# Role of Quantum Dipole Fluctuations in the Theory of Excitons and of the Dielectric Constant of Crystals

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(Received 4 April 1969; revised manuscript received 15 July 1969)

A general expression for the frequency-dependent dielectric constant of a molecular-crystal model, which has been derived in a previous paper by the author, is analyzed in an improved two-state model for the individual atoms or molecules. This expression includes explicitly the effect of quantum dipole fluctuations and is used to perform a detailed study of their role in various other properties. First, we obtain a simple expression for the correction in the polarizability of an individual atom arising from these fluctuations. This result agrees roughly with dielectric-constant measurements for the rare-gas crystals. Secondly, we derive detailed expressions for the effect of the dipole fluctuations on the energies of the long-wavelength tight-binding exciton modes. In addition to the usual longitudinal and transverse single-exciton states, a new class of cooperative double excitons is found, and their oscillator strength is determined. The double-exciton modes result directly from the dipole-fluctuation mechanism. All the effects which are calculated—corrections in the polarizability and in the exciton energies and oscillator strength of the transverse double excitation—appear to be quadratic in the refractivity. Except for the correction in the polarizability, these fluctuation effects are all fairly large. For example, the oscillator strength of the transverse double-exciton mode ranges between 1 and 15% of that of the single-exciton mode in the case of the rare-gas solids.

## I. INTRODUCTION

IN recent years the theory of excitons in insulators and especially in molecular crystals has been of considerable interest, as exemplified by the extensive reviews which have been published.[1,2] Two extreme exciton models, valid in opposite limits, are generally considered and are known conventionally as the Frenkel- and Wannier-type excitons, respectively.

The Frenkel tight-binding model is the one which is appropriate for describing the excited electronic states in molecular crystals. These crystals are bound essentially by van der Waals forces, and the overlap between the wave functions of neighboring atoms (molecules) is weak. A molecular crystal can thus be described in first approximation as a collection of individual atoms which do not overlap, even in the lowest excited states. An exciton is then viewed as an electronic excitation in which the excited electron is essentially localized on an individual atom while the excitation itself proceeds from lattice site to lattice site as a result of the Coulomb and exchange interactions. Such an exciton corresponds to a stationary state of the crystal, and its wave function has the form of a translationally invariant linear combination of wave functions describing excitations localized on different atoms.

In detailed treatments of this extreme tight-binding exciton model, it is found necessary to resort to simplified models[3–10] to describe the individual atoms them-

selves. The simplest such model, the so-called Drude-Lorentz model, represents the electron cloud in a real atom as an effective bound charge which oscillates harmonically about the charged core. This model is partly justified quantum-mechanically in the sense that the polarizability of an isolated atom can be written as a sum of contributions of a set of independent oscillators with appropriate frequencies and oscillator strengths. (In fact, some improvement over the original Drude-Lorentz model results if instead of just one oscillator one introduces, for each atom, a whole set of oscillators with frequencies corresponding to the atomic transitions.[4]) A better model, which seems to be valid for a number of organic molecular crystals as well as for the heavy rare gases, consists in describing the atoms effectively as two-state systems. However, except for a recent study by Mazo,[10] this model has always been treated approximately in a way which makes it effectively equivalent to the Drude-Lorentz model,[11] at least as far as the final results are concerned. In the framework of these models and with the further approximation of replacing the Coulomb interaction to lowest order by a dipole-dipole interaction, the excitons acquire quite interesting properties. They can be interpreted as independent Bose-type elementary excitations, i.e., as true eigenstates of the (harmonic) Hamiltonian. As was first observed by Hopfield,[5,6] the binding energy of the crystal is then simply given by the sum of

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[11] It has been shown explicitly by Anderson (Ref. 6) that the consistent treatment of the two-state model leads to the introduction of nonlinear interaction terms in the Hamiltonian and the usual results of the Drude-Lorentz model correspond to a linear approximation in such a treatment. However, no attempt has been made to study the higher-order nonlinear terms.

zero-point energies of these normal modes for all wave numbers in the first Brillouin zone.

However, the Drude-Lorentz model has some short-comings which show up very simply if one studies the dielectric constant, by considering the effect of an external applied field. It turns out that, for this model, the polarization induced on any individual atom is exactly described by the classical Lorentz local field effect, in which the polarizability of an individual atom (and, in particular, the polarizability which enters the local field expression) is replaced by the free-atom polarizability. Thus, in this model, the quantum-mechanical fluctuations of the individual dipoles do not affect the dielectric constant, nor any related quantities like the exciton energies. These fluctuations can be thought of as taking place about the average classical dipole moments induced in the presence of the external field, and they are coupled through the dipole-dipole interaction. The quantum dipole fluctuations in the absence of an external field give rise to the van der Waals interactions, as is well known. When the field is present, the matrix elements which describe the quantum fluctuations are perturbed, and therefore one expects that for real atoms (as opposed to Drude oscillators), these fluctuations will in general lead to corrections in the polarizability as well as in the exciton energies. In a recent paper, henceforth referred to as I,[12] we have studied this problem and derived a general expression describing the effect of dipole fluctuations on the polarizability for real atoms. Like the van der Waals interaction, the correction in the polarizability has the form of interactions between pairs proportional to $R^{-6}$, to lowest order. We have shown also that it represents a purely anharmonic effect, being expressible in terms of various anharmonicity parameters of the atoms. There is thus a qualitative difference between this effect and the van der Waals interaction, since the latter exists even when the atoms are treated effectively as harmonic oscillators (Drude model).

The purpose of the present paper is primarily to study the long-wavelength exciton modes in molecular crystals by examining the singularities of the general expression of the frequency-dependent dielectric constant (and of its inverse) obtained in I. The theory is made tractable by analyzing this expression in a two-state model for the individual atoms. This model is similar to the two-state model discussed above, except that here it is used without any further approximations, so that its inherent anharmonicities appear to be properly handled. However, the detailed analysis reveals the presence of a certain matrix element which implicitly requires the consideration of the effect of all the higher excited states as well. Thus, in reality, our model is intermediate between an exact anharmonic two-state model and the one which describes the real spectrum of an atom.

As usually, the excitons separate into transverse and longitudinal modes. In the Drude-like models the exciton frequencies (more precisely, the squares of the frequencies) involve only corrections linear in the refractivity, which correspond to the Lorentz field effect. In a monatomic crystal, the refractivity $z$ is defined by

$$z = 4\pi N \alpha_0(0), \tag{1}$$

where $N$ is the number density of individual atoms and $\alpha_0(0)$ the static polarizability of an isolated free atom. The dipole-fluctuation effect gives rise to significant additional corrections which are quadratic in the refractivity to lowest order. On the other hand, since the terms describing the fluctuation effect in the polarizability involves resonance denominators at frequencies equal to excitation energies of pairs of atoms, it leads to the existence of cooperative double excitons, which correspond to the simultaneous excitation of two neighboring atoms in the crystal. The oscillator strength of the transverse double exciton is quadratic in the refractivity and becomes, in fact, fairly large in certain cases. Thus the quantum dipole fluctuations provide a well-defined and effective mechanism for cooperative excitons in molecular crystals. Similar double excitons have been observed recently,[13,14] and have been discussed theoretically from various points of view for molecular crystals.[15-20] Double-exciton transitions have also been studied for Wannier excitons and the results have been applied to alkali halides.[21,22] Finally, with the present model the correction term in the polarizability itself assumes a very simple form, which seems to agree with experiment for the rare gases.

Section II starts with a general derivation of the expression of the frequency-dependent dielectric constant at finite long wavelengths in terms of an effective polarizability. This derivation is followed by the discussion of the basic expression for the dipolar-fluctuation effect in the polarizability, although the details are given in an Appendix. In Sec. III the energies and oscillator strengths of the long-wavelength single and double excitons are determined and a brief discussion of retardation effects is also presented. Numerical results and discussions are given in Sec. IV.

## II. DIELECTRIC CONSTANT

We begin this section with the derivation of a general expression of the frequency-dependent dielectric con-

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stant of a crystal, at finite long wavelengths, in terms of an arbitrary effective polarizability of a constituent atom (ion or molecule). This derivation clarifies certain points which, apparently, have not received sufficient attention before. We find it thus useful to discuss this derivation in some detail, although we shall not make use of all the results later on.

The macroscopic dielectric tensor is defined by the equation

$$\mathbf{P}(\mathbf{q},\omega) = (1/4\pi)[\mathbf{\epsilon}(\mathbf{q},\omega) - 1] \cdot \mathbf{E}(\mathbf{q},\omega), \qquad (2)$$

where $\mathbf{P}(\mathbf{q},\omega)$ and $\mathbf{E}(\mathbf{q},\omega)$ denote the Fourier components of the macroscopic polarization density and of the Maxwell field at wave number $\mathbf{q}$ and frequency $\omega$. By solving the complete system of Maxwell's equations for plane waves, one is led to the familiar equation[8,23,24]

$$q^2\{[\hat{q} \cdot \mathbf{E}(\mathbf{q},\omega)]\hat{q} - \mathbf{E}(\mathbf{q},\omega)\}$$
$$= -(\omega^2/c^2)[\mathbf{E}(\mathbf{q},\omega) + 4\pi\mathbf{P}(\mathbf{q},\omega)]$$
$$= -(\omega^2/c^2)\mathbf{\epsilon}(\mathbf{q},\omega) \cdot \mathbf{E}(\mathbf{q},\omega), \qquad (3)$$

which enables us to find the dispersion equation for the excitations in the crystal as well as to express $\mathbf{E}(\mathbf{q},\omega)$ in terms of $\mathbf{P}(\mathbf{q},\omega)$. For the Maxwell field we thus obtain the standard relationship

$$\mathbf{E}(\mathbf{q},\omega) = \mathbf{E}_{\mathrm{ext}}(\mathbf{q},\omega)$$
$$- 4\pi\left[\hat{q}\hat{q} - \frac{\omega^2}{c^2q^2 - \omega^2}(1 - \hat{q}\hat{q})\right] \cdot \mathbf{P}(\mathbf{q},\omega), \quad (4)$$

where we have added an arbitrary external field with Fourier components $\mathbf{E}_{\mathrm{ext}}(\mathbf{q},\omega)$. Here $\hat{q} = \mathbf{q}/q$, $\hat{q}\hat{q}$ denotes an outer product, and $1$ is the unit dyadic. The square bracket in (4) splits the polarization into its longitudinal and transverse components, the latter being smaller than the former by the factor $\omega^2/c^2q^2$, at low frequencies. Now in a monatomic crystal with $N$ atoms per unit volume having effective polarizabilities $\alpha(\omega)$, we have, in the local-field picture,

$$\mathbf{P}(\mathbf{q},\omega) = N\alpha(\omega)[\mathbf{E}_{\mathrm{ext}}(\mathbf{q},\omega) + (1/N)\mathbf{\Phi}(\mathbf{q},\omega) \cdot \mathbf{P}(\mathbf{q},\omega)], \quad (5)$$

where $\mathbf{\Phi}(\mathbf{q},\omega)$ is the Fourier transform of the retarded dipole interaction tensor. Using a modification of Ewald's summation method, Mahan[25] has recently shown that

$$\mathbf{\Phi}(\mathbf{q},\omega) = -\mathbf{T}(\mathbf{q}) + 4\pi N\frac{\omega^2}{c^2q^2 - \omega^2}(1 - \hat{q}\hat{q}) + O(\omega a/c)^2, \quad (6)$$

$\mathbf{T}(\mathbf{q})$ being the familiar lattice sum involved in the non-retarded (instantaneous) local field:

$$\mathbf{T}(\mathbf{q}) = \sum_{\lambda \neq 0} e^{i\mathbf{q} \cdot \mathbf{R}_{\lambda 0}}\mathbf{T}_{\lambda 0}, \qquad (7)$$

$$\mathbf{T}_{\lambda\mu} = \frac{1}{R_{\lambda\mu}^3}\left[1 - 3\frac{\mathbf{R}_{\lambda\mu}\mathbf{R}_{\lambda\mu}}{R_{\lambda\mu}^2}\right], \quad \mathbf{R}_{\lambda\mu} = \mathbf{R}_\lambda - \mathbf{R}_\mu. \quad (8)$$

Since $a$ denotes the lattice parameter, it is apparent that (6) is certainly valid in the optical frequency region and, furthermore, that the last term can be neglected compared to the second one for wavelengths large compared to $a$. This is, in fact, the same condition as that which is required for the definition of macroscopic fields in Maxwell's theory itself. In this approximation we now combine Eqs. (2)–(6) to obtain

$$\mathbf{\epsilon}(\mathbf{q},\omega) = 1 + \frac{4\pi N\alpha(\omega)}{1 + \alpha(\omega)\mathbf{T}(\mathbf{q}) - 4\pi N\alpha(\omega)\hat{q}\hat{q}}. \quad (9)$$

In an isotropic nongyrotropic medium and, in particular, in a cubic crystal in the long-wavelength limit (or at any wavelength in directions parallel to symmetry axis), the principal axes of $\mathbf{\epsilon}(\mathbf{q},\omega)$ are purely longitudinal and transverse, and we have[23]

$$\mathbf{\epsilon}(\mathbf{q},\omega) = \epsilon_l(q,\omega)\hat{q}\hat{q} + \epsilon_t(q,\omega)(1 - \hat{q}\hat{q}) \qquad (10)$$

as well as

$$\mathbf{T}(\mathbf{q}) = T_l(q)\hat{q}\hat{q} + T_t(q)(1 - \hat{q}\hat{q}), \qquad (11)$$

where the quantities with indices $l$ and $t$ denote longitudinal and transverse principal values. After some simple algebra, one finds from (9)–(11)

$$\epsilon_l(q,\omega) = 1 + \frac{4\pi N\alpha(\omega)}{1 + \alpha(\omega)T_l(q) - 4\pi N\alpha(\omega)}, \quad (12a)$$

$$\epsilon_t(q,\omega) = 1 + \frac{4\pi N\alpha(\omega)}{1 + \alpha(\omega)T_t(q)}. \quad (12b)$$

Since

$$\lim_{q \to 0} T_l(q) = (8\pi/3)N,$$

$$\lim_{q \to 0} T_t(q) = -(4\pi/3)N,$$

one finally has

$$\epsilon(\omega) \equiv \epsilon_l(0,\omega) = \epsilon_t(0,\omega) = 1 + \frac{4\pi N\alpha(\omega)}{1 - (4\pi/3)N\alpha(\omega)}, \quad (13)$$

which is the familiar Lorenz-Lorentz equation.

We now observe that expressions (9) and (12) for the dielectric constant at finite long wavelength appear to be independent of retardation or magnetic effects, to the extent that these effects do not affect $\alpha(\omega)$ itself (a point to be discussed shortly). However, our derivation shows that these equations are valid in the presence of electromagnetic retardation effects as well, provided only that $q$ is sufficiently small that the term $O(\omega a/c)^2$ can be neglected in comparison with the other retardation term in (6). The traditional and simplest way to discuss the effect of retardation on the excitations in the medium[5,8,23,24] is to use the dispersion equation which fol-

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lows from (3), with the additional simplification of replacing the dielectric constant by its limiting infinite-wavelength value (13). The validity of this approximation is supported by the fact that the singularities of $\varepsilon(\mathbf{q},\omega)$ and of $\varepsilon^{-1}(\mathbf{q},\omega)$, which determine the exciton energies, do not vary strongly with $\mathbf{q}$, especially at long wavelengths.[26] With these assumptions, Eq. (3) leads to the dispersion formulas

$$\epsilon(\omega)=0, \quad \text{longitudinal modes } [\mathbf{E}(\mathbf{q},\omega)\|\mathbf{q}] \quad (14)$$

$$c^2q^2/\omega^2=\epsilon(\omega), \quad \text{transverse modes } [\mathbf{E}(\mathbf{q},\omega)\perp\mathbf{q}] \quad (15)$$

since the electric field $\mathbf{E}(\mathbf{q},\omega)$ never vanishes identically. The first member of (15) defines, of course, the square of the refractive index $n$. It thus follows that the longitudinal modes are unaffected by retardation and that the nonretarded transverse modes, which correspond to the electrostatic approximation, are given by the poles of $\epsilon(\omega)$.[27] These results express the well-known fact that only the transverse electrostatic modes are effectively coupled to the electromagnetic field.

We now proceed with some general remarks about Eq. (13), which should be kept in mind in the course of later application of this equation. We note that the exact expression of the real part of $\epsilon(\omega)$ is of the general form

$$\text{Re}\epsilon(\omega)=1+\omega_p^2\sum_m\frac{F_{0m}}{\Omega_{m0}^2-\omega^2}, \quad (16)$$

which results from applying the Kramers-Heisenberg dispersion formula (at $q=0$) in the representation of the exact eigenstates of the crystal, whose transition energies and oscillator strengths are denoted by $\Omega_{m0}$ and $F_{0m}$, respectively. Here $P$ denotes the Cauchy principal value and $\omega_p^2$ is an effective plasma frequency. Now in Eq. (5) from which (13) is obtained, we have assumed that $\alpha(\omega)$ is real, which is correct at low frequencies. However, the polarizability exhibits resonances which correspond to the atomic transitions between the ground state and the various excited states when $\alpha(\omega)$ is chosen to be the free-atom polarizability, for example. Near such resonances, $\alpha(\omega)$ becomes complex through the appearance of infinitesimal imaginary parts $\pm is$ in the energy denominators. This feature arises as a result of switching on the external field adiabatically from the infinite past to a time $t$, by means of the usual exponential factor $e^{st}$. The complex dielectric constant of the crystal is then obtained by inserting this expression of

$\alpha(\omega)$ in Eq. (13), so that after reduction the resonance denominators in $\alpha(\omega)$ are replaced by resonance denominators in $\epsilon(\omega)$ itself, with infinitesimal imaginary parts of the form $isg(\omega)$. (An example which can be easily worked out in detail is the case of harmonic oscillators.) By going then to the limit $s\to 0$, one is led to an expression of $\text{Re}\epsilon(\omega)$ of the form (16), where principal parts are now taken at the resonance energies of the crystal.[28] In practice, of course, the same result is obtained by adding a principal-part symbol in front of the fraction in Eq. (13) and using for $\alpha(\omega)$ the low-frequency expression. The imaginary part of $\epsilon(\omega)$ can be found in a similar way but it is usually more expedient to obtain it from the Kramers-Kronig formula

$$\text{Im}\epsilon(\omega)=-\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega'[\text{Re}\epsilon(\omega')-1]P\left(\frac{1}{\omega-\omega'}\right). \quad (17)$$

Since the present theory does not take into account any damping effects (such as radiation damping or other decay processes like exciton-phonon interaction, etc.), the exciton energies are real and will thus be given by Eqs. (14) and (15), where $\epsilon(\omega)$ is replaced by $\text{Re}\epsilon(\omega)$.

In order to carry further our analysis of the electronic excitations in molecular crystals, we need a detailed expression of the polarizability $\alpha(\omega)$, which we shall now examine. As discussed in the Introduction, the model for the crystal is that of an array of nonoverlapping atoms. The interaction between the atoms is approximated by the instantaneous dipole-dipole interaction, which is the lowest-order term in the multipole expansion of the true Coulomb interaction. The Hamiltonian is then

$$H=\sum_\lambda H_{0\lambda}+\tfrac{1}{2}\sum_{\lambda\neq\mu}\mathbf{p}_\lambda\cdot\mathbf{T}_{\lambda\mu}\cdot\mathbf{p}_\mu, \quad (18)$$

where $H_{0\lambda}$ is the Hamiltonian of an individual atom and

$$\mathbf{p}_\lambda=-|e|\sum_{i=1}^{n}(\mathbf{r}_{i\lambda}-\mathbf{R}_\lambda) \quad (19)$$

is the dipole moment operator of the $n$-electron atom $\lambda$. Since we are interested in the electronic excitations of the crystal, we may disregard the phonons, because their energies are much lower, and assume that the nuclei are held fixed at the lattice sites.

In I we have presented a detailed analysis of the dielectric response of this system in a uniform external field $\mathbf{E}=\tfrac{1}{2}(\mathbf{E}_0e^{i\omega t}+\text{c.c.})$ of frequency $\omega$. The corresponding interaction term in the Hamiltonian is $-\sum_\lambda\mathbf{p}_\lambda\cdot\mathbf{E}$. The classical Lorentz field effect was diagonalized exactly in a first step. This enabled us to study, in a second step, the effect of the quantum fluctuations of the induced dipole moments, as discussed in the Introduc-

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[26] If more accurate results were needed at finite small $q$ values, one could include the effect of the $q$ dependence of $\varepsilon(\mathbf{q},\omega)$ by taking advantage of the numerical results for the eigenvalues and eigenvectors of $\mathbf{T}(q)$ which have been recently determined in another context: J. Heinrichs and A. Lucas, Bull. Soc. Belge Phys. 4, 55 (1964); A. Lucas, Physica 35, 353 (1967).

[27] The considered excitations are also called "polarization waves," which refers to their connection with a nonvanishing electric polarization in the crystal. In the crossover region of the excitons and virtual photons in the $(\omega,q)$ plane, one refers to the normal modes of the coupled system as "polaritons" (see Refs. 5 and 23).

[28] It would be incorrect, of course, to take the limit $s\to 0$ in $\alpha(\omega)$ itself and then substitute the result in Eq. (13). This is because the induced polarization is sensitive to the resonances in the crystal and not to those in the isolated atoms, which are in a sense irrelevant.

tion. The details are given in I and it is shown that the net effect of the dipole fluctuations is to replace the polarizability $\alpha_{0,\lambda}(\omega)$ of an isolated atom $\lambda$ by an effective polarizability

$$\alpha_\lambda(\omega)=\alpha_{0,\lambda}(\omega)+\Delta\alpha_\lambda(\omega),\qquad(20)$$

where $\Delta\alpha_\lambda(\omega)$ represents the correction due to the fluctuations. The expression of $\Delta\alpha_\lambda(\omega)$ has been derived in I in the general case of a real spectrum of excited states for the individual atoms. However, this expression appears to be too complicated to handle in detailed applications. Therefore, we shall attempt to simplify it here by using a much simpler model for the individual atoms. This model seems to describe adequately the essential features of the fluctuation effect for the rare gases (as well as for the electronically similar alkali-halide ions), and the indications are that it leads to quantitatively correct results.

As explained in the Introduction, we shall use a two-state model, assuming that the atoms can be treated effectively as systems having only one excited state. However, we shall see that this model must be somewhat amended in order to obtain a consistent treatment. For definiteness and in view of an application to the rare gases, we consider the important case where the first excited state of an atom $\lambda$ is a triply degenerate $P$ state denoted by $|1_i,\lambda\rangle$ $(i=x, y, z)$, while the ground state is an $S$ state $|0,\lambda\rangle$. We relegate, however, to the Appendix the details of the reduction of the general expression for $\Delta\alpha_\lambda(\omega)$ in this approximation, mainly because this is a technical and somewhat involved question, as a result of the complexity of the starting expression of I. Before discussing the final result some further remarks are in order.

In addition to assuming that the ground-state distribution of an individual atom is spherically symmetric, so that

$$\langle 0,\lambda|\,p_{i\lambda}{}^2|0,\lambda\rangle=\tfrac{1}{3}\langle 0,\lambda|\,p_\lambda{}^2|0,\lambda\rangle,\qquad(21)$$

we also assume that

$$\langle 0,\lambda|\,p_{i\lambda}\mathbf{p}_\lambda|0,\lambda\rangle=\langle 0,\lambda|\,p_{i\lambda}{}^2|0,\lambda\rangle\cdot\mathbf{e}_i\qquad(22)$$

as well as

$$\langle 1_i,\lambda|\,\mathbf{p}_\lambda|1_j,\lambda\rangle=0.\qquad(23)$$

Here the components of the dipole moment operator are labeled with an index $i$, and $\mathbf{e}_i$ is a unit vector in the $i$ direction. Equation (22) follows from the fact that the polarizability tensor reduces to a scalar for spherically symmetric atoms. Equation (23) is just a special case of an assumption which has been used throughout in I, namely, that the dipole moment operator is diagonal with respect to any subset of degenerate excited states. Its justification, in the case of many-electron atoms, relies on Laporte's rule according to which dipole transitions in an atom take place only between states of different parity.[29] Now, with these assumptions the

general expression of $\Delta\alpha_\lambda(\omega)$ reduces in the two-state approximation to an expression involving two kinds of ground-state expectation values: $\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle$ and $\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle=\tfrac{1}{3}\langle 0,\lambda|\,p_\lambda{}^4|0,\lambda\rangle$. The $z$ component and the magnitude of $\mathbf{p}_\lambda$ in this expression originate, respectively, from the external field term and from the dipole-dipole term in the Hamiltonian. It is important to recognize that while $\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle$ is uniquely expressed in terms of the transition matrix element $\langle 0,\lambda|\,p_{z\lambda}|1_z,\lambda\rangle$ by $\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle=|\langle 0,\lambda|\,p_{z\lambda}|1_z,\lambda\rangle|^2$, a similar reduction of $\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle$ in the two-state model is not feasible. In fact, such a reduction would not be unique, since by using (21)–(23) one could generate two different approximate values, $(\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle)^2$ or $3(\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle)^2$, for $\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle$ by considering the two different possibilities for inserting the completeness relation. This reflects the importance of the higher excited states in the value of $\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle$ and compels us, for consistency, to leave this expectation value in its present form. We then conclude that our model is in reality intermediate between a strict two-state model and a model describing the actual spectrum, since $\Delta\alpha_\lambda(\omega)$ includes terms depending on $\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle$, whose value cannot be approximated by using a two-state model. We introduce the parameter

$$\nu_\lambda=\langle 0,\lambda|\,p_{z\lambda}{}^2 p_\lambda{}^2|0,\lambda\rangle/(\langle 0,\lambda|\,p_{z\lambda}{}^2|0,\lambda\rangle)^2,\qquad(24)$$

whose direct determination will be discussed later. The appearance of the parameter $\nu_\lambda$, through which enters the effect of higher excited states, shows that the general expression for $\Delta\alpha_\lambda(\omega)$ is not completely defined in the limit of a two-state model. This is not surprising since, in evaluating it explicitly for the case of linear harmonic oscillators (for which it must vanish), one finds that not only the first two but rather the first three states contribute effectively to the final result. The dependence of $\Delta\alpha_\lambda(\omega)$ on this parameter was already noted in earlier theories of the dipole fluctuation effect,[30,31] whose validity has, however, been questioned.[12]

The expression of $\Delta\alpha(\omega)$ is obtained by applying (A5) to the case which we are considering, namely, that of a monatomic crystal. It is convenient to express the result in terms of the refractivity (1) and to introduce the quantity

$$\beta=\Delta E_0{}^{(0)}/\omega_{10},\qquad(25)$$

where $\Delta E_0{}^{(0)}$ is defined as minus the van der Waals pair interaction energy per particle. In the case of a cubic monatomic crystal, $\Delta E_0{}^{(0)}$ reduces to

$$\Delta E_0{}^{(0)}=\frac{1}{2}\frac{(\langle 0|\,p_z{}^2|0\rangle)^2}{2\omega_{10}}\,\mathrm{Tr}\sum_{\mu\,(\mu\neq\lambda)}\mathbf{T}_{\lambda\mu}{}^2,\qquad(26)$$

so that

$$\beta\sim z^2/48,$$

where the last line follows from (1), (A1), and (A3).

[29] G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944).

[30] L. Jansen and P. Mazur, Physica **21**, 1933 (1955).
[31] R. Yaris and B. Kirtman, J. Chem. Phys. **37**, 1775 (1962).

Using the new variable $t=\omega^2/\omega_{10}^2$, we obtain, finally, at off-resonance frequencies,

$$\Delta\alpha(\omega)$$
$$=-\alpha_0(0)\frac{2\beta}{3}\frac{(7-2\nu)t^2-(35-2\nu)t+4(16-3\nu)}{(1-t)^2(4-t)}, \quad (27)$$

where we have dropped the now unnecessary indices referring to atomic species. In the present notation, Eq. (A4) becomes

$$\alpha_0(\omega)=\alpha_0(0)/(1-t). \quad (28)$$

Substituting these expressions in (13) and using (28), we obtain for $\mathrm{Re}\epsilon(\omega)$

$$\mathrm{Re}\epsilon(\omega)=1+zP$$
$$\times\frac{(1-t)(4-t)-\tfrac{2}{3}\beta(at^2-bt+c)}{(1-t)(4-t)(1-\tfrac{1}{3}z-t)+(2/9)z\beta(at^2-bt+c)}, \quad (29)$$

where
$$a=7-2\nu, \quad b=35-2\nu, \quad c=4(16-3\nu). \quad (30)$$

In the next section we proceed with the study of the collective exciton modes, given by (14), (15), and (29).

### III. LONG-WAVELENGTH EXCITON MODES

We consider first the nonretarded or electrostatic case[9,24] in which the energies of the transverse modes are determined by the singularities of $\mathrm{Re}\epsilon(\omega)$, i.e., by the roots of the denominator in (29). To obtain these roots, it is sufficient to use an iteration procedure. Indeed, since (27) describes the fluctuation effect to $O(\beta)$ only [or equivalent to $O(R^{-6})$ or $O(z^2)$], it enables us to determine the exciton modes correctly only to this order. Our iteration procedure is then as follows. We factorize the third-degree polynomial in the denominator of the right-hand side of (29) in terms of its roots $t'$, $t''$, and $t'''$. To determine these roots iteratively, write

$$t'=t_0'+t_1'+\cdots, \quad t''=t_0''+t_1''+\cdots,$$
and
$$t'''=t_0'''+t_1'''+\cdots,$$

the zero-order values being $t_0'=1-\tfrac{1}{3}z$, $t_0''=4$, and $t_0'''=1$, and expand the polynomial in its factorized form to linear order in $\beta$. Comparison of terms with the same power of $t$ in this latter polynomial and in the denominator of (29) yields a system of three linear inhomogeneous equations which determine $t_1'$, $t_1''$, and $t_1'''$. A similar procedure is also used to find the roots of the numerator.

With this straightforward calculation, (29) is reduced to the form

$$\mathrm{Re}\epsilon(\omega)=1-z(1-\tfrac{2}{3}a\beta)P\frac{t-\tau'}{(t-t')(t-t'')}, \quad (31)$$

where

$$t'=\frac{\omega_t'^2}{\omega_{10}^2}=1-\tfrac{1}{3}z+\frac{2}{3(9+z)}$$
$$\times[3(a-b+c)-(2a-b)z+\tfrac{1}{3}az^2]\beta, \quad (32a)$$

$$t''=\frac{\omega_t''^2}{\omega_{10}^2}=4+\frac{2z}{9(9+z)}(16a-4b+c)\beta, \quad (32b)$$

$$\tau'=4+(2/9)(16a-4b+c)\beta. \quad (33)$$

The longitudinal modes are given by the solutions of $\mathrm{Re}\epsilon(\omega)=0$, and one finds without difficulty, to first order in $\beta$,

$$\frac{\omega_l'^2}{\omega_{10}^2}=1+\tfrac{2}{3}z+\frac{2}{3(3-\tfrac{2}{3}z)(9+z)}[9(a-b+c)$$
$$+(13a-7b+c)z+\tfrac{2}{3}(8a-b)z^2+(4/9)az^3]\beta, \quad (34a)$$

$$\frac{\omega_l''^2}{\omega_{10}^2}=4-\frac{4z}{27}(16a-4b+c)\frac{9+z^2}{(3-\tfrac{2}{3}z)(9+z)}\beta. \quad (34b)$$

We may rewrite (31) in a form similar to (16). Leaving out terms of $O(\beta^2)$, we obtain

$$\mathrm{Re}\epsilon(\omega)=1+z\left(1-\frac{7-2\nu}{72}z^2\right)$$
$$\times\omega_{10}^2P\left(\frac{f_t'}{\omega_t'^2-\omega^2}+\frac{f_t''}{\omega_t''^2-\omega^2}\right), \quad (35)$$

where

$$f_t''=\tfrac{9}{2}(\nu-1)z^2/(z+9)^2, \quad f_t'=1-f_t'' \quad (36)$$

are the oscillator strengths which correspond to the excitons of energy $\hbar\omega_t'$ and $\hbar\omega_t''$ and which satisfy the usual $f$ sum rule. The prefactor in (35) is interpreted as a renormalization of the plasma frequency, which is present in the general formula (16). We also determine $\mathrm{Im}\epsilon(\omega)$ by substituting (36) in (17) and by employing the integral identity

$$P\int_{-\infty}^{\infty}\frac{d\omega}{(\omega-\omega_1)(\omega-\omega_2)}=\pi^2\delta(\omega_1-\omega_2). \quad (37)$$

The result is

$$\mathrm{Im}\epsilon(\omega)=-\tfrac{1}{2}\pi z\left(1-\frac{7-2\nu}{72}z^2\right)\omega_{10}^2$$
$$\times\{(f_t'/\omega_t')[\delta(\omega-\omega_t')-\delta(\omega+\omega_t')]$$
$$+(f_t''/\omega_t'')[\delta(\omega-\omega_t'')-\delta(\omega+\omega_t'')]\}. \quad (38)$$

We also note that an alternative form of (35) is

$$\mathrm{Re}\epsilon(\omega)=P\frac{(\omega^2-\omega_l'^2)(\omega^2-\omega_l''^2)}{(\omega^2-\omega_t'^2)(\omega^2-\omega_t''^2)}. \quad (39)$$

By inserting (30) and the definitions (25) and (26) into Eqs. (32) and (34), we obtain the following final results for the exciton energies ($\hbar = 1$):

$$\omega_t'^2 = \omega_{10}^2\left((1-\tfrac{1}{3}z) + \frac{z^2}{72(9+z)}\right.$$

$$\left.\times[36(3-\nu) + (21+2\nu)z + (7-2\nu)\tfrac{1}{3}z^2]\right), \quad (40a)$$

$$\omega_t''^2 = 4\omega_{10}^2\left(1 - (\nu-1)\frac{z^3}{24(9+z)}\right), \quad (40b)$$

$$\omega_l'^2 = \omega_{10}^2\left((1+\tfrac{2}{3}z) + \frac{z^2}{24(9-2z)(9+z)}\right.$$

$$\times[108(3-\nu) - 6(15+4\nu)z + (14/3)(3-2\nu)z^2$$

$$\left.+ (4/9)(7-2\nu)z^3]\right), \quad (41a)$$

$$\omega_l''^2 = 4\omega_{10}^2\left(1 + \tfrac{1}{12}(\nu-1)z^3\frac{9+z^2}{(9-2z)(9+z)}\right). \quad (41b)$$

The terms of $O(z)$ in Eqs. (40a) and (41a) are proportional to the Lorentz local fields which are associated with transverse and longitudinal excitations, respectively (in a Drude model, they correspond to the contributions of these fields to the restoring force), while their difference $z$ corresponds to the depolarizing field, which exists for a longitudinal excitation but not for a transverse one. The remaining terms in these equations are the corrections due to the quantum dipole fluctuations. Since the latter effect has been treated only to $O(\beta)$ or, equivalently, $O(z^2)$, it is apparent, strictly speaking, that the correction in Eqs. (40) and (41), as well as Eq. (36), are correct only to $O(z^2)$. The higher-order terms which are present in these formulas arise from a mixing between the quantum and classical terms. However, we find it preferable to present the equations in the above more general form, because they describe exactly the lowest-order result of a perturbation expansion in terms of the quantum effects alone.

The present theory thus gives rise to the usual single- or one-exciton modes, whose energies are renormalized by the fluctuation effect. In addition, however, one obtains double cooperative excitons which involve the simultaneous excitation of two neighboring atoms, and whose energies are therefore of the order of $2\omega_{10}$. The double-excitation phenomenon predicted by the present theory arises as a natural consequence of the dipolar fluctuations.

The origin of the finite oscillator strength for double-exciton transitions in our discussion may be made somewhat more explicitly. The sum $M_t''$ of the squares of the transition matrix elements corresponding to the various possible double excitations, according to (35)

and (36), is proportional to

$$M_t'' \propto (\nu-1)z^3,$$

which becomes, after rewriting it in the original form of a contribution from interactions between pairs of separate atoms and using (24),

$$M_t'' \propto [\langle 0,\lambda | p_{z\lambda}^2 p_\lambda^2 | 0,\lambda\rangle$$

$$- (\langle 0,\lambda | p_{z\lambda}^2 | 0,\lambda\rangle)^2]\langle 0,\mu | p_{z\mu}^2 | 0,\mu\rangle$$

$$+\text{sym. term } \lambda \leftrightarrow \mu$$

$$= \sum_{i \neq 0, j \neq 0} |\langle 0,\lambda | p_{z\lambda}\mathbf{p}_\lambda | i,\lambda\rangle|^2 |\langle 0,\mu | \mathbf{p}_\mu | j,\mu\rangle|^2$$

$$+\text{sym. term } \lambda \leftrightarrow \mu.$$

As mentioned previously, the $z$ component of the dipole moment operator which appears in $\langle 0,\lambda | p_{z\lambda}^2 p_\lambda^2 | 0,\lambda\rangle$ arises from the coupling of the atoms to the external field, which causes the optical transitions, while all other operators in the above expression originate from the dipole-dipole coupling between the atoms. It is seen that an individual term in the above sum describes a combined process in which successively one of the atoms of the pair is excited to some intermediate state by absorption of a single photon and then both atoms are further excited to a doubly excited final state $|i,\lambda\rangle|j,\mu\rangle$ through the dipole-dipole interaction. The symmetric process in which the dipole-dipole term acts first is of course also included in the above expression. It follows from the dipolar selection rules that only those terms where the pair of states $|i,\lambda\rangle$ and $|j,\mu\rangle$ have different orbital symmetries, can possibly contribute to $M_t''$. This general picture of the double excitation process indicates, for instance, that two identical two-level atoms cannot be simultaneously excited by one photon. However, since the present theory ceases to be valid for strictly two-level atoms, it does not describe directly this limiting situation. We note also that, since in the double-exciton states with which we are concerned the two atoms are excited to different final states, the energy of the exciton will generally be different from $2\omega_{10}$, unless all the relevant atomic excited states are confined in a narrow range of energies of width small compared to $\omega_{10}$. This has been effectively assumed in obtaining the terms proportional to $\langle 0,\lambda | p_{z\lambda}^2 p_\lambda^2 | 0,\lambda\rangle$ in $\Delta\alpha|(\omega)$, since the only feature of a two-state model which can be used for these terms is the assumption of a single excitation energy. Therefore, in the present case, the total observable oscillator strength for double-exciton transitions is represented by the sum of the contributions from the various possible double-excitation processes.

The foregoing discussion shows that the double excitations considered here are in some respects very similar to those discussed in earlier treatments.[15,17] In the next section we shall present some numerical estimates of the oscillator strength for double excitations, as well as of the corrections in the exciton energies.

We now turn to a brief discussion of the role of the electromagnetic retardation effects which we have neglected so far. We shall not be concerned, however, with the effect of retardation on the calculation of $\Delta\alpha(\omega)$ itself. Just as in the ordinary van der Waals pair energy, this effect is significant only for pairs which are separated by distances $R$ of the order of an optical wavelength. The contribution of such distant pairs in $\Delta\alpha(\omega)$ is completely negligible in normal circumstances. When retardation effects are included, the transverse optical modes are given by the solutions of (15) rather than by the poles of $\mathrm{Re}\epsilon(\omega)$ as in the electrostatic case. In the absence of the (anharmonic) fluctuation effect, i.e., for a Drude-type model, the results are well known and correspond to the so-called "polaritons," which have been studied extensively both in the context of excitons[5] and in that of lattice vibrations.[24] Again, we require the solution of (15) only to first order in the parameter $\beta$ occuring in (31)–(33). We use an iteration procedure which is quite similar to the one described above. The coupling between the electromagnetic radiation and the nonretarded single and double transverse exciton modes gives rise to three new modes whose energies have the following expressions:

$$\frac{\omega_+^2}{\omega_{10}^2} = \tau_0^+ + [(h_1\tau_0^+ - k_1)\tau_0^+ + l_1]$$

$$\times \frac{\tau_0^- - 4}{(\tau_0^+ - \tau_0^-)[16 - 4(\tau_0^+ + \tau_0^-) + \tau_0^+\tau_0^-]}, \quad (42a)$$

$$\frac{\omega_-^2}{\omega_{10}^2} = \tau_0^- - [(h_1\tau_0^- - k_1)\tau_0^- + l_1]$$

$$\times \frac{\tau_0^+ - 4}{(\tau_0^+ - \tau_0^-)[16 - 4(\tau_0^+ + \tau_0^-) + \tau_0^+\tau_0^-]}, \quad (42b)$$

$$\frac{\omega'^2}{\omega_{10}^2} = 4 + [4(4h_1 - k_1) + l_1]$$

$$\times \frac{1}{16 - 4(\tau_0^+ + \tau_0^-) + \tau_0^+\tau_0^-}, \quad (43)$$

where

$$h_1 = \frac{z^2}{108(9+z)}[54(3-\nu) - 3(15-4\nu)z - (7-2\nu)z^2], \quad (44)$$

$$k_1 = \frac{z^2}{216(9+z)}\{8[54(3-\nu) - 3(6+5\nu)z - (4+\nu)z^2]$$

$$+ [108(3-\nu) + 3(33-10\nu)z + (7-2\nu)z^2]$$

$$\times (c^2q^2 \; \omega_{10}^2)\}, \quad (45)$$

$$l_1 = \frac{z^2}{54(9+z)}[108(3-\nu) + 3(24-\nu)z + (4+\nu)z^2]$$

$$\times (c^2q^2 \; \omega_{10}^2). \quad (46)$$

The frequencies $\tau_0^\pm$ are the solutions of (15) in the ab-

sence of the fluctuation effect, as given by Hopfield[5,32]:

$$\tau_0^\pm = \frac{1}{2}\left(1 + \tfrac{2}{3}z + \frac{c^2q^2}{\omega_{10}^2}\right)$$

$$\pm \frac{1}{2}\left[(1+\tfrac{2}{3}z)^2 - 2(1-\tfrac{4}{3}z)\frac{c^2q^2}{\omega_{10}^2} + \frac{c^4q^4}{\omega_{10}^2}\right]^{1/2}. \quad (47)$$

The characteristics and physical properties of these modes are well discussed elsewhere, e.g., Ref. 24. The additional retardation effects due to the presence of the dipole fluctuations turn out to be quite small, as can be seen by expanding the correction terms in (42) and (43) to $O(z^2)$. The result is

$$\omega_+^2 = \omega_{10}^2[\tau_0^+ + (3-\nu)z^2/18 + O(z^3)],$$

$$\omega_-^2 = \omega_{10}^2[\tau_0^- + O(z^3)],$$

$$\omega'^2 = 4\omega_{10}^2[1 + O(z^3)],$$

which shows that to this order the additional retardation effect vanishes altogether. Thus the double-exciton mode itself is completely unaffected by retardation to $O(z^2)$. In the case of the transverse single exciton, the retardation effect is quite pronounced, being essentially the same, however, as in the absence of the quantum correction term, i.e., as for the Drude model. Note that the degeneracy which occurs between the uncoupled double-exciton and photon energies at the crossing point of the dispersion equations is not removed. This is not a disturbing result in view of the fact that the double-exciton frequency does not represent a true normal mode, but corresponds only to the energy difference between two eigenstates of the Hamiltonian.

TABLE I. Comparison between theoretical and experimental values for the change in polarizability of the rare gases due to dipolar fluctuations. The theoretical values are based on Eq. (50) ($\nu=5$). The nearest-neighbor distances $R$ and the polarizabilities $\alpha_0(0)$ are taken from Refs. 35 and 36, respectively.

| | $R$ (Å) | $\alpha_0(0)$ (Å$^3$) | $z$ | $\Delta\alpha(0)/\alpha_0(0)$ Theory | Expt.[a] | Expt.[b] |
|---|---|---|---|---|---|---|
| Ne | 3.2 | 0.4 | 0.217 | −0.0007 | | |
| Ar | 3.83 | 1.64 | 0.52 | −0.0038 | −0.0085 | −0.0105 |
| Kr | 3.94 | 2.48 | 0.72 | −0.0072 | −0.0064 | −0.0129 |
| Xe | 4.41 | 4.04 | 0.837 | −0.0098 | −0.02 | −0.007 |

[a] Reference 37.
[b] Reference 38.

TABLE II. Results for the dipolar fluctuation effect $\Delta\alpha(\omega)/\alpha_0(\omega)$ at finite frequencies, as given by Eq. (27) ($\nu=5$, $t=\omega^2/\omega_{10}^2$).

| $t$ | Ne | Ar | Kr | Xe |
|---|---|---|---|---|
| 0 | −0.0007 | −0.0038 | −0.0072 | −0.0098 |
| 0.1 | −0.0003 | −0.0016 | −0.003 | −0.0041 |
| 0.157 | 0 | 0 | 0 | 0 |
| 0.2 | 0.0003 | 0.0014 | 0.0027 | 0.0036 |
| 0.3 | 0.001 | 0.0055 | 0.011 | 0.0142 |
| 0.4 | 0.002 | 0.0113 | 0.0217 | 0.0292 |

[32] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963).

TABLE III. Corrections in the energies of the transverse and longitudinal exciton modes and oscillator strength of the transverse double exciton ($\nu = 5$). In the results corresponding to $\omega_t'$ and $\omega_l'$ the second contribution is the Lorentz field effect and the third is the quantum correction.

|      | $\omega_t'^2/\omega_{10}^2$ | $\omega_t''^2/4\omega_{10}^2$ | $\omega_l'^2/\omega_{10}^2$ | $\omega_l''^2/4\omega_{10}^2$ | $-\frac{1}{9}z^2$ | $f_t''$ | $f_t''/f_t'$ |
|------|------|------|------|------|------|------|------|
| Ne   | $1-0.073-0.005$ | $1-0.0003$ | $1+0.146-0.007$ | $1-0.005$ | $-0.006$ | $0.01$ | $0.02$ |
| Ar   | $1-0.173-0.022$ | $1-0.003$ | $1+0.346-0.05$ | $1-0.006$ | $-0.03$ | $0.053$ | $0.055$ |
| Kr   | $1-0.24\ -0.038$ | $1-0.007$ | $1+0.48\ -0.113$ | $1-0.016$ | $-0.058$ | $0.098$ | $0.109$ |
| Xe   | $1-0.279-0.047$ | $1-0.01$ | $1+0.558-0.169$ | $1-0.027$ | $-0.078$ | $0.13$ | $0.149$ |

## IV. RESULTS AND DISCUSSION

In order to make quantitative predictions with the present theory, a simple procedure for estimating the parameter

$$\nu = \langle 0 | p_z^2 p^2 | 0 \rangle / (\langle 0 | p_z^2 | 0 \rangle)^2$$

appears to be highly desirable. For many-electron atoms, a direct determination of the numerator, based, for instance, on a Hartree-Fock approximation for the ground state, would be a very tedious task indeed. This which, when expressed in terms of the electron coordinates, involves various sums of $n$-particle terms ($n = 1$, 2, 3, 4). On the other hand, it is not clear at present whether the results of such detailed calculations could be expected to be significantly more accurate than those obtained from the much simpler procedure which we shall use below.

For hydrogen atoms, the parameter $\nu$ can be determined exactly, its value being 7.5. For He atoms, using a Slater determinant for the ground state and Slater one-electron wave functions, one finds $\nu = 6.25$.[30] The heavier rare gases are the simplest real systems to which we may attempt to apply the present theory since they seem to behave more closely as two-state systems. Another reason for studying the rare-gas crystals is that their refractivities are well known.[33] As far as the determination of $\nu$ is concerned, the heavy rare-gas atoms, which have closed electronic shells, seem to be adequately represented by the charge distribution of quantum harmonic oscillators

$$\rho(r) = |\psi_0(r)|^2 = (a\sqrt{\pi})^{-3} e^{-r^2/a^2}, \qquad (48)$$

i.e., by Gaussians. Formally, the use of this model in an approximate evaluation of the fluctuation effect is rather natural, since it is known that a zero-order approximation, which neglects this effect altogether, is precisely equivalent to the use of a Drude-Lorentz oscillator model for the atoms. If one uses (48), the result for $\nu$ is independent of $a$ and one finds[34]

$$\nu = 5. \qquad (49)$$

We shall use this value in the following estimates for

the rare gases. It is quite clear, however, that this determination of $\nu$ is not unique, since it is based on a highly simplified model. Thus a truly reliable test of its validity must still rely on comparison between theoretical and experimental results, although the accuracy of (49) is certainly much better than order-of-magnitude.

Along with the values of nearest-neighbor distances[35] and free-atom polarizabilities,[36] from which the refractivities $z$ are calculated, we present in Table I the results for the fractional change in the static polarizability obtained from (27):

$$\Delta\alpha(0)/\alpha_0(0) = -(16-3\nu)z^2/72. \qquad (50)$$

Our theoretical values are in rough agreement with recent experimental results for the variation of the Clausius-Mossotti function with density,[37,38] as determined by the difference between the values of this function in the solid and dilute gas phases. These results are shown in Table I.[39] This agreement provides a check on the validity of the Gaussian model for the determination of the parameter $\nu$ and justifies its use for making further detailed predictions concerning the excitons. Finally, we note that our expressions (27) and (50) for $\nu = 5$ differ from those of Mazo's theory,[10] which is based on an approximate Green's-function treatment of a second-quantization Hamiltonian, which is itself an approximation of (18).[40] Mazo's final result does not include any frequency dispersion effect and may be reduced to the form

$$\left(\frac{\Delta\alpha(\omega)}{\alpha_0(\omega)}\right)_M \simeq -\frac{z^2}{24}. \qquad (51)$$

We believe that our results are more accurate, since they are based on an exact treatment of the Hamiltonian (18). We note, incidentally, that (51) coincides exactly

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[33] In some respects, however, the localized tight-binding exciton model which we are considering seems to be better suited for certain organic molecular cystals (crystals of aromatic molecules) than for the rare gases. It appears indeed that charge-transfer processes (overlap effects) between neighboring atoms do play an important role in the rare-gas crystals (see Refs. 1 and 2).

[34] L. Jansen and A. D. Solem, Phys. Rev. 104, 1291 (1956).

[35] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

[36] A. Dalgarno, Advan. Phys. 11, 281 (1962).

[37] R. L. Amey and R. H. Cole, J. Chem. Phys. 40, 146 (1964).

[38] A. C. Sinnock and B. L. Smith, Phys. Letters 28A, 22 (1968).

[39] The refractivities computed with the density values corresponding to the Amey Cole measurements near the triple point differ only slightly (by 10% on the average) from those which are listed in Table I.

[40] As was noted in I, a factor 2 is missing in Mazo's final expression, so that values in Ref. 38 which are based on Mazo's theory should be multiplied by 2. In a strict two-state approximation, such as that used by Mazo, there are two possible values for $\nu$ (1 or 3), as discussed in Sec. II. For the rare gases the best choice would then correspond to $\nu = 3$. According to (50), this would lead to a correction of $-2.62\%$ for Ar, which is much larger than the correct result of Table I.

with the contribution of the first term in (A2), which represents the effect arising from the difference of the polarizabilities of the two states of the atoms.

Some typical results at finite frequencies obtained from Eq. (27) are given in Table II. These are relevant to the Lorentz-Lorenz equation for the refractive index, which is now

$$\frac{3}{4\pi}\frac{n^2-1}{n^2+2}=N\alpha_0(\omega)\left[1+\frac{\Delta\alpha(\omega)}{\alpha_0(\omega)}\right]. \qquad (52)$$

We note that (27) predicts some peculiar behavior at higher frequencies: $\Delta\alpha(\omega)$ vanishes at $t=0.157$ ($\omega=0.4\omega_{10}$) and becomes positive above this value, while being negative below it.

The most interesting results of the present study are probably those concerning the renormalization of the exciton energies, Eqs. (40) and (41) ,and the oscillator strength of the double-exciton mode, Eq. (36), as compared to that of the ordinary single exciton. Numerical results for these effects are listed in Table III. For comparison we have listed separately the numerical values of the classical and quantum contributions in the energies. To lowest order in $z$ the correction term in both (40a) and (41a) is $[(3-\nu)/18]z^2=-\frac{1}{9}z^2$, whose values are also given in Table III. The effect of the quantum fluctuations on the exciton energies appears to be quite significant. It is, in fact, of the same order of magnitude (but of opposite sign) as the effect which arises from short-range overlap forces, which has been studied recently by Doniach and Huggins,[38,41] using the shell model of Dick and Overhauser. This seems to suggest that the small observed shifts of the uv absorption frequencies in the solids from their gas values might be the result of a strong compensation between the short-range forces effect[38,41] on the one hand and the Lorentz field and dipole fluctuation effects on the other hand. However, in order to test this conjecture in detail the present theory would need to be generalized in such a way that overlap effects would be properly included.

The oscillator strength of the double exciton appears to be quite large for Ar, Kr, and Xe. The result for the ratio $f_t''/f_t'$, which ranges between 0.01 and 0.15, is somewhat larger than the value of about 0.01, which seems to be expected from the theory of Rice and co-workers,[17] as developed in their first paper.

In conclusion, the results of this paper indicate that while the effects of the quantum dipole fluctuations in the polarizability itself are small (in agreement with the experimental observations), they are much more pronounced in the properties of the tight-binding excitons. In particular, the quantum-fluctuation mechanism leads to the existence of cooperative double excitons of fairly large oscillator strength. This would then indicate that such excitations can be created fairly easily and should be observable in a variety of systems. The large

amount of theoretical evidence now available, compared to the meager experimental results, should be sufficient to stimulate some further experimental work on cooperative exciton absorption. Such work will be necessary in the future in order to prove or disprove the available theories.

## APPENDIX

Our purpose in this appendix is to discuss the detailed form of the general expression of the fluctuation effect, Eq. (3.45) of I, in the case where we restrict ourselves as far as possible to the contribution from one effective excited state $|1j,\lambda\rangle$ of thei ndividual atoms. Since the expression for $\Delta\alpha_\lambda(\omega)$ derived in I is valid for arbitrary species of atoms, it is of interest, for future reference, to carry out the present discussion with the same generality, in spite of the fact that the main body of the present work is concerned with monatomic crystals only. Indeed, in future work, we intend to generalize some of the results of this paper to crystals with two atoms per unit cell. This is a fairly important case since it includes lattice structures such as the alkali halides as well as typical molecular organic solids like anthracene and naphthalene.

On the other hand, in the static limit it has proved possible[42,43] to perform detailed calculations of $\Delta\alpha_\lambda(0)$, starting from an approximation which is less severe but easily related to the two-state approximation which we want to use here. This is the so-called Lennard-Jones-Unsöld approximation, which amounts to replacing all energy denominators in the second-order perturbation formula by a common average excitation energy. The analogous approximation in I, Eq. (3.45), is to replace all denominators involving pair excitation energies $\omega_{j,\lambda;0,\lambda}+\omega_{j,\mu;0,\mu}$ by an average value $\bar\omega_\lambda+\bar\omega_\mu$ as well as the excited-state polarizabilities $\alpha_{j,\lambda}(\omega)$ by an appropriate mean value $\bar\alpha_\lambda(\omega)$. Since in future work it might prove possible to carry out detailed studies in this "dynamic" Unsöld approximation, and also for the purpose of comparing the dynamic and static expressions (which is interesting), it is useful here to display the result in this approximation first. For the present purpose this result corresponds clearly to a first step in applying the two-state model. However, we specialize to cubic crystals and spherically symmetric atoms so that the polarizability is a scalar: $\alpha_\lambda(\omega)=[\alpha_{0,\lambda}(\omega)+\Delta\alpha_\lambda(\omega)]1$, and $\mathrm{Re}\Delta\alpha_\lambda(\omega)$ is typically given by the $zz$ component of Eq. (3.45) of I. We also have in this case

$$\sum_{\mu\,(\mu\neq\lambda)}T_{\lambda\mu}{}^2=\tfrac{1}{3}\,\mathrm{Tr}\sum_\mu T_{\lambda\mu}{}^2 1$$

$$=2\sum_\mu\frac{1}{R_{\lambda\mu}{}^6}1\simeq(4\pi N/3)^2 1. \qquad (A1)$$

Furthermore, as discussed in Sec. II, we need only the low-frequency result for $\Delta\alpha_\lambda(\omega)$ [or, more precisely, the

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value of $\Delta\alpha_\lambda(\omega)$ at off-resonance frequencies], which is readily obtained from I, Eq. (3.45), by putting the infinitesimal imaginary parts in all denominators equal to zero before taking the real part. From Eq. (3.45) of I, using Eqs. (3.15), (A2), (A3) of I and the completeness of the atomic states $|j,\lambda\rangle$, we then obtain

$$\Delta\alpha_\lambda(\omega) = -\tfrac{1}{6}\sum_{\mu(\mu\neq\lambda)} \mathrm{Tr}\mathbf{T}_{\lambda\mu}{}^2\langle 0,\mu|\,p_{z\mu}{}^2\,|0,\mu\rangle\left\{\frac{\langle 0,\lambda|\,p_\lambda{}^2\,|0,\lambda\rangle}{(\bar\omega_\lambda+\bar\omega_\mu)^2}[\alpha_{0,\lambda}(\omega)-\bar\alpha_\lambda(\omega)]\right.$$

$$+\frac{1}{\bar\omega_\lambda+\bar\omega_\mu-\omega}\sum_{k,l}\left(\frac{\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle\cdot\langle 0,\lambda|\,\mathbf{p}_\lambda\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|0,\lambda\rangle}{(\omega_{k,\lambda;0,\lambda}-\omega)(\omega_{l,\lambda;0,\lambda}-\omega)}\right.$$

$$+\frac{\langle 0,\lambda|\,\mathbf{p}_\lambda\,|k,\lambda\rangle\cdot(\langle k,\lambda|\,p_{z\lambda}\,|0,\lambda\rangle\langle 0,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle)\langle l,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle}{(\omega_{k,\lambda;0,\lambda}+\omega)(\omega_{l,\lambda;0,\lambda}+\omega)}\bigg)$$

$$+\frac{1}{\bar\omega_\lambda+\bar\omega_\mu+\omega}\sum_{k,l}\left(\frac{\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle\cdot\langle 0,\lambda|\,\mathbf{p}_\lambda\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|0,\lambda\rangle}{(\omega_{k,\lambda;0,\lambda}+\omega)(\omega_{l,\lambda;0,\lambda}+\omega)}\right.$$

$$+\frac{\langle 0,\lambda|\,\mathbf{p}_\lambda\,|k,\lambda\rangle\cdot(\langle k,\lambda|\,p_{z\lambda}\,|0,\lambda\rangle\langle 0,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle)\langle l,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle}{(\omega_{k,\lambda;0,\lambda}-\omega)(\omega_{l,\lambda;0,\lambda}-\omega)}\bigg)$$

$$+\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}\sum_{k,l}\left[\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle\cdot(\langle 0,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle)\langle l,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle\right.$$

$$\times\left(\frac{1}{(\omega_{k,\lambda;0,\lambda}+\omega)(\omega_{l,\lambda;0,\lambda}-\omega)}+\frac{1}{(\omega_{k,\lambda;0,\lambda}-\omega)(\omega_{l,\lambda;0,\lambda}+\omega)}\right)+\text{c.c.}\right]-\sum_{k,l}\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,p_\lambda{}^2\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|0,\lambda\rangle$$

$$\times\left(\frac{1}{(\omega_{k,\lambda;0,\lambda}-\omega)(\omega_{l,\lambda;0,\lambda}-\omega)(\bar\omega_\lambda+\bar\omega_\mu-\omega)}+\frac{1}{(\omega_{k,\lambda;0,\lambda}+\omega)(\omega_{l,\lambda;0,\lambda}+\omega)(\bar\omega_\lambda+\bar\omega_\mu+\omega)}\right)$$

$$-\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}\sum_{k,l\,(k\neq0)}\left[\frac{\langle 0,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,p_\lambda{}^2\,|0,\lambda\rangle}{\omega_{k,\lambda;0,\lambda}}\left(\frac{1}{\omega_{l,\lambda;0,\lambda}+\omega}+\frac{1}{\omega_{l,\lambda;0,\lambda}-\omega}\right)+\text{c.c.}\right]$$

$$+\frac{\langle 0,\lambda|\,p_\lambda{}^2\,|0,\lambda\rangle}{\bar\omega_\lambda+\bar\omega_\mu}\sum_k|\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle|^2\left(\frac{1}{(\omega_{k,\lambda;0,\lambda}+\omega)^2}+\frac{1}{(\omega_{k,\lambda;0,\lambda}-\omega)^2}\right)$$

$$-\sum_{j\neq0,k}\sum_{l\neq0}\left[\left[\langle 0,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle\langle k,\lambda|\,\mathbf{p}_\lambda\,|l,\lambda\rangle\cdot(\langle l,\lambda|\,p_{z\lambda}\,|j,\lambda\rangle)\langle j,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle\right.\right.$$

$$\times\left(\left(\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}-\frac{1}{\bar\omega_\lambda+\bar\omega_\mu+\omega}\right)\frac{1}{(\omega_{0,\lambda;k,\lambda}-\omega)(\omega_{j,\lambda;l,\lambda}-\omega)}\right.$$

$$+\left(\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}-\frac{1}{\bar\omega_\lambda+\bar\omega_\mu-\omega}\right)\frac{1}{(\omega_{0,\lambda;k,\lambda}+\omega)(\omega_{j,\lambda;l,\lambda}+\omega)}\bigg)\bigg]+\text{c.c.}\bigg]$$

$$+\left(\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}-\frac{1}{\bar\omega_\lambda+\bar\omega_\mu-\omega}\right)\sum_{j\neq0,k,l}\frac{\langle 0,\lambda|\,\mathbf{p}_\lambda\,|k,\lambda\rangle\cdot(\langle k,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|j,\lambda\rangle)\langle j,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle}{(\omega_{k,\lambda;l,\lambda}+\omega)(\omega_{j,\lambda;l,\lambda}+\omega)}$$

$$+\left(\frac{1}{\bar\omega_\lambda+\bar\omega_\mu}-\frac{1}{\bar\omega_\lambda+\bar\omega_\mu+\omega}\right)\sum_{j\neq0,k,l}\frac{\langle 0,\lambda|\,\mathbf{p}_\lambda\,|j,\lambda\rangle\cdot(\langle j,\lambda|\,p_{z\lambda}\,|l,\lambda\rangle\langle l,\lambda|\,p_{z\lambda}\,|k,\lambda\rangle)\langle k,\lambda|\,\mathbf{p}_\lambda\,|0,\lambda\rangle}{(\omega_{k,\lambda;l,\lambda}-\omega)(\omega_{j,\lambda;l,\lambda}-\omega)}\bigg\}$$

$$+\text{sym. term }\lambda\leftrightarrow\mu. \qquad (A2)$$

Here the expression "sym. term $\lambda \leftrightarrow \mu$" is used to designate the term which results from the replacement of $\lambda$ by $\mu$ in the term which is written out explicitly.

For the reader who is interested in the details of how (A2) is obtained from Eq. (3.45) of I, the following hints will be helpful. After having made the Unsöld approximation in Eq. (3.45), we remove summations over excited states $|j,\nu\rangle$ using the completeness relation, wherever this is possible. Next we separate all contributions with denominators involving only energy differences between the ground state and excited states of an atom. The terms which are left over are those which have either one or two denominators with energy differences between two excited states. The terms whose two denominators involve energy differences between excited states can be reduced somewhat further by making use of the unitarity of the operators $U_\lambda(t)$ in Eq. (3.39) of I which served to introduce the Lorentz field effect. At successive orders in the local field, their perturbation expansion is of the form

$$U_\lambda(t) = U_\lambda^{0\dagger}[1 - i(U_{+\lambda}^{(1)}e^{i\omega t} + U_{-\lambda}^{(1)}e^{-i\omega t}) - (U_{+\lambda}^{(2)}e^{2i\omega t} + U_{-\lambda}^{(2)}e^{-2i\omega t} + U_0^{(2)} + \cdots)]U_\lambda^0,$$

$$U_\lambda^0 = e^{-iH_{0\lambda}t}.$$

The condition $U_\lambda(t)U_\lambda^\dagger(t) = 1$ then leads to the relations

$$U_{+\lambda}^{(1)} = U_{-\lambda}^{(1)\dagger},$$

$$U_{+\lambda}^{(2)} + U_{-\lambda}^{(2)\dagger} = U_{-\lambda}^{(1)\dagger}U_{+\lambda}^{(1)},$$

$$U_{0\lambda}^{(2)} + U_{0\lambda}^{(2)\dagger} = U_{+\lambda}^{(1)\dagger}U_{+\lambda}^{(1)} + U_{-\lambda}^{(1)\dagger}U_{-\lambda}^{(1)}, \quad \text{etc.,}$$

and the matrix elements of $U_\lambda(t)$ are given in I. After suitable rearrangements of terms, one finally arrives at the expression (A2). It is important to note that in reducing Eq. (3.45) of I to the form (A2) no explicit use is made of the particular assumptions about the spectrum of the atoms, i.e., Eqs. (22) and (23).

It is seen that in the static limit those terms which involve energy differences between two excited states vanish identically. On the other hand, for spherically symmetric atoms the polarizability tensor has no off-diagonal elements and the static polarizability is simply

$$\alpha_{0,\nu}(0) = 2 \sum_k \frac{|\langle 0,\nu|p_{z\nu}|k,\nu\rangle|^2}{\omega_{k,\nu;0,\nu}}. \quad \text{(A3)}$$

One thus verifies immediately that in the static case (A2) reduces to Eq. (17) of Ref. 43.

Now, in applying the two-state model of Sec. II, we replace first of all $\bar{\omega}_\nu$ by $\bar{\omega}_\nu \equiv \omega_{1,\nu;0,\nu} = E_{1,\nu}^{(0)} - E_{0,\nu}^{(0)}$, the energy difference between the two states, and $\bar{\alpha}_\nu(\omega)$ by

$$\alpha_{1,\nu}(\omega) = -\alpha_{0,\nu}(\omega) = -2\frac{\langle 0,\nu|p_{z\nu}^2|0,\nu\rangle}{\omega_{1,\nu;0,\nu}^2 - \omega^2}\omega_{1,\nu;0,\nu}. \quad \text{(A4)}$$

Furthermore, using Eqs. (21)–(24) and the completeness relation (as approximated by the contribution of the first two states), we obtain after some algebra

$$\Delta\alpha_\lambda(\omega) = -\tfrac{1}{6}\operatorname{Tr}\sum_{\mu\,(\mu\neq\lambda)}T_{\lambda\mu}^2\frac{\langle 0,\mu|p_{z\mu}^2|0,\mu\rangle(\langle 0,\lambda|p_{z\lambda}^2|0,\lambda\rangle)^2}{(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2[(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2-\omega^2](\omega_{1,\lambda;0,\lambda}^2-\omega^2)^2}$$

$$\times\{4[3\omega_{1,\lambda;0,\lambda}+(4-\nu_\lambda)(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})][(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2-\omega^2](\omega_{1,\lambda;0,\lambda}^2-\omega^2)$$

$$+4(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})[3(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2-2\omega^2](\omega_{1,\lambda;0,\lambda}^2+\omega^2)-[(\nu_\lambda(\omega_{1,\lambda;0,\lambda}+\omega)^2+(\omega_{1,\lambda;0,\lambda}-\omega)^2)$$

$$\times(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu}+\omega)(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2+\text{sym. term } \omega \leftrightarrow -\omega]\}+\text{sym. term } \lambda \leftrightarrow \mu. \quad \text{(A5)}$$

This is the final result for $\Delta\alpha_\lambda(\omega)$ in the case of arbitrary species of atoms.

As discussed in Sec. II, the parameter $\nu_\lambda$ is not defined in a two-state model. This corresponds to the fact that the general expression (3.45) in I is itself partly undefined within this model and depends, in fact, rather crucially on the higher excited states. Therefore, in reducing (A2) one has to be careful not to eliminate any of the inherent indeterminacies associated with $\nu_\lambda$, which could happen as a result of choosing arbitrarily one of the possible two-state values. An exception must be made, however, for those terms in (A2) involving one or two denominators with energy differences between two excited states. They appear in the last three terms in (A2), and by applying the two-state-like model in the same way as above, their sum is reduced to

$$-\tfrac{1}{3}\sum_{\mu\,(\mu\neq\lambda)}\operatorname{Tr}T_{\lambda\mu}^2\frac{\langle 0,\mu|p_{\lambda\mu}^2|0,\mu\rangle(\langle 0,\lambda|p_{z\lambda}^2|0,\lambda\rangle)^2(1-\nu_\lambda)}{(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})\omega}$$

$$\times\frac{(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})(\omega^2-\omega_{1,\lambda;0,\lambda}^2+2\omega_{1,\lambda;0,\lambda}\omega)+2\omega^3}{[(\omega_{1,\lambda;0,\lambda}+\omega_{1,\mu;0,\mu})^2-\omega^2](\omega_{1,\lambda;0,\lambda}^2-\omega^2)}+\text{sym. term } \lambda \leftrightarrow \mu.$$

This contribution must vanish in order for our procedure to be consistent with the general theory, and in particular with Eq. (A2), in which all excited-state degeneracies at $\omega = 0$ are assumed to be properly treated.[12] Thus in these terms, but only in these, we must use the particular two-state value $\nu_\lambda = 1$.