad (1)$$

and one obtains

$$\Delta E_{AB} = -\frac{1}{8} \omega_0 \alpha_0^2 \text{Tr} \bar{\mathbf{T}}_{AB}^2 \quad (2)$$

which is the familiar London formula. Here $|0, A\rangle$ denotes the ground state of atom A , $p_{z,A}$ the z component of the dipole moment operator of the n -electron atom A ,

$$\bar{\mathbf{P}}_A = -|e| \sum_{i=1}^n \left(\bar{\mathbf{r}}_{iA} - \bar{\mathbf{R}}_A \right),$$

$$\text{and } \bar{\mathbf{T}}_{AB} = (1/R_{AB}^3) [\bar{\mathbf{I}} - 3(\bar{\mathbf{R}}_{AB} \bar{\mathbf{R}}_{AB}/R_{AB}^2)] \quad (3)$$

is the dipolar tensor.

For our purposes it is important to recognize that Eq. (2) may also be obtained formally in two alternative ways. The first one consists in retaining only the contribution from the first excited state of the atoms in the general expressions of both ΔE_{AB} and α_0 . For convenience we choose the first excited state to be a triply degenerate P state $|1_i, A\rangle$ ($i = x, y, z$), the ground state being an S state, and we have the usual selection rule

$$\langle 0, A | p_{jA} | 1_i, A \rangle = \langle 0, A | p_{iA} | 1_i, A \rangle \delta_{i,j}.$$

In this approximation ΔE_{AB} retains the form (2) but α_0 is now given by

$$\alpha_0 \simeq (2/\omega_0) |\langle 0, A | p_{zA} | 1_z, A \rangle|^2. \quad (4)$$

The second procedure consists in approximating the real spectrum of the atoms by a pair of effective states, a ground state $|0, A\rangle$, and a triply degenerate excited state $|1, A\rangle$, their energy difference being ω_0 . In particular, we have in this case the closure relation

$$|0, A\rangle \langle 0, A| + \sum_i |1_i, A\rangle \langle 1_i, A| = 1, \quad (5)$$

which implies that

$$\langle 0, A | p_{zA}^2 | 0, A \rangle = |\langle 0, A | p_{zA} | 1_z, A \rangle|^2,$$

so that α_0 has the form of Eq. (1). These remarks are of no real significance and help in the study of ΔE_{AB} , but they do provide much insight in finding the best approximation for the correction $\Delta \bar{\alpha}_{AB}(\omega)$. As we shall now see, the distinction between the two approximations is fundamental since they lead to quite different results for $\Delta \bar{\alpha}_{AB}(\omega)$. First, we recall that in the Ünsöld approximation $\Delta \bar{\alpha}_{AB}(\omega)$ still involves summations over all excited states

of an atom¹³ which cannot be eliminated in favor of the ground-state polarizability.¹² Thus, in order to make further progress one is naturally led to use one of the two procedures just described. In addition, these approximation procedures play an essential role in obtaining a useful definition of the average polarizability of an excited state which arises in the Ünsöld result.¹⁴ We confine the discussion to the static correction $\Delta \bar{\alpha}_{AB}(0)$. Consider first the approximation where we retain only the contribution which arises from the first excited state of the free atoms. Using Eq. (A2) of II, where in this case we replace the mean values $\bar{\omega}$ and $\bar{\alpha}(0)$ by ω_0 and $\alpha_1 = -\alpha_0$, respectively, we obtain

$$\Delta \bar{\alpha}_{AB}(0) = -\frac{1}{8} \alpha_0^3 [(2 \text{Tr} \bar{\mathbf{T}}_{AB}^2) \bar{\mathbf{I}} + 3 \bar{\mathbf{T}}_{AB}^2]. \quad (6)$$

Next, we examine the alternative approximation where we use an effective two-state model and apply, in particular, the closure relation (5). Such a model has been very useful in the study of exciton states, which will also be discussed in this paper. The reduction of Eq. (A2) of II in the two-state model approximation is straightforward; use is made of (1), (5), and of the symmetry properties

$$\langle 0, A | \bar{p}_A \bar{p}_A | 0, A \rangle = \langle 0, A | p_{zA}^2 | 0, A \rangle \bar{\mathbf{I}} \quad (7)$$

(isotropy of the atomic polarizability),

$$\langle 1_i, A | \bar{p}_A | 1_j, A \rangle = 0, \quad (8)$$

$$\text{and } \langle 0, A | p_{xA}^2 p_{yA}^2 | 0, A \rangle = \frac{1}{3} \langle 0, A | p_{zA}^4 | 0, A \rangle \quad (9)$$

(with similar relations arising from permutations of x, y, z). Equation (8) expresses diagonality of \bar{p}_A with respect to the subset of degenerate states $|1_i, A\rangle$ (Ref. 12) and Eq. (9) can be quite generally established for atoms with spherically symmetric charge distributions in the ground state. One then obtains

$$\Delta \bar{\alpha}_{AB}(0) = -\frac{1}{8} \alpha_0^3 [(4 - \frac{3}{5} \nu) (\text{Tr} \bar{\mathbf{T}}_{AB}^2) \bar{\mathbf{I}} + 2(2 - \frac{3}{5} \nu) \bar{\mathbf{T}}_{AB}^2], \quad (10)$$

where ν is defined by

$$\nu = \langle 0, A | p_{xA}^2 p_{yA}^2 | 0, A \rangle / (\langle 0, A | p_{zA}^2 | 0, A \rangle)^2. \quad (11)$$

Now, upon insertion of (5) into (11), using (7), it follows at once that ν could take the two values 1 and 3 in the effective two-state model. This ambiguity indicates that those terms in Eq. (A2) of II which depend on ν , when all excitation energies are replaced by ω_0 (in the spirit of an average-excitation-energy approximation), are not strictly defined in an effective two-state model. They are, in fact, very sensitive to the effect of the higher excited states since the parameter ν reaches its actual unique value only when the contribution of these states is properly included.¹² In order to take this

effect into account we must calculate (11) explicitly, i. e., without making use of the effective two-state model.

To summarize then, it appears that Eq. (10) [and Eq. (11)] corresponds to the following well-defined, and probably valid, approximation scheme: It is based on the two-state-model approximation of those terms, in Eq. (A2) of II, which are well defined and determined sufficiently accurately with this model; on the other hand, those terms which are not defined in the two-state model are approximated by replacing the excitation energies in the denominators by the constant value ω_0 , while the parameter ν arising in the numerator is defined by the actual value of (11), which includes large contributions from the higher excited states. We note, incidentally, that by summing Eq. (10) over neighbors in a cubic monatomic lattice, using the approximate relation

$$\sum_{B \neq A} \vec{T}_{AB}^2 = \left(\frac{1}{3}\right) \sum_{B \neq A} \text{Tr} \vec{T}_{AB}^2 \vec{1} \approx \left(\frac{4}{3}\pi N\right)^2 \vec{1} \quad (12)$$

(N is the number density of atoms and $\vec{1}$ is the unit tensor), one is led exactly to Eq. (50) of II. The actual value of ν for the rare-gas configurations is about 5, as was suggested previously¹² and as will be shown here by more detailed calculations. This then indicates the existence of a large numerical discrepancy between Eqs. (10) and (6) which is due to the effect of the higher excited states, which is completely neglected in (6). Therefore, the approximation of retaining only the contribution from the first excited state of the atoms is not valid and must be rejected in the study of $\Delta \vec{\alpha}_{AB}(0)$, although it is suitable in the study of the van der Waals interaction ΔE_{AB} .

The importance of the higher excited states in $\Delta \vec{\alpha}_{AB}(0)$ is tied to the fact that this correction arises purely from anharmonic properties of the real atoms, being thus exactly zero in a harmonic (Drude) model.¹¹ On the other hand, a detailed evaluation of the general expression of $\Delta \vec{\alpha}_{AB}(0)$ [Eq. (2.43) of I] for harmonic oscillators shows that individual terms do not vanish separately but that instead an exact cancellation between the various terms does occur; but only a few excited states of the oscillators (actually the first two) contribute effectively in these terms. These features of the result for harmonic oscillators lead us to suspect that for real atoms very substantial effects will arise from the higher excited states which are mixed in as a result of the electronic anharmonicities. One important consequence of including the effect of the higher excited states (through the parameter ν) is the existence of two-quantum excitations, which would be completely absent in an effective two-state model.¹²

The aim of the present paper is to study, along similar lines as in II, the detailed effects of induced dipole-dipole interactions on the polarizability and on the excited states of individual atoms in cases where two interacting species are involved in a crystal. This includes the study of various effects in pure diatomic ionic crystals like the alkali halides as well as the study of deep impurity states in monatomic crystals like the rare gases.⁵ Our treatment will be based on the approximations discussed above. In all the mentioned applications we find reasonable agreement between the theory and the results deduced from experimental data. This shows the relevance of both the theory and the individual atom model on which it is based to actual dielectric properties in these solids. This feature was less evident in II, where we dealt only with monatomic situations for which the variety of experimental effects to compare with is necessarily more restricted. Specifically, we shall apply the theory to the study of the polarizability of alkali halide ions, to the electronic excited states of rare gas and molecular impurities in rare-gas solids, and finally to two-quantum excitations in alkali halides. Concerning the polarizability, the theory accounts quantitatively for a correction in the additivity rule of ion polarizabilities, which has been obtained by Pirene and Kartheuser,⁸ from an empirical analysis of dielectric constant data. It also explains essentially the frequency dispersion effects in the polarizability of these crystals. When applied to impurity states in rare-gas solids, it agrees rather well with the empirical van der Waals contribution to the total shift of the excited states of various impurities. These shifts have been determined by Roncin¹⁵ from an empirical fit of the experimental data to 6-12 pair potentials. Finally, our numerical results for the oscillator strength of two-quantum excitations in alkali halides are intermediate between the results of earlier calculations by Hermanson¹⁶ and Miyakawa,¹⁷ both of which are based on the electronic polaron model. The present work clearly shows, however, that the oscillator strength for two-quantum transitions depends rather strongly on the lattice parameter, polarizabilities, and other electronic properties of the individual atoms. Weak two-quantum exciton transitions have apparently been observed very recently in the rare gases.¹⁸

The paper is organized as follows. In Sec. II, we derive the approximate expression for the frequency-dependent correction $\Delta \vec{\alpha}_{AB}(\omega)$ in the polarizability. In Sec. III, we analyze this correction in the static limit and show how it enables us to interpret the empirical results for alkali halide ion polarizabilities. In Sec. IV, we discuss and solve the dispersion equation for the excitation frequen-

cies of an isolated pair and apply the results to impurity states in rare-gas solids. In Sec. V, we study the oscillator strength of two-quantum excitations and some final comments follow in Sec. VI.

II. POLARIZABILITY OF A PAIR OF UNLIKE ATOMS

The various problems of interest in this paper can be handled, without loss of generality, starting from the expression $\Delta\bar{\alpha}_{AB}(\omega)$ of the correction in the polarizability for an isolated pair of interacting atoms. This is physically obvious since all the effects to be considered are pairwise additive. In I and II, our interest was focused directly on perfect cubic lattices, but in the case of a single pair some modifications do occur both in the derivation and in the final form of the correction. We present a brief account of these modifications and display the final result in the Unsöld approximation in Appendix A, Eq. (A6). We now proceed with the further reduction of (A6) using the effective two-state model together with the modifications which enable us to deal properly with the higher excited states in the terms where their effect is most prominent (see Sec. I).

First, however, we discuss the important question of the choice of the average polarizability $\bar{\alpha}_A(\omega)$ of a free atom in an excited state. So far, both in Secs. I and II, we have only considered the choice

$$\bar{\alpha}_C(\omega) = \alpha_{1C}(\omega) = -\alpha_{0C}(\omega), \quad C \equiv A, B \quad (13)$$

which would seem the most natural one to make in the framework of an effective two-state model. We would like to emphasize, however, that this is by no means the only choice which is compatible with our proposed approximation scheme for $\Delta\bar{\alpha}_{AB}(\omega)$: In fact, it may be necessary, in addition (in some cases), to take into account the effect of the higher excited states in $\bar{\alpha}_C(\omega)$, as it already turned out to be essential for the terms depending on ν .¹⁹ First, we note that the term involving $\bar{\alpha}_C(\omega)$ in Eq. (A6) has a quite different structure than the others. This follows from the fact that in the perturbation expression for the polarizability of an excited state of an isolated atom, all terms but one involve energy differences which correspond to two excited states. In addition, one finds that, in the static limit, all other terms in (A6) involving energy differences between two excited states vanish identically.¹² Thus, a different approximation for $\bar{\alpha}_C(\omega)$ is not formally inconceivable. On the other hand, the contribution from virtual transitions between excited states in $\bar{\alpha}_C(\omega)$ may be quite large (among other things, as a result of the smallness of the corresponding energy denominators) and even exceed that which arises from the transition to the ground state, the only one which

is taken into account in (13). Such a situation, which will usually make $\bar{\alpha}_C(0)$ positive, has been discussed previously at $\omega=0$.¹⁴ The above remarks lead us to distinguish two cases as far as the value of $\bar{\alpha}_C(\omega)$ is concerned: In the first case the higher excited states are unimportant and Eq. (13) is approximately valid, whereas in the second case their effect is so large that it cannot be ignored.

We now discuss the derivation of an explicit expression for $\bar{\alpha}_C(\omega)$ in the case where the higher excited states are important. Instead of using a specific atomic model (which would be quite complicated to construct), the expression of $\bar{\alpha}_C(\omega)$ will be chosen such as to obtain an optimum value for the perturbation expression of $\Delta\bar{\alpha}_{AB}(\omega)$ in the average-excitation-energy approximation (A6). Therefore, the use of the result may even be justified to some extent for atoms or ions where the higher excited states do not have such a drastic effect on the excited states polarizabilities. The argument which will be used is suggested by Kirkwood's variational version²⁰ of the Unsöld average-excitation-energy approximation in second-order (stationary) perturbation theory. In this method the optimum average excitation energy is determined to be the average of the true excitation energies weighted with the matrix elements of the perturbation V under consideration. This is also equal to the ratio of the expectation values of $V(H_0 - E_0)V$ and V^2 , where H_0 and E_0 denote the unperturbed Hamiltonian and the ground-state energy, respectively. Rather than actually carrying out a similar variational treatment to obtain an expression for $\bar{\alpha}_C(\omega)$, and because of the appealing simplicity of Kirkwood's result, we shall postulate the form of $\bar{\alpha}_C(\omega)$ by analogy with Kirkwood's result. This leads us to define $\bar{\alpha}_A(\omega)$ ($\bar{\alpha}_B(\omega)$) in (A6) as an average of the induced dipole moment operator weighted with respect to the dipole-dipole interaction

$$\begin{aligned} W_{AB} &= \vec{p}_A \cdot \vec{T}_{AB} \cdot \vec{p}_B, \\ \bar{\alpha}_A(\omega) &= \frac{1}{2} \vec{F}_{0A} e^{i\omega t} + \text{c. c.} \\ &= 2 \frac{\langle 0, A; 0, B | U_A' \dagger W_{AB} \vec{p}_A \cdot \vec{T}_{AB} W_{AB} U_A' | 0, A; 0, B \rangle}{\langle 0, A; 0, B | W_{AB} | 0, A; 0, B \rangle}. \quad (14) \end{aligned}$$

Here $U_A' | 0, A \rangle$ denotes the ground state of the free atom A as perturbed by the effect of the Lorentz local field²¹

$$\frac{1}{2} (\vec{F}_{0A} e^{i\omega t} + \text{c. c.}),$$

and the factor 2 has the same origin as a similar factor in the usual ground-state polarizability. With Eq. (7) the second member of (14) becomes

$$2 \frac{\langle 0, A | U_A' \dagger \vec{p}_A \cdot \vec{T}_{AB} \vec{p}_A \cdot \vec{T}_{AB} U_A' | 0, A \rangle}{\langle 0, A | \vec{p}_A \cdot \vec{T}_{AB} \cdot \vec{T}_{AB} \cdot \vec{p}_A | 0, A \rangle}.$$

We shall simplify somewhat this definition of $\bar{\alpha}_A(\omega)$ by replacing $\bar{\mathbb{T}}_{AB}^2$ with its average $\langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av}$ over-all orientations of the axis of the pair AB:

$$\langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av} = (2/R_{AB}^6) \bar{\mathbb{T}}. \quad (15)$$

The explicit result is obtained by expanding through linear order in $\bar{\mathbb{F}}_{0A}$ and by substituting the matrix elements of U'_A as given, for instance, in I. This gives

$$\begin{aligned} \bar{\alpha}_A(\omega) = & \frac{1}{3} \frac{2}{\langle 0, A | p_{zA}^2 | 0, A \rangle} \\ & \times \sum_j \left(\frac{\langle 0, A | p_{zA} p_A^2 | j, A \rangle \langle j, A | p_{zA} | 0, A \rangle}{\omega_{j, A; 0, A} + \omega} \right. \\ & \left. + \frac{\langle 0, A | p_{zA} | j, A \rangle \langle j, A | p_{zA} p_A^2 | 0, A \rangle}{\omega_{j, A; 0, A} - \omega} \right). \end{aligned} \quad (16)$$

Applying the approximation scheme discussed in Sec. I, we obtain finally

$$\bar{\alpha}_A(\omega) \approx \bar{\alpha}_A(0) \omega_A^2 / (\omega_A^2 - \omega^2), \quad (17)$$

where $\bar{\alpha}_A(0) = \frac{2}{3} \nu_A \alpha_{0A}$. (18)

ν_A and α_{0A} refer to the parameters introduced earlier as defined for atom A. Because of the presence of ν_A the above definition emphasizes the effect of the higher excited states, as is also apparent from the fact that $\bar{\alpha}_A(0)$ is positive. Therefore, this definition does not apply to atoms or ions in which the effect of the higher excited states is unimportant as, for instance, in the two-state model.

It is to be noted that (17) has the same frequency dependence as $\alpha_{0A}(\omega)$, given by

$$\alpha_{0A}(\omega) = \alpha_{0A} \omega_A^2 / (\omega_A^2 - \omega^2). \quad (19)$$

For the purpose of later use, we introduce the new parameter

$$\beta_A = 1 - \bar{\alpha}_A(0) / \alpha_{0A}, \quad (20)$$

so that

$$\alpha_{0A}(\omega) - \bar{\alpha}_A(\omega) = \beta_A \alpha_{0A} \omega_A^2 / (\omega_A^2 - \omega^2). \quad (21)$$

In the case of (13) we have $\beta_A = 2$ whereas in the case of (17) $\beta_A = 1 - \frac{2}{3} \nu_A$. Judging from the success of the Kirkwood method in calculations of atomic polarizabilities and of van der Waals interaction constants²² we may expect (17) and (18) to give a reasonable estimate of $\bar{\alpha}_A(\omega)$, at least as far as the calculation of $\Delta \bar{\alpha}_{AB}(\omega)$ is concerned. This will be especially true for systems whose polarizability in a low-lying excited state differs strongly from Eq. (13).

We now turn to the explicit reduction of (A6) using the approximation scheme discussed in II¹² and in Sec. I. Accordingly, we replace $\bar{\omega}_A$ and $\bar{\omega}_B$ as well as all excitation energies from the ground state of A and B by ω_A and ω_B , respectively (these are the analogs of ω_0 in Sec. I), and we use the closure relation. As noted earlier (in II) we drop all terms in the last five lines of (A6) which involve energy differences between two excited states.

This is done for reasons of consistency of our approximation scheme with the general theory of I, at $\omega = 0$. Further simplifications follow from Eqs. (7) and (9) which enable us to show that all ground-state expectation values arising in the course of approximating (A6) reduce to the value

$$\langle \langle 0, A | p_{zA}^2 | 0, A \rangle \rangle^2 \bar{\mathbb{T}}_{AB}^2,$$

except two of them which are

$$\langle 0, A | \vec{p}_A \cdot \bar{\mathbb{T}}_{AB}^2 \cdot \vec{p}_A | 0, A \rangle = \langle 0, A | p_{zA}^2 | 0, A \rangle \text{Tr} \bar{\mathbb{T}}_{AB}^2$$

and

$$\begin{aligned} \langle 0, A | \vec{p}_A (\vec{p}_A \cdot \bar{\mathbb{T}}_{AB}^2 \cdot \vec{p}_A) \vec{p}_A | 0, A \rangle \\ = \frac{1}{3} \langle 0, A | p_{zA}^2 p_A^2 | 0, A \rangle [(\text{Tr} \bar{\mathbb{T}}_{AB}^2) \bar{\mathbb{T}} + 2 \bar{\mathbb{T}}_{AB}^2]. \end{aligned}$$

Finally, using (1), (11), and (21) we obtain from (A6)²³

$$\begin{aligned} \Delta \bar{\alpha}_{AB}(\omega) = & -\frac{1}{8} \frac{\alpha_{0A}^2 \alpha_{0B}}{\omega_A + \omega_B} \frac{\omega_A^2 \omega_B}{(\omega_A^2 - \omega^2)^2 [(\omega_A + \omega_B)^2 - \omega^2]} \left(2[(\omega_A + \omega_B)^2 - \omega^2] \left[\frac{\beta_A \omega_A}{\omega_A + \omega_B} (\omega_A^2 - \omega^2) + 3\omega_A^2 - \omega^2 \right] \right. \\ & \times (\text{Tr} \bar{\mathbb{T}}_{AB}^2) \bar{\mathbb{T}} + \{(\omega_A + \omega)^2 (\omega_A + \omega_B) (\omega_A + \omega_B + \omega) + (\omega_A - \omega)^2 (\omega_A + \omega_B) (\omega_A + \omega_B - \omega) + 2(3\omega_A^2 - \omega^2) [(\omega_A + \omega_B)^2 \\ & - \omega^2]\} \bar{\mathbb{T}}_{AB}^2 - \frac{1}{3} \nu_A \{(\omega_A + \omega)^2 (\omega_A + \omega_B) (\omega_A + \omega_B + \omega) + (\omega_A - \omega)^2 (\omega_A + \omega_B) \\ & \times (\omega_A + \omega_B - \omega) + 4(\omega_A^2 - \omega^2) [(\omega_A + \omega_B)^2 - \omega^2]\} [(\text{Tr} \bar{\mathbb{T}}_{AB}^2) \bar{\mathbb{T}} + 2 \bar{\mathbb{T}}_{AB}^2] \left. \right). \end{aligned} \quad (22)$$

The correction $\Delta \bar{\alpha}_{BA}(\omega)$ is obtained from (22) by interchanging A and B.

In the following we shall be concerned exclusive-

ly with problems involving cubic crystals which will be either pure diatomic crystals or monatomic crystals containing impurities at substitutional

sites. In the latter case we shall concentrate on the effects of the surrounding matrix on the impurity states. In these problems, the correction in the polarizability of the atom A due to the interactions with its neighbors is isotropic. In particular, the contribution to $\Delta\vec{\alpha}_A(\omega)$ due to a given shell of neighbors B will be equal to the number of atoms in that shell multiplied by the average of (22) over all orientations of the axis AB . Thus for our purposes, we may replace Eq. (22) by its orientational average using (15). The result is

$$\begin{aligned} \langle \Delta\vec{\alpha}_{AB}(\omega) \rangle_{\text{av}} &= \frac{1}{2} \frac{\alpha_{0A}^2 \alpha_{0B}}{R_{AB}^6} \frac{\omega_A^2 \omega_B}{\omega_A + \omega_B} \\ &\times \frac{1}{(\omega^2 - \omega_A^2)^2 [\omega^2 - (\omega_A + \omega_B)^2]} \\ &\times (k'_{AB} \omega^4 + k'_{AB} \omega^2 + k_{AB}) , \end{aligned} \quad (23)$$

where the quantities k'_{AB} , k'_{AB} , and k_{AB} are defined by

$$k'_{AB} = 3\beta_A \omega_A / (\omega_A + \omega_B) - 2\nu_A + 4 , \quad (24)$$

$$\begin{aligned} k'_{AB} &= -3[\omega_A^2 + (\omega_A + \omega_B)^2] \beta_A \omega_A / (\omega_A + \omega_B) \\ &- 13\omega_A^2 - 3\omega_B^2 - 4\omega_A \omega_B + \nu_A (\omega_A^2 + \omega_B^2) , \end{aligned} \quad (25)$$

$$k_{AB} = \omega_A^2 (\omega_A + \omega_B)^2 [3\beta_A \omega_A / (\omega_A + \omega_B) + 13 - 3\nu_A] . \quad (26)$$

In the following sections we shall examine three different types of applications of these results.

III. APPLICATION TO THE POLARIZABILITY OF ALKALI HALIDE IONS

We shall first discuss in detail the static polarizability of alkali halide ions, but later on we shall also consider the frequency-dispersion effects. These problems are of considerable interest for the following reasons. It is well known from the classic paper of Tessman *et al.*,⁷ that in the alkali halides the polarizabilities of the cations (A) and anions (B) nearly obey an additivity rule of the form

$$\alpha_{AB} = \alpha_A + \alpha_B . \quad (27)$$

This result follows also from the classical Lorentz field theory which leads to the Clausius-Mossotti equation.^{7,8} Moreover, the individual polarizabilities α_A (α_B) determined by means of (27) from the knowledge of the experimental values α_{AB} are remarkably close to the polarizabilities α_{0A} (α_{0B}) of the free ions. This is demonstrated very convincingly by the improved empirical analysis of Pirenne and Kartheuser (PK).⁸ An assertion that is often made, and according to which in the crystal the cation polarizability is larger and the anion polarizability is smaller than for the free ions, is ap-

parently disproved by their more careful treatment. Another very interesting feature of the work of PK is the evidence they obtain for the existence of a correction term to (27). In their work they chose this term phenomenologically to be of the form $\lambda\alpha_A\alpha_B$, so that

$$\alpha_{AB} = \alpha_A + \alpha_B + \lambda\alpha_A\alpha_B . \quad (28)$$

The parameter λ is positive and changes discontinuously with the crystal structure.⁸ The relative magnitude of the correction term in (28) varies roughly between 1 and 10% for the alkali halides. The existence of the correction term in (28) has later been confirmed by a similar empirical analysis of frequency-dispersion effects in the polarizability.²⁴ This suffices to demonstrate the particular interest of making a detailed comparison of the present theory, which is based on the individual (free) ion model, with the above-mentioned results for alkali halides. For completeness we mention two previous theoretical studies of polarizabilities of alkali halides,^{25,26} which differ both in emphasis and in presentation from the present work.

We now turn to the calculation of the total static correction in the polarizability for the alkali halide ions. In the case of halogen ions, the second-neighbor halogen ions give large contributions in $\Delta\vec{\alpha}_A(0)$ because of their large polarizabilities. Therefore, in order to obtain a reasonable approximation for the total correction in the polarizability of an ion A in the crystal, we have to sum (22) over two shells of neighbors. We denote by n and R the number and distance of first neighbors of a given ion; respectively, and by m and R' the same parameters for the second neighbors. Using (15) we then obtain the following expression for the total correction in the polarizability of A due to the interaction with first (B) and second (A) neighbors:

$$\begin{aligned} \frac{\Delta\alpha_A(0)}{\alpha_{0A}} &= -\frac{n}{2} \frac{\alpha_{0A}\alpha_{0B}}{R^6} \frac{1}{1+x} \left(3\beta_A \frac{x}{1+x} - 3\nu_A + 13 \right) \\ &- \frac{m}{4} \frac{\alpha_{0A}^2}{R'^6} \left(\frac{3}{2}\beta_A - 3\nu_A + 13 \right) , \end{aligned} \quad (29)$$

where the notation

$$x = \omega_A / \omega_B , \quad y = \omega_B / \omega_A \quad (30)$$

will be used throughout in this paper. The same results could be obtained, of course, by starting from Eq. (23). Numerical values of R, R' are given in Table I while free-ion polarizabilities and values of ω_A are listed in Table II. For the alkali ions we have chosen ω_A to be the excitation energy of the first excited 1P state of the free ion. For the halogen ion the values of Table II correspond to average values of the lowest absorption frequency of the five corresponding alkali halides, as ob-

TABLE I. Distances between neighbors in alkali halides in units of Å, taken from the work of C. Kittel [Introduction to Solid State Physics (Wiley, New York, 1956)]. The first number is the nearest-neighbor distance and the second number the distance between second neighbors. All values are for crystals with the NaCl structure except those for CsCl, CsBr, and CsI which are for the CsCl structure.

	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	2.31 3.267	2.67 3.776	2.82 3.988	3.005 4.25
Cl ⁻	2.815 3.981	3.14 4.441	3.27 4.625	3.559 4.11
Br ⁻	2.98 4.214	3.295 4.66	3.425 4.844	3.715 4.29
I ⁻	3.23 4.568	3.525 4.985	3.665 5.183	3.949 4.56

tained in Ref. 24. This latter choice is motivated by the fact that, as noted by PK, the first excited state of the free anions (which lie apparently at the bottom of the continuum) is expected to be strongly shifted by crystal-field effects. This then leaves the anion absorption frequencies in the crystals as the most meaningful values of excitation energies for the present calculations.²⁴

The major remaining task in applying Eq. (29) to the alkali halides is the determination of the parameter ν_A given by (11). For the H atom the exact value of ν is 7.5 while an approximate value of 6.25 is found for He atoms by using Slater orbitals. In II we have introduced a Gaussian model to determine this parameter for the heavier rare gases, which leads to $\nu = 5$. Although this value seems quite reasonable, it suffers from the objection of being determined unphysically. Therefore we have now undertaken a more realistic calculation of the parameter ν for the free alkali and halogen ions and for the rare-gas atoms. The expectation values involved in ν are obtained from an explicit calculation of the contribution of the outermost shell of electrons (ns^2np^6). The ground state is represented by a Slater determinant of Slater one-electron orbitals.²⁷ Some further details of this calculation are given in Appendix B. The final result is obtained by substituting (B10) and (B11) in (11), which leads to

$$\nu = \frac{4(n^* + 1)(48n^{*2} + 232n^* + 149) + 25(2n^* + 1)^3}{10(2n^* + 1)(2n^* + 3)^2} \quad (31)$$

n^* is Slater's effective principal quantum number whose values are listed in Table II. For later use we note that the values of n^* for the sequence Ne, Ar, Kr, Xe are the same as for the isoelectronic sequence F⁻, Cl⁻, Br⁻, I⁻, respectively. The values obtained for ν from (31) are also listed in Table II which shows that they lie, in fact, surprisingly close to the Gaussian-model result $\nu = 5$.

Finally, for the excited-states polarizability to be used in β_A we have to make a choice between Eqs. (13) and (18). In the case of the rare gases we have chosen Eq. (13)¹² which led us to small negative corrections $\Delta\alpha_A(0)$, in reasonable agreement with the density dependence of the refractive index of these crystals. The use of (13) would also lead to small negative corrections for the alkali halide ions, while the empirical corrections of PK are positive.⁸ With Eq. (28), on the other hand, the correction $\Delta\alpha_A(0)$ becomes positive. The PK results thus suggest the use of this latter expression, but this requires further justification if we want to make theoretical predictions rather than a fit to the empirical results. Fortunately, there is a physical reason for preferring (18) to (13) in the case of the halogen ions, which clearly contribute the dominant effect in the total correction to the additivity formula for the polarizabilities (except for the fluorides). Physically, the fact that all the excited states of these ions lie practically in the continuum suggests that the polarizabilities $\bar{\alpha}_A(0)$ will depend rather strongly on the virtual transitions between excited states. Now, as seen earlier, this is typically an effect which is included in Eq. (18), which should therefore be preferred for the halogen ions. A further reason for adopting this expression is the fact that it corresponds to an optimum approximation for the perturbation expression of $\Delta\alpha_A(0)$, as suggested by Kirkwood's results.²⁰ For these reasons we have carried out the calculations of the relative corrections $\Delta\alpha_A(0)/\alpha_{0A}$ for the alkali halide ions on the basis of Eq. (18) for $\bar{\alpha}_A(0)$. In Tables III and IV, we present the numerical results for cations (A) and anions (B), respectively. For the crystals of the NaCl structure

TABLE II. Values of parameters defined in the text. The polarizabilities α_{0A} and the excitation energies ω_A are taken from Refs. 8 and 24, respectively.

	F ⁻	Cl ⁻	Br ⁻	I ⁻	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
α_{0A} (Å ³)	1.0	3.5	4.15	6.37	0.152	0.9	1.7	2.7
ω_A (eV)	9.5	7.6	6.6	5.6	32.85	20.15	15.68	15.23
n^*	2	3	3.7	4	2	3	3.7	4
ν_A	5.218	5.116	5.075	5.062	5.218	5.116	5.075	5.062
ω_B^2/ω_A^2	0.049	0.0766	0.1015	0.141	0.0041	0.0109	0.018	0.0191

TABLE III. Relative polarizability corrections $\Delta\alpha_A(0)/\alpha_{0A}$ for A ions in percent. All values are for crystals with the NaCl structure, except those for CsCl, CsBr, and CsI which are for the CsCl structure.

$B \setminus A$	Na*	K*	Rb*	Cs*
F ⁻	1.02	2.24	3.81	4.92
Cl ⁻	0.54	2.24	3.87	5.6
Br ⁻	0.41	1.83	3.21	4.7
I ⁻	0.34	1.68	2.9	4.31

$n = 6$ and $m = 12$ while for those of the CsCl structure (CsCl, CsBr, and CsI) $n = 8$ and $m = 6$. A feature which emerges from these tables is that the correction for a given ion stays relatively constant in the four alkali halide crystals, especially in the case of the anions. In Table V, we compare the total relative corrections calculated in the present work with the values obtained empirically by PK.⁸ It is seen that except for the sodium compounds the agreement is quite good both in sign and in magnitude. The theoretical results for the correction in the polarizability range from 2.4% for the least polarizable crystal to 8.5% for the most polarizable one.

At this point we would like to discuss briefly the variation of the dipole-fluctuation effect in the polarizability with the frequency ω . More specifically, our aim is to compare the frequency-dispersion effect which results from this correction with a similar effect derived empirically by PK²⁴ from an analysis of frequency-dispersion data for the alkali halides. By postulating the empirical correction to be of the same form at nonzero frequency than at $\omega = 0$,²⁴ it follows that the contribution κ'_{AB} of the correction term to the frequency-dispersion effect is given by

$$\kappa'_{AB}(\omega) = \frac{\lambda[\alpha_A(\omega)\delta\alpha_B(\omega) + \alpha_B(\omega)\delta\alpha_A(\omega)]}{\delta\alpha_A(\omega) + \delta\alpha_B(\omega)}, \quad (32)$$

where

$$\delta\alpha_C(\omega) = \alpha_C(\omega) - \alpha_C(0), \quad C \equiv A, B. \quad (33)$$

The PK analysis provides us with a set of values for $\alpha_A(\omega)$ and $\delta\alpha_A(\omega)$ for the alkali halide ions, for the frequency $\omega = \omega_D$ of the sodium D line at which

TABLE IV. Relative polarizability corrections $\Delta\alpha_B(0)/\alpha_{0B}$ for B ions in percent. All values are for crystals with the NaCl structure, except those for CsCl, CsBr, and CsI which are for the CsCl structure.

$B \setminus A$	Na*	K*	Rb*	Cs*
F ⁻	2.6	3.21	3.93	4.06
Cl ⁻	6.49	5.96	6.87	8.17
Br ⁻	6.12	5.56	6.33	7.62
I ⁻	8.4	7.18	7.63	9.38

the experimental refractive indices have been measured. These values can be used to compute $\kappa'_{AB}(\omega_D)$ for the alkali halide ions.

Similarly, the correction in the polarizability due to dipole fluctuations leads to a contribution κ_{AB} to the frequency-dispersion effect given by

$$\kappa_{AB}(\omega) = \frac{\Delta\alpha_A(\omega) - \Delta\alpha_A(0) + \Delta\alpha_B(\omega) - \Delta\alpha_B(0)}{\delta\alpha_{0A}(\omega) + \delta\alpha_{0B}(\omega)}, \quad (34)$$

where

$$\delta\alpha_{0C}(\omega) = \alpha_{0C}(\omega) - \alpha_{0C}, \quad C \equiv A, B. \quad (35)$$

Now, since for the alkali halide ions the ratio ω_D^2/ω_A^2 is in most cases less than 0.1 (see Table II) it will be quite sufficient to approximate the numerator and the denominator in (34) by the first term of series expansions in powers of ω^2/ω_A^2 and ω^2/ω_B^2 . Carrying out these calculations in (22) and summing the results over the first two shells of neighboring ions of A (and similarly for B) we obtain, after some algebra,

$$\begin{aligned} \frac{\Delta\alpha_A(\omega) - \Delta\alpha_A(0)}{\alpha_{0A}(\omega)} = & -\frac{n}{2} \frac{\alpha_{0A}\alpha_{0B}}{R^6} \frac{\omega^2}{\omega_B^2} \frac{y^3}{y+1} \\ & \times \left[20 + \frac{3\beta_A}{1+y} - (\nu_A - 1) \left(\frac{1}{y^2 + 2y + 1} + \frac{2}{y+1} + 3 \right) \right. \\ & \left. - 4\nu_A \right] - \frac{m}{8} \frac{\alpha_{0A}^2}{R^6} \frac{\omega^2}{\omega_A^2} \\ & \times (48.5 + 3\beta_A - 12.5\nu_A) + 0(\omega^4), \end{aligned} \quad (36)$$

and from (19) we have

$$\delta\alpha_{0C}(\omega) = (\omega^2/\omega_C^2)\alpha_{0C} + 0(\omega^4), \quad C \equiv A, B. \quad (37)$$

Note that

$$\Delta\alpha_B(\omega) - \Delta\alpha_B(0)$$

is obtained from (36) by interchanging A and B and

TABLE V. Comparison of total relative theoretical and empirical corrections in the polarizability for the alkali halides (in percent). The first number is the correction $[\Delta\alpha_A(0) + \Delta\alpha_B(0)]/(\alpha_{0A} + \alpha_{0B})$ calculated in the present work; the second number is the empirical correction $(\lambda\alpha_A\alpha_B)/(\alpha_A + \alpha_B)$ as obtained from the results of Ref. 8. All values are for crystals with the NaCl structure, where $\lambda = 0.076A^3$ except those for CsCl, CsBr, and CsI, where $\lambda = 0.046A^3$.

$B \setminus A$	Na*	K*	Rb*	Cs*
F ⁻	2.39	2.75	3.86	4.69
	1.66	3.61	4.3	3.04
Cl ⁻	6.24	5.2	5.88	7.05
	2.01	5.82	7.83	6.46
Br ⁻	6.05	4.9	5.43	6.47
	2.07	6.26	8.65	7.42
I ⁻	8.21	6.49	6.63	7.87
	2.11	6.71	9.53	8.54

TABLE VI. Comparison between relative theoretical and empirical frequency-dispersion effects in the polarizability, as defined by Eqs. (32) and (34) in the text, respectively. Both numbers are given in percent, the first one being the theoretical value and the second one the empirical value. All values are for crystals with the NaCl structure (where $\lambda=0.076A^3$) except those for CsCl, CsBr, and CsI which are for the CsCl structure (where $\lambda=0.046A^3$).

$B \backslash A$	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	7.01	9.46	11.26	14
	2.43	7.44	9.07	6.35
Cl ⁻	14.67	17.28	20.4	23.79
	2.42	9.17	13.9	12.67
Br ⁻	13.5	16.11	19.31	23.13
	2.38	9.11	14.2	13.6
I ⁻	17.86	19.66	22.7	28.41
	2.34	8.89	14.1	14.1

replacing y by x . The numerical estimate of (34) and (36) for the alkali halides at $\omega = \omega_D$ is carried out in a way similar to the calculation of $\Delta\alpha_A(0)$ using the values of Tables I and II and determining β_A from (18). In Table VI, we compare the values of $\kappa_{AB}(\omega_D)$ to the values of $\kappa'_{AB}(\omega_D)$ obtained from the PK results.²⁴ It is seen that both values agree in sign while the theoretical values are larger by a factor of 2 or less than the empirical PK values (except for the sodium halides). No special significance can be attached to this discrepancy in magnitude because of the unknown effect of experimental uncertainties on the PK results on the one hand and the simplified nature of the present theory on the other hand.

IV. DEEP IMPURITY STATES IN RARE-GAS SOLIDS

In this section, we would like to discuss the effect of the dipole-dipole interactions on the electronic excited states of impurity atoms or nonpolar molecules which are trapped at substitutional sites in nonpolar crystal matrices. The treatment could be readily generalized, of course, to the case where the matrix is a nonpolar liquid or a compressed gas. In general, the surrounding matrix has several kinds of effects on the optical properties of the impurity center; shifts of its energy levels, changes of intensity, and width of its absorption lines and production of new sidebands occurring at combination frequencies of the impurities and the atoms of the matrix.

The problem of the dipole-dipole interaction effects on the impurity states can be formulated quite generally in terms of the self-consistent equations for the effective local fields acting on the individual atoms and on the impurity when an optical excitation is present in the system. This treat-

ment requires only the knowledge of the effective polarizability of an individual atom, which has been studied in Sec. II. Since the spectral shifts which result from the interaction between the impurity and the matrix atoms are additive, their study may be reduced to that of a single pair of unlike atoms A and B , one of them being the impurity (A) and the other one an atom (B) of the surrounding matrix. When the pair is in an excited state, the amplitudes of the local fields acting on A and B , as a result of the induced dipolar interaction, satisfy the pair of coupled equations

$$\vec{F}_A = -\vec{T}_{AB} \cdot [\alpha_{0B}(\omega)\vec{I} + \Delta\vec{\alpha}_{BA}(\omega)] \cdot \vec{F}_B, \quad (38a)$$

$$\vec{F}_B = -\vec{T}_{BA} \cdot [\alpha_{0A}(\omega)\vec{I} + \Delta\vec{\alpha}_{AB}(\omega)] \cdot \vec{F}_A. \quad (38b)$$

This system has solutions only if

$$\det \left| \vec{I} - \vec{T}_{AB} \cdot [\alpha_{0A}(\omega)\vec{I} + \Delta\vec{\alpha}_{AB}(\omega)] \cdot \vec{T}_{AB} \cdot [\alpha_{0B}(\omega)\vec{I} + \Delta\vec{\alpha}_{BA}(\omega)] \right| = 0, \quad (39)$$

which determines the frequencies of the excitations of the impurity-matrix-atom pair. Clearly, for an isolated pair we expect normal-mode oscillations parallel and perpendicular to the axis of the pair, which differ slightly in frequency as a result of the difference between the longitudinal and transverse local field perturbations. On the other hand, in a matrix of cubic symmetry the contribution of a particular shell of neighbors to the energy shift of the impurity corresponds to a certain average of the above frequency perturbations (multiplied by the number of atoms in the shell). This average frequency shift per atom is defined by a dispersion equation of the form (39) suitably averaged over orientations as follows. First, instead of Eqs. (38) we introduce fictitious local fields, \vec{F}_A and \vec{F}_B , defined as the fields which are induced when the polarizability of each member of the pair is replaced by the average over orientations (isotropic part). The resulting dispersion equation is then further averaged, replacing the tensors \vec{T}_{AB}^2 by $\langle \vec{T}_{AB}^2 \rangle_{av}$. To lowest order, the equation to be solved thus becomes [using (15)]

$$\vec{I} - (2/R_{AB}^6)[\alpha_{0A}(\omega)\alpha_{0B}(\omega)\vec{I} + \alpha_{0A}(\omega)\langle \Delta\vec{\alpha}_{BA}(\omega) \rangle_{av} + \alpha_{0B}(\omega)\langle \Delta\vec{\alpha}_{AB}(\omega) \rangle_{av}] = 0, \quad (40)$$

which is considerably simpler than (39). We note that an alternative averaging procedure which would consist in averaging directly the whole matrix in (39) does not seem correct to us because it gives rise to some unphysical results: In particular, the use of these results in the monatomic limit leads to an energy shift which differs slightly from the correct value as obtained in II. The reason for this difference is that

$$\langle \overline{T}_{AB}^4 \rangle_{av} \neq \langle \overline{T}_{AB}^2 \rangle_{av}^2 .$$

Finally, we note that Eq. (40) does not allow us to study the effect of the isolated impurity on the levels of a neighboring matrix particle because this latter effect is obviously quite anisotropic.

We now proceed with the solution of (40) where we substitute (19) and (23) explicitly. By defining the classical excitation energies ω_{\pm} , which are the solutions of (40) in the absence of the quantum correction in the polarizability, the equation becomes

$$\begin{aligned} & (\omega^2 - \omega_A^2)(\omega^2 - \omega_B^2)[\omega^2 - (\omega_A + \omega_B)^2](\omega^2 - \omega_+^2)(\omega^2 - \omega_-^2) \\ & + \lambda (\alpha_{0A} \alpha_{0B} / R_{AB}^6) \omega_B \omega_A [\omega_A(\omega^2 - \omega_A^2) \\ & \times (k''_{BA} \omega^4 + k'_{BA} \omega^2 + k_{BA}) + \text{same } A \leftrightarrow B] = 0, \end{aligned} \quad (41)$$

where

$$\lambda = \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \omega_A \frac{1}{x+1}, \quad (42)$$

and we have

$$\begin{aligned} \omega_{\pm}^2 = & \frac{1}{2} \{ \omega_A^2 + \omega_B^2 \pm [(\omega_A^2 - \omega_B^2)^2 \\ & + 8(\alpha_{0A} \alpha_{0B} / R_{AB}^6) \omega_A^2 \omega_B^2]^{1/2} \}. \end{aligned} \quad (43)$$

In the present case of a pair of unlike atoms, the expansion of (43) to lowest order is

$$\omega_+^2 = \omega_A^2 \left(1 + 2 \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \frac{1}{x^2 - 1} \right) + O(R_{AB}^{-12}), \quad (44a)$$

$$\omega_-^2 = \omega_B^2 \left(1 - 2 \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \frac{1}{x^2 - 1} \right) + O(R_{AB}^{-12}). \quad (44b)$$

We note, incidentally, that in the limit of identical atoms the excitation energies (43) include the usual so-called resonance interaction which is proportional to R_{AB}^{-3} . Since the corrections

$$\langle \Delta \overline{\alpha}_{AB}(\omega) \rangle_{av} \quad \langle \langle \Delta \overline{\alpha}_{BA}(\omega) \rangle_{av} \rangle$$

in (40) have been restricted to the lowest-order effect proportional to R_{AB}^{-6} , we only require the corrections linear in λ in the solutions of (41). These can be determined by means of an iteration procedure which will be discussed after introducing a simplification, which reduces by one the degree of the equation to be solved. Namely, we observe that through first order in λ the solutions of (41) are obtained from those of

$$\begin{aligned} & (\omega^2 - \omega_A^2)[\omega^2 - (\omega_A + \omega_B)^2](\omega^2 - \omega_+^2)(\omega^2 - \omega_-^2) \\ & + \lambda \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \omega_A \omega_B^2 (k''_{AB} \omega^4 + k'_{AB} \omega^2 + k_{AB}) = 0 \end{aligned} \quad (45)$$

and of the symmetric equation $A \leftrightarrow B$. Denoting by t_A , t_{AB} , ω'_+ , ω''_+ the corrections linear in λ in the solutions of (45) and by t_B , t_{BA} , ω''_+ , ω'_+ those

in the solutions of the symmetric equation, one sees that the solution of (42), through first order, will simply be $\omega_A^2 + t_A$, $\omega_B^2 + t_B$, $(\omega_A + \omega_B)^2 + t_{AB} + t_{BA}$, $\omega_+^2 + \omega'_+ + \omega''_+$, and $\omega_-^2 + \omega'_- + \omega''_-$. Furthermore, t_{BA} , ω''_+ and ω'_- are obtained from t_{AB} , ω'_+ and ω''_- by interchanging A and B .

In order to solve (45) one formally factorizes the polynomial on the left-hand side in terms of its roots $\omega_A^2 + t_A$, $(\omega_A + \omega_B)^2 + t_{AB}$ and $\omega_+^2 + \omega'_+$, $\omega_-^2 + \omega''_-$ to linear order in λ . Next one expands the factorized form, retaining only linear terms, and one equates the coefficients of the same powers of ω^2 in these terms and in the λ term of (45). The so-obtained system of four linear inhomogeneous equations for t_A , t_{AB} , ω'_+ , and ω''_+ is easily solved analytically by means of a judicious use of the properties of determinants. The final results through $O(R_{AB}^{-6})$ are

$$\omega'_+ = \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \omega_A^2 \left(\frac{2x^2 + 11x + 5}{2x^2 + 3x + 1} - \nu_A \right), \quad (46a)$$

$$\omega'_- = \text{same } A \leftrightarrow B, \quad x \leftrightarrow y, \quad (46b)$$

$$t_A = - \frac{\lambda}{2\omega_A} \frac{1}{\omega_B(\omega_B + 2\omega_A)} (\omega_A^4 k''_{AB} + \omega_A^2 k'_{AB} + k_{AB}), \quad (47)$$

$$\begin{aligned} t_{AB} = & -\lambda \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \frac{1}{(\omega_A + 2\omega_B)(\omega_B + 2\omega_A)^2} \\ & \times [(\omega_A + \omega_B)^4 k''_{AB} + (\omega_A + \omega_B)^2 k'_{AB} + k_{AB}], \end{aligned} \quad (48)$$

whereas one finds that ω''_+ and ω''_- are both of $O(R_{AB}^{-12})$. Thus the absorption frequency Ω_A of the impurity, including the orientationally averaged effects of the dipolar interaction with a matrix atom at a distance R_{AB} , is given by

$$\Omega_A = \omega_A \left[1 + \frac{1}{2} \frac{\alpha_{0A} \alpha_{0B}}{R_{AB}^6} \left(\frac{2}{x^2 - 1} + \frac{2x^2 + 11x + 5}{2x^2 + 3x + 1} - \nu_A \right) \right], \quad (49)$$

through $O(R_{AB}^{-6})$. The restriction to the lowest-order contribution of the classical term in (43) is a very good approximation here since the numerical value of the expansion parameter

$$\alpha_{0A} \alpha_{0B} / R_{AB}^6 (x^2 - 1)$$

does not exceed 0.01 for any of the systems considered below.

For the purpose of later application, it is convenient to write down the explicit expression of the average polarizability of the pair, which is defined by

$$\langle \alpha_{AB}(\omega) \rangle_{av} \overline{\mathbf{E}}_0 = \overline{\alpha}_A(\omega) \overline{\mathbf{F}}_A + \overline{\alpha}_B(\omega) \overline{\mathbf{F}}_B, \quad (50)$$

where $\overline{\alpha}_A(\omega) \overline{\mathbf{I}} = \alpha_{0A}(\omega) \overline{\mathbf{I}} + \langle \Delta \overline{\alpha}_{AB}(\omega) \rangle_{av}$ and $\overline{\mathbf{F}}_A$, $\overline{\mathbf{F}}_B$, which are parallel to $\overline{\mathbf{E}}_0$, are averages of the fictitious fields which correspond to the

average values of the polarizabilities. To obtain the expression of $\bar{\mathbb{F}}_A$ we thus first replace the polarizabilities in Eq. (A2) by the averages over orientations $\bar{\alpha}_A(\omega)$ and $\bar{\alpha}_B(\omega)$. Furthermore, since the denominator in (A2) determines the energy shifts, which for individual atoms in a cubic crystal correspond to averages over all orientations, we replace $\bar{\mathbb{T}}_{AB}^2$ by its average $\langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av}$, as discussed before. This would not be correct, however, for the study of the frequency shift of a matrix atom interacting with other matrix atoms and with a nearby substitutional impurity because the dipole field is then quite anisotropic. But it is valid for the ions in a perfect cubic diatomic crystal since any shell of neighbors of a given ion includes only one species. Therefore, we emphasize that the expression given below [Eq. (52)] is only use-

$$\langle \alpha_{AB}(\omega) \rangle_{av} = \frac{\alpha_{0A}(\omega) - \sqrt{2}\alpha_{0A}(\omega)\alpha_{0B}(\omega)R_{AB}^{-3} + \langle \Delta\alpha_{AB}(\omega) \rangle_{av}}{1 - 2[\alpha_{0A}(\omega)\alpha_{0B}(\omega) + \alpha_{0A}(\omega)\langle \Delta\alpha_{BA}(\omega) \rangle_{av} + \alpha_{0B}(\omega)\langle \Delta\alpha_{AB}(\omega) \rangle_{av}]R_{AB}^{-6}} + \text{same } A \leftrightarrow B. \quad (52)$$

Unfortunately, this expression cannot be used for the study of the terms proportional to R_{AB}^{-3} in the total susceptibility of an infinite crystal because the summation over neighbors $\sum_{B \neq A} R_{AB}^{-3}$ diverges. This is not surprising because it is well known that the angular factor in the dipole-dipole interaction is essential to obtain the finite $\frac{4}{3}\pi$ value of the Lorentz factor. The same remark applies to the R_{AB}^{-3} correction in the classical frequencies (43) in the limit of identical atoms; it leads to a divergent result for the otherwise finite effect of the Lorentz field on the exciton energies in monatomic crystals.¹² However, we shall not attempt to improve the treatment of the terms proportional to R_{AB}^{-3} because their effects are well known in the classical Lorentz field theory and are thus of little interest here. It must be emphasized, however, that our treatment of the R_{AB}^{-6} terms as applied to cubic crystals is strictly rigorous both intuitively and mathematically, as shown by the comparison of the various results with those obtained exactly for monatomic crystals.¹²

We now proceed with the determination of the roots of the numerator of (52). There are four of

ful for applications concerning perfect monatomic or diatomic crystals. To complete the definition of $\bar{\mathbb{F}}_A$ ($\bar{\mathbb{F}}_B$) it would then be tempting to replace $\bar{\mathbb{T}}_{AB}$ in the numerator of (A2), also by the average value $\langle \bar{\mathbb{T}}_{AB} \rangle_{av} = 0$. But this is incorrect for applications to crystals since the Lorentz field is proportional to R_{AB}^{-3} , to lowest order, and therefore the susceptibility also includes terms of this order. On the other hand, the averaging of $\bar{\mathbb{T}}_{AB}^2$ suggests to replace $\bar{\mathbb{T}}_{AB}$ by $\langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av}^{1/2}$, which circumvents in principle the above mentioned difficulty. We thus write

$$\bar{\mathbb{F}}_A = \frac{1 - \langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av}^{1/2} \bar{\alpha}_B(\omega)}{1 - \langle \bar{\mathbb{T}}_{AB}^2 \rangle_{av} \bar{\alpha}_A(\omega) \bar{\alpha}_B(\omega)} \bar{\mathbb{E}}_0, \quad (51)$$

and by using (15) we obtain to lowest order

them which we denote by $\omega_A^2 + t'_A$, $\omega_B^2 + t'_B$, $(\omega_A + \omega_B)^2 + t'^2$, and where the second terms are the first-order corrections to be determined. These corrections may be obtained by a calculation which is exactly similar to that described above. The results are

$$t'_A = t_A + O(R_{AB}^{-9}), \quad (53)$$

$$t'_B = t_B + O(R_{AB}^{-9}), \quad (54)$$

$$t'^2_{AB} = \frac{\lambda}{2} \frac{\alpha_{0A}}{\omega_B^3} \frac{x^2(x+2)}{(1+2x)[\alpha_{0A}x^3(x+2) + \alpha_{0B}(1+2x)]} \times [(\omega_A + \omega_B)^4 k'_{AB} + (\omega_A + \omega_B)^2 k'_{AB} + k_{AB}] + \text{same } A \leftrightarrow B + O(R_{AB}^{-9}), \quad (55)$$

$$t^2 = \frac{\omega_A^2}{\alpha_{0A}x^2 + \alpha_{0B}} \left(\alpha_{0A} + \alpha_{0B} - 2\sqrt{2} \frac{\alpha_{0A}\alpha_{0B}}{R_{AB}^3} \right), \quad (56)$$

$$t' = \frac{\lambda}{2} \frac{\alpha_{0B}}{\omega_A} \frac{1}{(\alpha_{0A}x^2 + \alpha_{0B})[(\omega_A + \omega_B)^2 - t'^2]} \times (t^4 k'_{AB} + t^2 k'_{AB} + k_{AB}) + \text{same } A \leftrightarrow B + O(R_{AB}^{-9}). \quad (57)$$

The final expression of (52) in terms of the roots of the numerator and of the denominator is then, through $O(R_{AB}^{-6})$,

$$\langle \alpha_{AB}(\omega) \rangle_{av} = -\omega_B^2 (\alpha_{0A}x^2 + \alpha_{0B}) \left[1 - \frac{\lambda}{2\omega_B} \frac{\alpha_{0A}k'_{AB}x + \alpha_{0B}k'_{BA}}{\alpha_{0A}x^2 + \alpha_{0B}} \right] \frac{[\omega^2 - (\omega_A + \omega_B)^2 - t'^2](\omega^2 - t^2 - t')}{[\omega^2 - (\omega_A + \omega_B)^2 - t_{AB}](\omega^2 - \omega_+^2 - \omega_-^2)(\omega^2 - \omega_+^2 - \omega_-^2)}. \quad (58)$$

Before using these results in detailed applications some further comments are in order. First, a very important feature of the frequency shift in (49) is its independence on the parameter β_A , describing the polarizability of an atomic excited state. From this we may infer that calculations of frequency shifts of impurities based on (49) will be less model dependent, in general, than the results for the correction in the polarizability [Eq. (29)], which depend directly on this parameter.

Second, we note that the shift of the impurity absorption frequency in (49) includes both a classical and a quantum term at $O(R_{AB}^{-6})$. We normally expect the classical correction to be dominant because it is the only one which is present in a harmonic approximation for the atoms (Drude model), whereas the quantum correction arises purely from anharmonicities of the real atoms.^{11,12} This is found to be the case in the examples discussed below which indicate, however, that the quantum term is usually rather large also. Among previous discussions of electronic spectral shifts arising from dipole-dipole interactions of nonpolar molecules in nonpolar matrices, the most detailed and closest to the present approach is that of Longuet-Higgins and Pople.²⁸ All of these discussions have been based on quantum-mechanical second-order perturbation theory, whose drawback is, however, that it does not allow a natural distinction between classical and quantum effects to be made. Considering the Longuet-Higgins-Pople treatment, we note that the final result [Eq. (14) of Ref. 28] involves no parameter which depends in an essential way on the higher excited states, as does, for instance, our parameter ν . If we apply the effective two-state model to the final formula of Ref. 28 we obtain for the absorption frequency

$$\Omega_{A, L-H-P} = \omega_A \left(1 - \frac{1}{8} \alpha_{0A} \alpha_{0B} / R_{AB}^6 \right), \quad (59)$$

which is derived for $x \ll 1$.²⁸ Comparison with Eq. (49) in this limit shows that agreement in sign and in qualitative form exists with our classical correction; which is, however, about eight times larger than the correction in (59). Therefore the numerical coefficient in (59) appears to be rather unrealistic. The quantum correction is very small for $x \ll 1$ and has therefore little effect on this conclusion.

As a check of the present calculation, we note that in the monatomic crystal limit the summation of the quantum correction in (49) over all neighboring atoms of A , using (12), coincides with the lowest-order results obtained in II.

Turning to applications, we note that Eq. (49) could of course be used to estimate the effects proportional to R_{AB}^{-6} in the tight-binding exciton frequencies of perfect diatomic crystals, like the alkali

halides. Here, we prefer however to illustrate its application to impurity states in the rare-gas solids, for which many experimental data are now available. Furthermore, these data have recently been analyzed in a form which is suitable for direct comparison with the present theory. To this end let us introduce two van der Waals interaction constants, ${}^0C(A, B)$ and ${}^1C(A^*, B)$, where ${}^0C(A, B)$ characterizes the interaction $-{}^0C(A, B)/R_{AB}^6$ of a single pair $A-B$ in the ground state and ${}^1C(A^*, B)$ the interaction $-{}^1C(A^*, B)/R_{AB}^6$ in the case where A is in an excited state (and B not). From London's approximate formula, discussed in Sec. I, we have

$${}^0C(A, B) = \frac{3}{2} \alpha_{0A} \alpha_{0B} \omega_A / (x + 1), \quad (60)$$

which may be combined with (49) to yield

$${}^1C(A^*, B) = -\frac{1}{2} \alpha_{0A} \alpha_{0B} \omega_A \left[\frac{2}{x^2 - 1} + \frac{2x^2 + 11x + 5}{2x^2 + 3x + 1} - \nu_A - \frac{3}{x + 1} \right]. \quad (61)$$

Roncin¹⁵ has recently carried out an empirical fit of the experimental shifts of electronic absorption frequencies of rare-gas and simple molecular impurities in rare-gas matrices^{29,30} in terms of 6-12 pair potentials, thereby obtaining a set of values for the parameters ϵ_{A^*B} (potential-well depth) and σ_{A^*B} (separation at which the potential vanishes) for the interaction between the excited impurity (A) and a matrix atom (B) in the ground state. This is probably the simplest way of separating the contributions due to van der Waals type of interactions from the short-range exchange interactions. Roncin's results are based on the assumption that the Lennard-Jones parameters ϵ and σ are not very different for the same impurity in different matrices but that their variations upon excitation of the impurity are much more appreciable. Using the results of Ref. 15 and applying the usual combining rules which relate the Lennard-Jones parameters of the interaction between A and B atoms to those of the interaction between two A atoms and two B atoms,¹⁵ we obtain the values of Tables VII and VIII for ϵ_{A^*B} and σ_{A^*B} , for various excited rare-gas and molecular impurities in rare-gas matrices. From these results we then compute the empirical van der Waals constants of the interaction of the excited impurity with an atom of the matrix,

$${}^1C(A^*, B)_{\text{emp}} = 4\epsilon_{A^*B} \sigma_{A^*B}^6. \quad (62)$$

It is thus interesting to compare the empirical values obtained from (62) with those calculated by means of (61). The ground- and excited-state, as well as the free-atom (molecule), parameters in-

TABLE VII. Lennard-Jones parameter ϵ_{A^*-B} for excited states of impurities (A) in rare-gas matrices (B), in units 10^{-2} eV. For Xe impurities the results are given for singlet and triplet excited P states. The excited states for Kr, Hg, CO, and N_2O are 3P , 1P , $A^1\pi$, and \tilde{B} , respectively.

$B \setminus A$	Kr	Xe	Hg	CO	N_2O
Ne	0.775	0.749(3P) 0.702(1P)	1.485	0.857	0.554
Ar	1.441	1.392(3P) 1.304(1P)	2.758	1.593	1.03
Kr	...	1.723(3P) 1.615(1P)	3.415	1.971	1.275
Xe	1.955	...	3.741	2.161	1.397

involved in (61) are listed in Table IX for the systems which have been analyzed by Roncin.¹⁵ The polarizabilities of the rare-gas atoms are taken from Ref. 31, those of Hg, CO, and N_2O from Ref. 32. In the case of the rare gases we take for ω_A the average values of the excitation energies to the triplet and singlet P states as listed in Ref. 29 for Ar, Kr, Xe and in Ref. 33 for Ne. The values of ω_A for CO and N_2O are from Ref. 34. The values of ν_A for the rare gases are those calculated from (31), while for Hg, CO, and N_2O we use the Gaussian-model result as a rough estimate, neglecting molecular anisotropies. In Table X, we compare the theoretical values ${}^1C(A^*, B)$ obtained from (61) to the empirical values given by (62). In the case of Xe we have listed the averages of the empirical values obtained for the triplet and singlet states. It appears that theoretical and empirical excited-states van der Waals constants have the same sign and agree surprisingly well in magnitude, in the cases of Ar, Kr, and Xe matrices. This is especially true considering that theoretical results for the ground-state van der Waals constants ${}^0C(A, B)$ in pure substances are usually smaller by a factor of 2, or more, than the empirical results.³⁵ A similar discrepancy has been found also for the excited-states interaction con-

TABLE VIII. Lennard-Jones parameter σ_{A^*-B} for excited states of impurities (A) in rare-gas matrices (B), in units of Å. Excited states are the same as for Table VII.

$B \setminus A$	Kr	Xe	Hg	CO	N_2O
Ne	3.72	3.795(3P) 3.895(1P)	3.52	3.27	3.77
Ar	4.035	4.11(3P) 4.21(1P)	3.835	3.585	4.085
Kr	...	4.205(3P) 4.305(1P)	3.93	3.68	4.18
Xe	4.355	...	4.155	3.905	4.405

TABLE IX. Ground and excited states of various atoms and molecules and numerical values of parameters defined in the text. The values of the excitation energies ω_A for the rare-gas atoms are averages of excitation energies to the singlet and triplet P states. The polarizabilities for CO and N_2O are averages of parallel and perpendicular molecular polarizabilities.

	Ne	Ar	Kr	Xe	Hg	CO	N_2O
Ground state	$1s$	$1s$	$1s$	$1s$	$1s$	$X^1\Sigma^+$	$\tilde{X}^1\Sigma^+$
Excited states	$^3P, ^1P$	$^3P, ^1P$	$^3P, ^1P$	$^3P, ^1P$	1P	$A^1\pi$	\tilde{B}
α_{0A} (\AA^3)	0.4	1.64	2.48	4.04	5.03	1.95	3
ω_A (eV)	16.725	11.725	10.295	9	6.698	8.026	7.386
ν_A	5.218	5.116	5.075	5.062	5	5	5

stants of impurities of Ca, Ar, and Na in compressed rare gases.³⁶ These constants have been obtained empirically from collision-broadening data and theoretically from a formula which is not directly related to (61).³⁶ For completeness, we note that a theoretical value ${}^1C(A^*, B) = 60.69$ eV Å⁶ for Ar in Ne has been found previously by Gold⁴ using the Buckingham variational method.²² Furthermore, for an excited Hg atom interacting with an Ar atom in the ground state a value ${}^1C(A^*, B) = 82$ eV Å⁶ has been obtained by Margenau in an early calculation based on perturbation theory and the use of spectroscopic data.³⁷ This value agrees less well with the empirical one than the result of Eq. (61). Finally, in Table XI, we compare the three different additive contributions in ${}^1C(A^*, B)$,

$$\Delta C_{\text{class}} = -\frac{\alpha_{0A}\alpha_{0B}\omega_A}{x^2 - 1}, \quad (63)$$

$$\Delta C_{\text{quant}} = -\frac{1}{2}\alpha_{0A}\alpha_{0B}\omega_A\left(\frac{2x^2 + 11x + 5}{2x^2 + 3x + 1} - \nu_A\right), \quad (64)$$

and ${}^0C(A, B)$, given by (60). It appears that although the classical effect always dominates in cases of heavy impurities trapped in lighter matrices, the quantum effects are nonetheless large. In most of these cases, in fact, the sum of ${}^0C(A, B)$ and of the quantum correction in the frequency shift (ΔC_{quant}) is nearly equal to the classical shift ΔC_{class} . We also note the difference in sign between the classical and quantum contributions for the cases of lighter rare-gas impurities in heavier matrices, which leads sometimes to negative constants ${}^1C(A^*, B)$ and therefore to a repulsive interaction. This is partly in agreement with an argument of Margenau,³⁷ according to which the interaction should be repulsive if the electronic excitation energy of the matrix atoms is smaller than that of the impurity. This is precisely the case for lighter rare-gas atoms in heavier matrices. The present treatment shows, however, that the additional "detailed balance" criterion

TABLE X. van der Waals interaction constants for impurities (*A*) in excited states in various rare-gas matrices (*B*) in units $\text{eV } \text{\AA}^6$. The first number is the theoretical value given by Eq. (61) and the second one is the empirical value as defined by Eq. (62). For the rare-gas impurities the empirical values are the averages of those corresponding to the singlet and triplet excited *P* states, respectively.

$B \backslash A$	Ne	Ar	Kr	Xe	Hg	CO	N ₂ O
Ne	...	28.680	34.09	45.35	39.24	18.54	25.66
		60.69 ^a	80.02	93.73	112.99	41.91	63.62
Ar	10.26	...	257	249	179.77	92.05	121.8
			248.72	279.34	350.95	135.27	191.45
					82 ^b		
Kr	21.72	-73.57	...	541.78	294.84	165.72	206.95
				395.99	503.28	195.81	272.04
Xe	41.24	31.71	-147.72	...	553.41	419.7	429.09
					769.97	306.5	408.26

^aA. Gold, Ref. 4.

^bReference 37.

$$\Delta C_{\text{class}} + \Delta C_{\text{quant}} + {}^0C(A, B) < 0 \quad (65)$$

must be satisfied in order for the net interaction of the excited impurity to be repulsive. In a similar context we may observe that if we use the results of Tables VII and VIII to compute ${}^1C(A^*-B)$ for Kr in Xe we obtain the value 532.14, in clear disagreement with the negative theoretical value of -147.72 of Table X. This would suggest that the empirical results of Roncin cannot be used to predict interaction constants for lighter excited impurities in heavier matrices. Such situations have not been studied experimentally so far, which would obviously be very interesting.

A last remark concerns the application of (61) in the case of molecular impurities CO and N₂O, where we have neglected possible anisotropy effects by taking average polarizabilities. Of course

this may only be valid in first approximation. Work is now in progress on the anisotropy effects of the dipole-dipole correction in the polarizability and in energy shifts of impurities by using a proper generalization of the present treatment.

V. TWO-QUANTUM EXCITATIONS IN ALKALI HALIDES

A specific effect of the quantum dipole fluctuations when the higher excited states of the individual atoms are taken into account is the existence of a nonzero oscillator strength for two-quantum absorption. In this process two atoms are simultaneously excited by one photon as a result of the combined effect of the external field and of the dipole-dipole correlation.¹² The present theory enables us to calculate this oscillator strength for pure diatomic crystals like the alkali halides.

TABLE XI. Comparison of the various contributions to the theoretical value of the van der Waals interaction constant for impurities (*A*) in excited states, trapped in various solid rare-gas matrices (*B*). The first number is the classical contribution ΔC_{class} , the second number is the quantum contribution ΔC_{quant} , which represents the quantum shift of the impurity-absorption frequency, and finally the third number is the van der Waals constant 0C of the interaction in the ground state (in units of $\text{eV } \text{\AA}^6$).

$B \backslash A$	Ne	Ar	Kr	Xe	Hg	CO	N ₂ O
Ne	...	15.110	16.450	20.45	16.49	8.13	11.01
	...	6.78	8.17	10.62	7.92	4.06	5.43
	...	6.78	9.48	14.18	14.84	6.35	9.22
Ar	-10.62	...	182.85	144.38	84.26	48.34	60.26
	14.09	...	40.72	53.96	41.29	20.87	28.09
	6.78	...	33.44	50.65	54.22	22.85	33.44
Kr	-10.11	-160.57	...	382.09	149.1	99.02	113.07
	22.35	53.55	...	87.51	67.72	34	45.88
	9.48	33.44	...	72.18	78.03	32.71	48
Xe	-11.02	-111.3	-333.82	...	313.68	309.95	274.6
	38.08	92.41	113.93	...	119.4	59.63	80.75
	14.18	50.6	72.17	...	120.33	50.13	73.74

As noted earlier, and as far as the pair interaction effects are concerned, the absorption frequencies and the associated oscillator strengths in perfect cubic crystals can be discussed rigorously by using the expression for the polarizability of an isolated pair suitably averaged over orientations as in (58). In particular, the calculation of oscillator strengths is performed by reducing $\langle \alpha_{AB}(\omega) \rangle_{av}$ to the usual Kramers-Heisenberg form involving a summation over all possible excitations of the system, with the resonance energies in the denominators and the corresponding oscillator strengths in the numerators. This may be achieved with

$$\langle \alpha_{AB}(\omega) \rangle_{av} = - \left(1 - \frac{\lambda}{2\omega_B} \frac{\alpha_{0A} k'_{AB} x + \alpha_{0B} k'_{BA}}{\alpha_{0A} x^2 + \alpha_{0B}} \right) \left\{ \left[1 - \frac{f_{AB}}{\omega_B^2(1+2x)} + \frac{1}{\alpha_{0A}\omega_B^2 x^2(x^2-1)} (\alpha_{0B} g_{AB} + \alpha_{0A} x^2 g_{BA}) \right] \right. \\ \left. \times \frac{\alpha_{0A}\omega_A^2}{\omega^2 - \omega_+^2 - \omega_-^2} + \text{same } A \leftrightarrow B, \omega_+ \leftrightarrow \omega_- + f_{AB} \left[\frac{\alpha_{0A}\omega_A^2}{\omega_B^2(1+2x)} + \frac{\alpha_{0B}\omega_B^2}{\omega_A^2(1+2y)} \right] \frac{1}{\omega^2 - (\omega_A + \omega_B)^2 - t_{AB}} \right\}, \quad (67)$$

where

$$f_{AB} = f_{BA} = -t'_{AB} = \frac{1}{2} \frac{\alpha_{0A}\alpha_{0B}}{R_{AB}^6}$$

$$\times \omega_A \omega_B \frac{(x+1)}{x^3(x+2)\gamma + (1+2x)} \\ \times \left[\gamma \frac{x^2(x+2)}{2x+1} (4x^2+4x+1)(\nu_A-1) \right. \\ \left. + \frac{(2x+1)}{x(x+2)} (x^2+4x+4)(\nu_B-1) \right], \quad (68)$$

$$g_{AB} = \sqrt{2} \frac{\alpha_{0A}}{R_{AB}^3} \omega_A^2 + \frac{\alpha_{0A}\alpha_{0B}}{R_{AB}^6} \omega_A^2 \left(\frac{2}{x^2-1} + \frac{2x^2+11x+5}{2x^2+3x+1} \right. \\ \left. - \nu_A - \frac{\gamma x^3}{2(x+1)(\gamma x^2+1)[x^3(x+2)\gamma + y^3(y+2)]} \right) \\ \times \left\{ 3\beta_A \gamma x(x-1)[x^3(x+2)\gamma + y^3(y+2)] \right. \\ \left. + 2[2x^2+11x+5 - \nu_A(2x^2+3x+1)] \right. \\ \left. + \gamma^2 x^2 [13x^4+26x^3-4x+1 - \nu_A(3x^4+6x^3+2x^2+1)] \right. \\ \left. + \gamma x^2 [13x^4+48x^3+18x^2-4x \right. \\ \left. - 3 - \nu_A(5x^4+12x^3+8x^2-1)] \right\}, \quad (69)$$

and $\gamma = \alpha_{0A}/\alpha_{0B}$. (70)

We note that in the classical limit [neglect of terms $\langle \Delta\alpha_{AB}(\omega) \rangle_{av}$ and $\langle \Delta\alpha_{BA}(\omega) \rangle_{av}$] one obtains

$$\langle \alpha_{AB, \text{class}}(\omega) \rangle_{av} = - \left[1 + 2\sqrt{2} \frac{\alpha_{0B}}{R_{AB}^3} \frac{1}{x^2-1} \right. \\ \left. + 2 \frac{\alpha_{0B}^2}{R_{AB}^6} \frac{(1-\gamma x^2)}{(x^2-1)^2} \right] \frac{\alpha_{0A}\omega_A^2}{\omega^2 - \omega_+^2}$$

(58) by means of repeated use of identities like

$$\frac{\omega^2 - u}{\omega^2 - v} = 1 + \frac{v-u}{\omega^2 - v} \quad (66a)$$

and

$$\frac{1}{(\omega^2 - u)(\omega^2 - v)} = \frac{1}{u-v} \left(\frac{1}{\omega^2 - u} - \frac{1}{\omega^2 - v} \right), \quad (66b)$$

where (66a) serves to remove the frequency dependence in the numerator without modifying the pole in the denominator. After a series of straightforward but tedious manipulations, using Eqs. (55) to (58) and (24) to (26), we obtain

+ same $A \leftrightarrow B, \omega_+ \leftrightarrow \omega_-$. (71)

Thus, for unlike atoms, the oscillator strength of the ordinary classical excitons is modified by the dipole-dipole interaction, while, of course, no such effect exists for identical atoms, as can be easily verified. It follows from (67) that the ratio ξ of the total oscillator strength for double excitation of a pair of nearest-neighbor atoms (two-quantum excitation) and of that for the excitation of the individual atoms in the crystal is given by

$$\xi = \frac{\gamma x^2 h_A + h_B}{1 + \gamma x^2 - (\gamma x^2 h_A + h_B)}, \quad (72)$$

where $h_A = \sum_{B \neq A} \frac{f_{AB}}{\omega_B^2(1+2x)}$ (73)

and h_B is obtained by interchanging A and B . The summation extends over nearest neighbors only, and by using (68) we obtain

$$h_A = \frac{n}{2} \frac{\alpha_{0A}\alpha_{0B}}{R^6} \frac{x(x+1)}{(1+2x)[(1+2x) + \gamma(x+2)x^3]} \\ \times \left[\frac{\gamma(x+2)(4x^2+4x+1)x^2}{2x+1} (\nu_A-1) \right. \\ \left. + \frac{(2x+1)(x^2+4x+4)}{x(x+2)} (\nu_B-1) \right]. \quad (74)$$

Similarly, we may define the ratio ξ'_{AB} (and ξ'_{BA}) which represents the relative oscillator strength for double excitation of a pair of second neighbors AA (BB) in a diatomic crystal whose other atoms are of type B (A). According to (67) and (68) this is given by

$$\xi'_{AB} = h'_A / (1 - h'_A), \quad (75)$$

$$\text{where } h'_A = m(\alpha_{0A}^2 / R'^6)(\nu_A - 1). \quad (76)$$

We note that, like ${}^1C(A^*, B)$, ξ and ξ'_{AB} (ξ'_{BA}) do not depend on β_A , which leads us to anticipate, again, that numerical calculations of this quantity will be less model dependent than $\Delta\alpha_A(\omega)$ itself. In Tables XII–XIV, we collect the results of the computation of ξ , ξ'_{AB} , and ξ'_{BA} for the various alkali halide crystals. It appears that for the crystals with the NaCl structure ξ varies from 4.5 to 20% while for those with the CsCl structure it rises to 30%. The relative oscillator strength for double excitation of a pair of second-neighbor halogen ions is also fairly large because of the large polarizabilities of these ions. Finally, we note that in the limit of monatomic cubic crystals the expressions for ξ and ξ'_{AB} reduce to Eq. (36) of II if the summations over neighbors are performed by means of (12). Since in this case there is only a single frequency of double excitation, all neighbors contribute additively to the oscillator strength.

The previous treatments of two-quantum excitations in alkali halides have led to the very different results $\xi \approx 0.01$ (Hermanson¹⁶) and $\xi \approx 1.5$ (Miyakawa¹⁷); those of the present work fall between these limits, being however much less than 1 as anticipated. In addition, the present results illustrate a new feature of the two-quantum oscillator strength which is its strong dependence on specific parameters of the individual ions. This is demonstrated by the large spread in the values obtained for the various crystals.

Stephan *et al.*³⁸ have recently observed peaks in the reflection spectra of KBr and KCl at 27.8 and 28.5 eV, respectively, which they attribute tentatively to double excitation of neighboring pairs of ions in the crystal. We note that these energies are very close to those at which the present analysis predicts the onset of double excitation (see Table II).

VI. CONCLUDING REMARKS

In this paper, we have presented detailed calculations for several effects of practical interest

TABLE XII. Numerical values of oscillator strengths for two-quantum nearest-neighbor excitations relative to those of one-quantum excitations in alkali halide crystals (in percent).

$B \backslash A$	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	4.52	9.36	11.4	12.49
Cl ⁻	4.36	13.03	17.92	24.9
Br ⁻	4.05	12.76	17.45	25.03
I ⁻	4.16	14.47	19.66	30.29

TABLE XIII. Relative oscillator strengths (in percent) for double excitation of pairs of second-neighbor A ions in alkali halides.

$B \backslash A$	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	0.1	1.43	3.77	6.43
Cl ⁻	0.03	0.52	1.48	3.86
Br ⁻	0.02	0.39	1.1	2.93
I ⁻	0.01	0.26	0.73	2.04

(correction in the polarizability and frequency-dispersion effects in alkali halide crystals, deep impurity states in solid rare gases, and two-quantum excitations) from a unified point of view. This is in contrast with the numerous discussions which have been devoted in the past to each of these problems in particular. As a result, a variety of points of view have been adopted to treat these problems, and many different approximation schemes have been developed. On the other hand, because of the simplified nature of the individual-atom model which forms the basis of the theory which we have applied here,¹¹ we are omitting completely the effects arising from the overlap between neighboring atoms, which have been considered in more detail by other authors (the relevant references are discussed in Sec. I).

The final analytical expressions of this paper, particularly Eqs. (29), (36), (61), (72), (74), and (75), can be expected to have more general validity than the simple assumptions about the electronic spectrum of the atoms which underly their derivation. This is because the physical parameters involved in these expressions (polarizabilities, excitation energies, and parameter ν_A) have a general meaning. This may be especially true in the case of Eqs. (61), (72), (74), and (75) which do not depend on the parameter β_A , which is the most sensitive to particular models.

APPENDIX A

The general formalism described in I does not aim directly at the calculation of the induced dipole-dipole correction in the polarizability of an individual atom itself. Instead, it determines a

TABLE XIV. Relative oscillator strengths (in percent) for double excitation of pairs of second-neighbor B ions in alkali halides.

$B \backslash A$	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	4.34	1.78	1.28	0.87
Cl ⁻	17.91	8.53	6.63	6.67
Br ⁻	17.7	8.97	6.97	7.2
I ⁻	27.81	14.78	11.41	12.52

certain energy correction (which reduces only in the static limit to the total induced polarization energy) from which the correction to the polarizability of the individual atoms may then be obtained. This requires however the use of a separate additional argument. Namely, one assumes that the susceptibility tensor $\vec{\chi}(\omega)$, which determines the total polarization $\vec{P} = \vec{\chi}(\omega) \cdot \vec{E}_0$ induced by the external field \vec{E}_0 , has the same formal structure as the classical expression resulting from the Lorentz local field theory. The corrections $\Delta\vec{\alpha}_A(\omega)$ in the individual polarizabilities are then obtained by identifying the first-order change in $\vec{\chi}(\omega)$, resulting from small changes of the polarizabilities from the free-atom values, with the energy correction just mentioned. The success of this procedure depends on our ability to solve the system of coupled equations for the local fields. In I, we applied it in the case of cubic crystals where the local fields are the same at all lattice sites, so that these equations may be readily solved indeed. For an isolated pair of unlike atoms, the situation is slightly different since the local fields acting on the two atoms are different. Therefore, it would seem necessary to repeat an argument similar to that given above, in order to obtain the correction $\Delta\vec{\alpha}_{AB}(\omega)$ which arises when we are considering an isolated pair rather than a whole collection of atoms arranged on a cubic lattice. This is done below. The total polarizability of the pair is defined by

$$\vec{\alpha}_{AB}(\omega) \cdot \vec{E}_0 = \vec{\alpha}_A(\omega) \cdot \vec{F}_A + \vec{\alpha}_B(\omega) \cdot \vec{F}_B, \quad (\text{A1})$$

where \vec{E}_0 denotes the amplitude of the external field

$$\vec{E} = \frac{1}{2} (\vec{E}_0 e^{i\omega t} + \text{c. c.})$$

of frequency ω and \vec{F}_A, \vec{F}_B the amplitudes of the local fields which are given by

$$\vec{F}_A = \frac{\vec{I} - \vec{T}_{AB} \cdot \vec{\alpha}_B(\omega)}{\vec{I} - \vec{T}_{AB} \cdot \vec{\alpha}_B(\omega) \cdot \vec{T}_{AB} \cdot \vec{\alpha}_A(\omega)} \cdot \vec{E}_0 \quad (\text{A2})$$

and a similar expression for \vec{F}_B . Note, incidentally, the reduction which occurs for identical spher-

ically symmetric atoms. The polarizabilities $\vec{\alpha}_A(\omega)$ ($\vec{\alpha}_B(\omega)$) are assumed to be the sum of the free-atom polarizability and small deviations $\Delta\vec{\alpha}_{AB}(\omega)$ and $\Delta\vec{\alpha}_{BA}(\omega)$ so that, for instance,

$$\vec{\alpha}_A(\omega) = \alpha_{0A}(\omega) \vec{I} + \Delta\vec{\alpha}_{AB}(\omega) \quad (\text{A3})$$

Next, we write

$$\vec{F}_A = \vec{F}_{0A} + \Delta\vec{F}_A,$$

where \vec{F}_{0A} is defined by (A2) after replacing $\vec{\alpha}_A(\omega)$ and $\vec{\alpha}_B(\omega)$ by $\alpha_{0A}(\omega)$ and $\alpha_{0B}(\omega)$, respectively, and $\Delta\vec{F}_A$ is chosen to be linear in the deviations (A3). We then obtain

$$\Delta\vec{F}_A = \frac{\vec{T}_{AB}}{\vec{I} - \alpha_{0B}(\omega) \alpha_{0A}(\omega) \vec{T}_{AB}^2} \times \left[\alpha_{0B}(\omega) \vec{T}_{AB} \cdot \Delta\vec{\alpha}_{AB} \cdot \vec{F}_{0A} - \Delta\vec{\alpha}_{BA} \cdot \vec{F}_{0B} \right] \quad (\text{A4})$$

and a similar expression for $\Delta\vec{F}_B$. Finally, upon substitution in (A1), we obtain through linear order

$$\begin{aligned} \vec{E}_0 \cdot \vec{\alpha}_{AB}(\omega) \cdot \vec{E}_0 &= \vec{E}_0 \cdot \alpha_{0A}(\omega) \cdot \vec{F}_{0A} + \vec{E}_0 \cdot \alpha_{0B}(\omega) \cdot \vec{F}_{0B} \\ &+ \vec{F}_{0A} \cdot \Delta\vec{\alpha}_{AB}(\omega) \cdot \vec{F}_{0A} + \vec{F}_{0B} \cdot \Delta\vec{\alpha}_{BA}(\omega) \cdot \vec{F}_{0B} \quad (\text{A5}) \end{aligned}$$

The remainder of the argument follows the same pattern as in I, and shows that the expression of the correction $\Delta\vec{\alpha}_{AB}(\omega)$ in the case of a pair AB is obtained by the following simple modifications of Eq. (3.45) of I: Replace λ by A , μ by B , and delete the summation sign $\sum_{\mu \neq \lambda}$; multiply by 2 and delete the addition "sym term $\lambda \leftrightarrow \mu$." Similar modifications in the case of a pair of spherically symmetric atoms must then also be introduced in the result obtained in the Unsöld approximation, Eq. (A2) of II. In addition, we already discussed some further obvious modifications of Eq. (A2) of II for a pair.¹³ The final result for the correction in the polarizability of atom A due to its interaction with atom B is, in the Unsöld approximation,

$$\begin{aligned} \Delta\vec{\alpha}_{AB}(\omega) &= -\langle 0, B | \hat{p}_{AB}^2 | 0, B \rangle \left(\frac{\langle 0, A | \vec{p}_A \cdot \vec{T}_{AB}^2 \cdot \vec{p}_A | 0, A \rangle}{(\omega_A + \omega_B)^2} [\alpha_{0A}(\omega) - \bar{\alpha}_A(\omega)] \vec{I} + \frac{1}{\omega_A + \omega_B - \omega} \right. \\ &\times \sum_{k,l} \left[\frac{\langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A | 0, A \rangle \cdot \vec{T}_{AB}^2 \cdot \langle 0, A | \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | 0, A \rangle}{(\omega_{k,A;0,A} - \omega)(\omega_{l,A;0,A} - \omega)} \right. \\ &\left. + \frac{\langle 0, A | \vec{p}_A | k, A \rangle \cdot \vec{T}_{AB}^2 \langle k, A | \vec{p}_A | 0, A \rangle \langle 0, A | \vec{p}_A | l, A \rangle \cdot \langle l, A | \vec{p}_A | 0, A \rangle}{(\omega_{k,A;0,A} + \omega)(\omega_{l,A;0,A} + \omega)} \right] + \frac{1}{\omega_A + \omega_B + \omega} \\ &\times \sum_{k,l} \left[\frac{\langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A | 0, A \rangle \cdot \vec{T}_{AB}^2 \cdot \langle 0, A | \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | 0, A \rangle}{(\omega_{k,A;0,A} + \omega)(\omega_{l,A;0,A} + \omega)} \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{\langle 0, A | \vec{p}_A | k, A \rangle \cdot \vec{T}_{AB}^2 \langle k, A | \vec{p}_A | 0, A \rangle \langle 0, A | \vec{p}_A | l, A \rangle \cdot \langle l, A | \vec{p}_A | 0, A \rangle}{(\omega_{r,A;0,A} - \omega)(\omega_{l,A;0,A} - \omega)} \Big] + \frac{1}{\bar{\omega}_A + \bar{\omega}_B} \\
& \times \sum_{k,l} \left\{ \langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A | 0, A \rangle \cdot \vec{T}_{AB}^2 \langle 0, A | \vec{p}_A | l, A \rangle (\cdot \langle l, A | \vec{p}_A | 0, A \rangle) \right. \\
& \times \left[\frac{1}{(\omega_{r,A;0,A} + \omega)(\omega_{l,A;0,A} - \omega)} + \frac{1}{(\omega_{r,A;0,A} - \omega)(\omega_{l,A;0,A} + \omega)} \right] + \text{c.c.} \\
& - \sum_{k,l} \langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A \cdot \vec{T}_{AB}^2 \cdot \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | 0, A \rangle \\
& \times \left[\frac{1}{(\omega_{r,A;0,A} - \omega)(\omega_{l,A;0,A} - \omega)(\bar{\omega}_A + \bar{\omega}_B - \omega)} + \frac{1}{(\omega_{r,A;0,A} + \omega)(\omega_{l,A;0,A} + \omega)(\bar{\omega}_A + \bar{\omega}_B + \omega)} \right] - \frac{1}{\bar{\omega}_A + \bar{\omega}_B} \\
& \times \sum_{\substack{k,l \\ k \neq 0}} \left[\frac{\langle 0, A | \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A \cdot \vec{T}_{AB}^2 \cdot \vec{p}_A | 0, A \rangle}{\omega_{k,A;0,A}} \right. \\
& \times \left. \left(\frac{1}{\omega_{l,A;0,A} + \omega} + \frac{1}{\omega_{l,A;0,A} - \omega} \right) + \text{c.c.} \right] \\
& + \frac{\langle 0, A | \vec{p}_A \cdot \vec{T}_{AB}^2 \cdot \vec{p}_A | 0, A \rangle}{\bar{\omega}_A + \bar{\omega}_B} \sum_k \langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A | 0, A \rangle \left[\frac{1}{(\omega_{k,A;0,A} + \omega)^2} + \frac{1}{(\omega_{k,A;0,A} - \omega)^2} \right] \\
& - \sum_{\substack{j \neq 0 \\ k}} \sum_{\substack{l \neq 0 \\ k}} \left\{ \langle 0, A | \vec{p}_A | k, A \rangle \langle k, A | \vec{p}_A | l, A \rangle \cdot \vec{T}_{AB}^2 \langle l, A | \vec{p}_A | j, A \rangle (\cdot \langle j, A | \vec{p}_A | 0, A \rangle) \right. \\
& \times \left[\left(\frac{1}{\bar{\omega}_A + \bar{\omega}_B} - \frac{1}{\bar{\omega}_A + \bar{\omega}_B + \omega} \right) \frac{1}{(\omega_{0,A;k,A} - \omega)(\omega_{j,A;l,A} - \omega)} \right. \\
& \left. \left. + \left(\frac{1}{\bar{\omega}_A + \bar{\omega}_B} - \frac{1}{\bar{\omega}_A + \bar{\omega}_B - \omega} \right) \frac{1}{(\omega_{0,A;k,A} + \omega)(\omega_{j,A;l,A} + \omega)} \right] + \text{c.c.} \right] + \left(\frac{1}{\bar{\omega}_A + \bar{\omega}_B} - \frac{1}{\bar{\omega}_A + \bar{\omega}_B - \omega} \right) \\
& \times \sum_{\substack{j \neq 0 \\ k,l}} \frac{\langle 0, A | \vec{p}_A | k, A \rangle \cdot \vec{T}_{AB}^2 \langle k, A | \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | j, A \rangle (\cdot \langle j, A | \vec{p}_A | 0, A \rangle)}{(\omega_{r,A;l,A} + \omega)(\omega_{j,A;l,A} + \omega)} + \left(\frac{1}{\bar{\omega}_A + \bar{\omega}_B} - \frac{1}{\bar{\omega}_A + \bar{\omega}_B + \omega} \right) \\
& \times \sum_{\substack{j \neq 0 \\ k,l}} \frac{\langle 0, A | \vec{p}_A | j, A \rangle \cdot \vec{T}_{AB}^2 \langle j, A | \vec{p}_A | l, A \rangle \langle l, A | \vec{p}_A | k, A \rangle (\cdot \langle k, A | \vec{p}_A | 0, A \rangle)}{(\omega_{r,A;l,A} - \omega)(\omega_{j,A;l,A} - \omega)} \Big) . \tag{A6}
\end{aligned}$$

Here the manifolds $|i, A\rangle$ and $|i, B\rangle$ denote the complete sets of eigenstates of the Hamiltonians of the free atoms and

$$\omega_{i,A;j,A} = E_{i,A}^{(0)} - E_{j,A}^{(0)}, \quad \omega_{i,B;j,B} = E_{i,B}^{(0)} - E_{j,B}^{(0)}$$

are the energy differences between the states i, j of atoms A and B , respectively. The pair excitation energy $\bar{\omega}_A + \bar{\omega}_B$ is the average value by which the denominators in the original exact second-order perturbation formula have been replaced. $\bar{\alpha}_A(\omega)$ and $\bar{\alpha}_B(\omega)$ denote average polarizabilities of the free species in excited states, which arise also in the framework of the Unsöld approximation in the second-order perturbation formula. Some details concerning the derivation of (A6) from the exact general expression Eq. (3.45) of I have been given in II and will not be repeated here.

APPENDIX B

In this Appendix, we sketch the calculation of the parameter ν [Eq. (11)] using Slater one-electron orbitals. We only include the effect of the outermost shell of electrons whose spectroscopic configuration is ns^2np^6 for all the rare-gas and alkali halide ions, except He and Li^+ which are not considered here. Thus the core electrons and the nucleus are treated effectively as a static structureless entity. Each electron in this shell is represented by a one-electron wave function of the form

$$\psi_{n^*,l,m} = \varphi_{n^*}(r) Y_{l,m}(\theta\varphi) . \tag{B1}$$

The functions $Y_{l,m}(\theta\varphi)$ are the normalized spherical harmonics and the $\varphi_{n^*}(r)$ are the normalized radial Slater orbitals²⁷

$$\varphi_{n^*}(r) = N(n^*)(r/a_0)^{n^*-1} \exp[-(Z-S)r/a_0 n^*],$$

$$a_0 = (\text{Bohr radius}) \quad (\text{B2})$$

$$N^2(n^*) = \frac{1}{(2n^*)!} \left[\frac{2(Z-S)}{n^*} \right]^{2n^*+1}, \quad (\text{B3})$$

depending on an effective quantum number n^* and an effective nuclear charge (screening constant) $Z-S$. The ground state of the external shell of eight electrons is then represented as a Slater determinant of one-electron functions (B1), supplemented by the appropriate spin functions.

The problem is to calculate the expectation values of the operators

$$p_x^2 = e^2 \sum_{i,j} z_i z_j, \quad (\text{B4})$$

$$p_x^2 p^2 = e^4 \sum_{i,j,k,l} z_i z_j \vec{r}_k \cdot \vec{r}_l \quad (\text{B5})$$

in the ground state of the external shell of electrons (we assume the atom to be centered at the origin). The summations are over all electrons in this shell. We note that (B4) contains sums of one- and two-electron terms while (B5) involves different sums of one- up to four-electron terms: More explicitly, (B4) contains one-electron terms z_i^2 and two-electron terms $z_i z_j$ ($i \neq j$) whereas (B5) has one-electron terms $z_i^2 r_i^2$, four different kinds of two-electron terms; $z_i^2 \vec{r}_i \cdot \vec{r}_j$, $z_i z_j r_j^2$, $z_i^2 r_j^2$, and $z_i z_j \vec{r}_i \cdot \vec{r}_j$, three kinds of three-electron terms: $z_i^2 \vec{r}_k \cdot \vec{r}_l$, $z_i z_k r_l^2$, $z_i z_k \vec{r}_l \cdot \vec{r}_i$ ($i \neq k, k \neq l, l \neq i$), and finally, the four-electron term $z_i z_j \times \vec{r}_k \cdot \vec{r}_l$ (all indices \neq). The first step in the calculation of the above expectation values consists in transforming the original expectation values of sums of n -electron terms into sums, over all one-electron states, of matrix elements of just one of the n -electron operators. In the case of one- and two-electron operators, the procedure is well known.³⁹ Denoting, for brevity, the one-electron states in the Slater determinant $|0\rangle$ by greek letters $\alpha, \beta, \gamma, \dots$, one finds for arbitrary one-electron operators A_i, B_i, \dots ,

$$\sum_i \langle 0 | A_i | 0 \rangle = \sum_{\alpha} \langle \alpha | A_i | \alpha \rangle, \quad (\text{B6})$$

$$\sum_{i,j; i \neq j} \langle 0 | A_i B_j | 0 \rangle = \sum_{\alpha, \beta} (\langle \alpha \beta | A_1 B_2 | \alpha \beta \rangle - \langle \alpha \beta | A_1 B_2 | \beta \alpha \rangle), \quad (\text{B7})$$

where the summations in the second numbers extend over all different one-electron states occurring in the Slater determinant. The last term in (B7) evidently corresponds to electron-exchange effects. It is not difficult to generalize these results to the case of an n -electron operator $A_{i_1} A_{i_2}, \dots, A_{i_n}$. One simply finds, in obvious notations,

$$\sum_{i_1, i_2, \dots, i_n} \langle 0 | A_{i_1} A_{i_2} \dots A_{i_n} | 0 \rangle = \sum_{\alpha_1, \dots, \alpha_n} \times \sum_{\substack{\text{perm } \nu_{\alpha_1} \dots \nu_{\alpha_n} \\ \text{of } \alpha_1 \dots \alpha_n}} \text{sign} \left(\begin{array}{c} \nu_{\alpha_1} \dots \nu_{\alpha_n} \\ \alpha_1 \dots \alpha_n \end{array} \right) \times \langle \alpha_1 \dots \alpha_n | A_{i_1} A_{i_2} \dots A_{i_n} | \nu_{\alpha_1} \dots \nu_{\alpha_n} \rangle. \quad (\text{B8})$$

The next and most laborious task consists in the identification, counting, and explicit evaluation of all nonzero terms in the various sums over one-electron states. This analysis is simplified by choosing the representation

$$\vec{r}_1 \cdot \vec{r}_2 = \frac{1}{2} [(x_1 + iy_1)(x_2 - iy_2) + \text{c. c.}] + z_1 z_2, \quad (\text{B9})$$

which permits an easy use of the dipole selection rules for the individual matrix elements. By following these lines carefully and making systematic use of selection rules, the detailed calculation turns out to be less formidable than it might seem at first. Space limitation does not permit us to go into more details here, and we shall simply quote the final results. These are

$$\langle 0 | p_x^2 | 0 \rangle = \frac{1}{3} e^2 a_0^2 (2n^* + 1)(2n^* + 3) [n^{*2}/(Z-S)^2], \quad (\text{B10})$$

$$\langle 0 | p_x^2 p^2 | 0 \rangle = \frac{2}{3} e^4 a_0^4 (2n^* + 1) [n^{*4}/(Z-S)^4] \{ (n^* + 1) \times [(n^* + 2)(2n^* + 3) + \frac{1}{15}(2n^* + 1)(139n^* + 124) - \frac{13}{3}(2n^* + 1)^2] + \frac{5}{12}(2n^* + 1)^3 \}. \quad (\text{B11})$$

Finally, we note that the restriction to the effect of the outermost shell of electrons probably affects the accuracy of the ratio ν to a lesser extent than the individual expectation values (for which it is expected to be rather good, however) themselves.

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¹³The result of II which is derived specifically for cubic monatomic crystals has to be slightly modified in order to apply to an isolated pair of identical atoms. First, all combinations of operators of the form $\frac{1}{3} \text{Tr} \sum_{\mu \neq \lambda} \vec{T}_{\lambda\mu}^2 (\cdots \vec{p}_\lambda \cdots \vec{p}_\lambda \cdots)$ should be replaced by $\vec{p}_\lambda \cdot \vec{T}_{\lambda\mu}^2 \cdot \vec{p}_\mu$. Second, all products involving two operators $\vec{p}_{2\lambda}$ have to be replaced by the outer product of the two vectors \vec{p}_λ because for one pair the tensor $\Delta \vec{\alpha}_{\lambda\mu}(\omega)$ is neither proportional to 1 nor diagonal for a general orientation of the axis of the pair.

¹⁴J. Heinrichs, *Chem. Phys. Letters* **4**, 151 (1969). The two Eqs. (16) of this reference contain a misprint and should be divided by $\langle 0|AB|0\rangle$ and $\langle 0|ABC|0\rangle$, respectively.

¹⁵J. Y. Roncin, *Chem. Phys. Letters* **3**, 408 (1969).

¹⁶J. Hermanson, *Phys. Rev.* **177**, 1234 (1969).

¹⁷T. Miyakawa, *J. Phys. Soc. Japan* **17**, 1898 (1962).

¹⁸R. Haensel *et al.*, *Phys. Rev. Letters* **23**, 530 (1969). For a complete list of earlier experimental and theoretical references on double excitons, especially in molecular crystals, see Ref. 12.

¹⁹In this connection, a statement made in an earlier paper (Ref. 14), according to which $\vec{\alpha}_A(\omega)$ is closely given by the two-state model value $-\alpha_{0A}(\omega)$ for the rare-gases and for the alkali halide ions, appears to be largely unwarranted. It turns out, however, that with this latter value one obtains reasonable agreement between the calculations and the experimental refractive index data in the case of the rare-gas solids, while the use of Eq. (18) below would destroy this agreement because it would reverse the sign of $\Delta \vec{\alpha}_{AB}(0)$.

²⁰J. G. Kirkwood, *Physik. Z.* **33**, 57 (1922); see also, J. P. Vinti, *Phys. Rev.* **41**, 813 (1932).

²¹In terms of the operator U_A introduced in I, we have $U'_A = e^{-iH_{0A}t} U_A e^{iH_{0A}t}$, where H_{0A} is the Hamiltonian of the free atom A.

²²R. A. Buckingham, *Proc. Roy. Soc. (London)* **A160**, 94 (1937); **A160** 113 (1937).

²³A check of the calculations is possible in the case of cubic crystals where the correction in the polarizability is obtained by summing (22) over neighboring atoms B using Eq. (12). The result can be compared to Eq. (A5) of II. The two expressions coincide, as they should, but it is interesting to note that they have been derived in slightly different ways whose equivalence is thereby established. In II, we assumed that the tensor $\Delta \vec{\alpha}_A(\omega)$ reduces to a scalar in a cubic crystal, which enabled us to work only with the zz component of the general expression from the outset. In the present case, however, we start from the result for an isolated pair and we do not make this assumption *a priori*. Instead, we have reduced all matrix elements using only the electronic symmetry properties [Eqs. (7) and (9)] of the individual atoms. It is comforting to find that the two procedures lead to coinciding results and therefore that for cubic crystals the general expression of $\Delta \vec{\alpha}_A(\omega)$ [Eq. (3.45) of I] reduces explicitly to a scalar without an *a priori* assumption.

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²⁵A. R. Ruffa, *Phys. Rev.* **130**, 1412 (1963).

²⁶E. M. Ledovskaya, *Phys. Status Solidi* **31**, 507 (1969).

²⁷See, for instance, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 951.

²⁸H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.* **27**, 192 (1957); for other references on spectral shifts, especially in organic systems, see B. Linder, *Advan. Chem. Phys.* **12**, 225 (1967); see also, J. Jortner and C. A. Coulson, *Mol. Phys.* **4**, 451 (1961).

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³⁰J.-Y. Roncin, N. Damany, and J. Romand, *J. Mol. Spectr.* **22**, 154 (1967).

³¹A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

³²*Landolt-Börnstein Tabellen*, Vol. I (Springer, Berlin, 1955).

³³E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., Cambridge, England, 1959).

³⁴G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950).

³⁵See Ref. 27, p. 966.

³⁶W. R. Hindmarch, A. D. Petford, and G. Smith, *Proc. Roy. Soc. (London)* **297**, 296 (1967).

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³⁸G. Stephan, E. Garignon, and S. Robin, *Compt. Rend.* **268**, B408 (1968); G. Stephan and S. Robin, *Opt. Commun.* **1**, 40 (1969).

³⁹D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957), p. 39.