# Diagram method of calculating the polarizabilities of interacting atoms and molecules

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Diagram rules for the calculation of diagonal and off-diagonal elements of arbitrary operators with nondegenerate spectra are constructed on the basis of a modification of the diagram technique for the ground-state energy of the interacting system. A method for partially summing the diagrams for the susceptibility of the system on going to the polarizabilities of individual particles is indicated. The hyperpolarizabilities of isolated atoms of inert gases and of atoms interacting via dispersion forces are calculated. It is shown that an integral relation sets in between the molecule polarizabilities of different orders (with respect to the external field) when the interaction between the particles is turned on.

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## 1. INTRODUCTION

The calculation of the dielectric constant $\epsilon(\mathbf{k}, \omega)$ of a medium by the polarization-operator method, carried out by Dzyaloshinskiĭ and Pitaevskiĭ,[1] does not call for introducing the polarizabilities of the individual molecules into the theory. In various problems of the physics of the condensed state, however, knowledge of the polarizabilities of the particles, and also of the connection between the microscopic and macroscopic characteristic of the medium is necessary in principle. It is therefore of interest to use quantum field theoretical methods of statistical physics[2] to calculate the linear and nonlinear polarizabilities of interacting atoms and molecules, since the difficulties of the analytic approach increase rapidly with increasing order of the linearity in terms of the external field and with increasing complexity of the intermolecular interaction.

It will be shown in this paper that by generalizing the known[3] diagram technique for the ground-state energy of an interacting system it is possible to develop a technique for calculating the diagonal and off-diagonal matrix elements of arbitrary operators for an arbitrary character of the interaction in the system. With the aid of the corresponding diagrams for the dipole-moment operator $\hat{p}$ it is possible, in principle, to calculate the polarizability of any order with respect to the field of the interacting molecules, if the single-particle matrix elements of the operator $\hat{p}$ are known. The necessary partial summation of the diagram series is realized here with the aid of a certain integral equation of the Dyson type, which is derived by the self-consistent-field method.

By way of illustration of the developed procedure we shall calculate the hyperpolarizability $\gamma_0$ (third order in the external field $E_0$) of free inert-gas atoms, and the correction $\Delta\gamma$ necessitated by the dipole-dipole (DD) interaction of the corresponding atoms in liquids. The last calculation, hitherto not reported in the literature (probably because it is unusually laborious), shows that the change in the hyperpolarizability of atoms of heavy inert gases reaches several dozen per cent on account of the dispersion forces acting in the condensed phases of the medium.

## 2. MATRIX ELEMENTS OF ARBITRARY OPERATORS

It is known[3] that the connection between the ground-state energy of a system placed in a constant field E, on the one hand, and the vacuum amplitude R(t), on the other,

$$W_0(E)-W_0(0)=i\lim_{t\to\infty(1-i\eta)}\frac{d}{dt}[\ln R(t)] \tag{1}$$

makes it possible to use the diagram series of the nonstationary theory for the calculation of the energy in the stationary Rayleigh-Schrödinger perturbation theory. Let us see how to obtain, on the basis of the diagram rules for the system energy, the rules for calculating the matrix elements of an arbitrary operator $\hat{F}$ with a nondegenerate spectrum.

Let the wave functions

$$|0\rangle=\Psi_0^{(n)} \tag{2}$$

of the ground state of the total Hamiltonian

$$\hat{H}=\hat{H}_0+\hat{V}_0 \tag{3}$$

be specified in n-th order of perturbation theory in $\hat{V}_0$. The diagonal matrix elements of the operator $\hat{F}$

$$\langle 0|\hat{F}|0\rangle=\int\Psi_0^{(n)*}\hat{F}\Psi_0^{(n)}d\tau, \tag{4}$$

calculated with the aid of the wave functions (2), will be of n-th order in $\hat{V}_0$. However, the same wave functions (2) determine the correction to the ground-state energy of the total Hamiltonian (3) in the n-th order in $\hat{V}_0$ and in first order in a certain additional interaction $\hat{V}_1$;

$$W_0^{(1)}=\langle 0|\hat{V}_1|0\rangle=\int\Psi_0^{(n)*}\hat{V}_1\Psi_0^{(n)}d\tau. \tag{5}$$

From a comparison of (4) and (5) we see that the rules for calculating the diagonal matrix element of the operator $\hat{F}$ in the n-th order in the perturbation $V_0$ should coincide with the diagram rules for the ground-state energy in the (n + 1)-st order of perturbation theory (n-th in $\hat{V}_0$ and first in $\hat{V}_1$), if we replace in the latter the operator $\hat{V}_1$ by the measured operator $\hat{F}$.

The foregoing is illustrated in Fig. 1 (where the cross represents the measured operator $\hat{F}$), to which corresponds the expression

$$(-1)^3\sum_{k\neq 0}\sum_{l\neq 0}\frac{V_{0k}F_{k0}V_{0l}V_{l0}}{(W_0-W_k)(W_0-W_l)(W_0-W_k+W_0-W_l)}, \tag{6}$$

that enters in the matrix element $\langle 0|\hat{F}|0\rangle$ and is obtained directly with the aid of the rules[3] for the energy of the ground state of the system.

To calculate the off-diagonal matrix element $\langle m|\hat{F}|n\rangle$ we can use the same diagrams, but in the numerator of the expression of the type (6) it is necessary to replace all the subscripts 0 to the left of the operator $\hat{F}$ by the subscript m, and those to the right

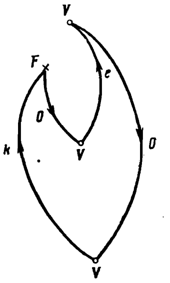

FIG. 1. Diagram that enters in the matrix element of the measured operator $\hat{F}$ in third order in the interaction $\hat{V}$.

by the subscript n. In addition, in the energy denominator of the lines located in the diagram ahead of $\hat{F}$ are replaced in accordance with the rule $W_k \rightarrow W_k + W_0 - W_m$, while the energies of the lines located past $\hat{F}$ are replaced in accord with the rule $W_l \rightarrow W_l + W_0 - W_n$. Thus, the diagram in Fig. 1 describes simultaneously the expression

$$(-1)^3 \sum_{k\neq m} \sum_{l\neq n} \frac{V_{mk} F_{kn} V_{nl} V_{ln}}{(W_m - W_k)(W_n - W_l)(W_m - W_l + W_n - W_k)}, \tag{7}$$

which enters in the matrix element $\langle m|\hat{F}|n\rangle$.

## 3. DIAGRAM RULES FOR THE SUSCEPTIBILITY OF THE SYSTEM

A perturbation-theory analytic calculation of the linear polarizability $\hat{\alpha}_2$ of atoms and molecules that interact with electric multipole forces was carried out by Jansen and Mazur[4] and by Jansen.[5] Considering for simplicity the case of DD interaction between particles, we shall use the results of the preceding section to construct a diagram technique directly for the dipole-moment operator $\hat{p}$ of the interacting particles, and the diagonal matrix elements of the operator yield expressions for the polarizabilities of all orders in the external field $E_0$. The diagram rules derived below remain valid also in the case of an arbitrary type of molecule interaction.

The total Hamiltonian of an interacting system consisting of N particles and situated in an external electric field is

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}, \tag{8}$$

where the interaction Hamiltonian consists of two parts:

$$\hat{H}_{int} = \hat{H}_{int_1} + \hat{H}_{int_2} = -\sum_{i=1}^{N} \hat{p}_\alpha^{(i)} E_{0\alpha} - \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i} \hat{p}_\alpha^{(i)} T_{\alpha\beta}^{(ij)} \hat{p}_\beta^{(j)}. \tag{9}$$

Here $T_{\alpha\beta}^{(ij)}$ is the DD-interaction tensor

$$T_{\alpha\beta}^{(ij)} = r_{ij}^{-3} (3 r_\alpha^{(ij)} r_\beta^{(ij)} - \delta_{\alpha\beta}), \tag{10}$$

$\mathbf{r}^{(ij)}$ is the radius vector joining the particle centers. The problem is to calculate the mean value $\langle \mathbf{p}^{(i)} \rangle^{(n)}$ of the operator $\hat{\mathbf{p}}^{(i)}$ over the ground state $|0\rangle = \Psi_0^{(n)}$ of the total Hamiltonian (8) in a specified order n of perturbation theory in the interaction Hamiltonian (9).

It is necessary to distinguish in what follows between the proper polarizability $\hat{\alpha}$ of the molecules and the system susceptibility $\hat{\beta}$ per molecule, i.e., the effective polarizability of the molecule. By definition, the susceptibility tensor $\hat{\beta}_s^{(i)}$ enters in the relation

$$\langle \hat{p}_\alpha^{(i)} \rangle = \sum_{s=0}^{\infty} \frac{1}{s!} \beta_{\alpha\beta_1\ldots\beta_s}^{(i)} E_{0\beta_1} \ldots E_{0\beta_s}, \tag{11}$$

being the response of the molecule directly to the external field $E_0$. The perturbation theory is constructed for this tensor.[4,5] The molecule polarizability proper can be introduced in the interacting system only as the response to a certain local self-consistent field $E_{loc}^{(i)}$ produced by the external field $E_0$ and by the fields induced by the neighboring particles. Within the framework of the DD approximation, the local field is equal to[6]

$$E_{loc\,\alpha}^{(i)} = E_{0\alpha} + \sum_{j\neq i} T_{\alpha\beta}^{(ij)} \langle \hat{p}_\beta^{(j)} \rangle. \tag{12}$$

According to the foregoing, the polarizability tensor $\hat{\alpha}_s^{(i)}$ enters in the relation

$$\langle \hat{p}_\alpha^{(i)} \rangle = \sum_{s=0}^{\infty} \frac{1}{s!} \alpha_{\alpha\beta_1\ldots\beta_s}^{(i)} E_{loc\,\beta_1}^{(i)} \ldots E_{loc\,\beta_s}^{(i)}. \tag{13}$$

The difference between the definitions (11) and (13) of the tensors $\hat{\beta}^{(i)}$ and $\hat{\alpha}^{(i)}$ plays the principal role in the calculation of the polarizability of the molecules, and will be used in the next section. Here we reformulate the rules for the ground-state energy of the system directly into rules for calculating the susceptibility of the particles in any order of nonlinearity in the external field and in the particle interaction. We shall list these rules, for the sake of simplicity, for the case of a constant external field $E_0$. The transition to the nonstationary case can be effected in accordance with the general rules.[2]

In n-th order of perturbation theory, which is composed of the orders in the external field and in the interparticle interaction, the diagonal matrix element $\langle 0|\mathbf{p}^{(i)}|0\rangle^{(n)}$ of the dipole-moment operator of the interacting particle is calculated in the following manner:

1. The ensemble of particles participating in the binary, ternary, etc. interactions is represented by a chain of loops that correspond to the individual particles. The interaction between the particles is represented by wavy lines, which are set in correspondence with the matrix elements of the corresponding interaction Hamiltonian, of the form

$$\langle \varkappa_i \varkappa_j | \hat{H}_{int_2}^{(ij)} | \lambda_i \lambda_j \rangle = -(p_\alpha^{(i)})_{\varkappa_i\lambda_i} T_{\alpha\beta}^{(ij)} (p_\beta^{(j)})_{\varkappa_j\lambda_j}, \tag{14}$$

where $\kappa_i, \ldots, \lambda_j$ are single-particle states described by the wave functions $u^{(i)}$ of the free particles, so that the single-particle matrix elements in (14) are equal to

$$(\mathbf{p}^{(i)})_{\varkappa_i\lambda_i} = \int u_\varkappa^{(i)*} \hat{\mathbf{p}}^{(i)} u_\lambda^{(i)} d\tau^{(i)}. \tag{15}$$

2. The interaction of a given particle with the external field $E_0$ is represented by a point on the loop of the particle. This point is set in correspondence with the matrix element of the operator $\hat{H}_{int_1}^{(i)}$ in (9), taken between the corresponding single-particle states. The operator $\hat{p}^{(i)}$ whose mean value is calculated is represented by a cross on the loop of the given particle.

3. The product of the matrix elements of all the operators (including the ends of the interparticle-interaction lines), which are represented on the particle loops, is written out in the numerator of the analytic expression for the given diagram. The denominator of the expression is the product of the algebraic sums of the energies of the single particle states, with energies $-W_{\kappa_i}$ ($\kappa_i \neq 0$) assigned to the "particle" lines and ground-state energies $+W_{0_i}$ assigned to the "hole" lines. The sign of the expression is $(-1)^{k+l}$, where k is the number of loops and $l$ is the number of hole lines on the entire diagram. The obtained expression is

summed over all the intermediate indices of the "particles" and over the numbers i, j, ..., of all the loops.

4. The expression for the matrix element $\langle 0|\hat{p}^{(i)}|0\rangle^{(n)}$ is obtained by summing all the diagrams that preserve the given order of perturbation theory and obtained by all possible permutations of the operators on the particle loops.

In accord with the definition (11), the susceptibility tensor $\beta_{\alpha\beta_1\ldots\beta_s}$ is obtained from the expression for $\langle\hat{p}^{(i)}\rangle^{(n)}$ by differentiation with respect to the external field $E_0$ and by symmetrization of the obtained expression over all the uncontracted tensor indices. The use of the indicated rules makes it possible to dispense with the laborious procedure of calculating the wave functions of the interacting system and automatizes the method of calculating the molecule susceptibility in any order of nonlinearity.

## 4. DIAGRAMS FOR THE POLARIZABILITY. PARTIAL SUMMATION

Unlike the susceptibility tensor $\hat{\beta}^{(i)}$, the expression for the polarizability tensor $\hat{\alpha}^{(i)}$ cannot be obtained by simple differentiation of the matrix element $\langle\hat{p}^{(i)}\rangle$ with respect to $E_{loc}^{(i)}$, inasmuch as according to (12) the local field itself depends on $\widehat{\langle p\rangle}$. However, the self-consistency of Eqs. (12) and (13) allows us to construct another procedure for calculating $\hat{\alpha}^{(i)}$. We consider first the connection between the linear tensors $\hat{\beta}_2^{(i)}$ and $\hat{\alpha}_2^{(i)}$.

Relations (11)—(13) for classical systems allow us to derive[6] the following relations between the tensors of the linear susceptibility and the polarizability of the particles:

$$\beta_{2\alpha\beta}^{(i)}=\alpha_{2\alpha\mu}^{(i)}\Big(\delta_{\mu\beta}+\sum_{j\neq i}T_{\mu\nu}^{(ij)}\beta_{2\nu\beta}^{(j)}\Big). \qquad (16)$$

We shall show that (16) is the classical analog of Dyson's equation in quantum electrodynamics. Indeed, the diagrams discussed in the preceding section for the linear susceptibility of the molecules $\hat{\beta}_2^{(i)}$ are analogs of Feynman diagrams of linear vacuum electrodynamics. namics. The molecule loops correspond to the fermion loops of charged particles, the lines of the intermolecular-interaction $T^{(ij)}$ can be set in correspondence with the internal photon propagators $D_c$, and the lines of the stationary external field in both techniques simply coincides (they can be represented on the diagrams for the susceptibility by dashed lines).

In view of the indicated analogy between the diagram techniques, the expression for the susceptibility of the molecules $\hat{\beta}_2^{(i)}$, which generally speaking should contain the entire series in the intermolecular interaction $T^{(ij)}$ (i.e., both compact and noncompact wavy-lines diagrams), is the analog of the photon self-energy function $K^{(0,2)}$ (in the notation of Akhiezer and Berestetskiĭ[7]). Dyson's equation for this function is of the form[7]

$$K^{(0,2)}(k)=\Pi(k)\,[1-D_c(k)\Pi(k)]^{-1}, \qquad (17)$$

where $\Pi(k)$ is the polarization operator of quantum electrodynamics, i.e., the sum of all the compact photon self-energy diagrams. Rewriting (17) in the form

$$K^{(0,2)}(k)=\Pi(k)\,[1+D_c(k)K^{(0,2)}(k)] \qquad (18)$$

and comparing with (16) we conclude (with allowance for the statements made above concerning the equivalence of the corresponding elements of the two techniques) that the linear polarizability of the molecules $\hat{\alpha}_2^{(i)}$ should be represented by the sum of all the diagrams that are compact in the lines of the interparticle interaction $T^{(ij)}$ and enter in the diagram series for the susceptibility $\hat{\beta}_2^{(i)}$.

Thus, the linear polarizability of the molecules $\hat{\alpha}_2^{(i)}$ in quantum theory is the polarization operator $\hat{\Pi}(k)$, which is the direct analog of the operator $\Pi(k)$ of quantum electrodynamics. It is interesting to note that the polarization operator $\pi(k)$ of quantum statistics, introduced by Dzyaloshinskiĭ and Pitaevskiĭ[1] and describing the behavior of all of matter in an external field, is directly connected with the linear susceptibility of the particles $\hat{\beta}_2^{(i)}(k)$. The polarization operator $\pi(k)$ is by definition an irreducible self-energy part relative to the lines of the long-wave photons of the external field. This operator, however, becomes naturally reducible with respect to the lines of the "short-wave" interaction $T^{(ij)}$ if matter is considered as an aggregate of interacting molecules.

In the nonlinear case, in a nonstationary external field, the algebraic equations of the type (16) go over into integral equations obtained earlier[8] and connecting the tensors of the nonlinear polarizability $\hat{\alpha}_s^{(i)}(k_1,\ldots,k_s)$ and susceptibility $\hat{\beta}_s^{(i)}(k_1,\ldots,k_s)$ of the molecules. These integral equations (which are too cumbersome to present here) were obtained on the basis of the extraneous-current method proposed in[1] and developed in[9] for the case of arbitrary order in the external field. These nonlinear equations were solved by an iteration method[8] and a recurrence relation between the tensors $\hat{\alpha}_s$ and $\hat{\beta}_s$ of different order was obtained. From an analysis of the solution given in[8] it is seen that, just as the linear case, the separation of the molecule polarizability $\hat{\alpha}_s^{(i)}$ reduces to a product of partial summation in the diagram series for the susceptibility $\hat{\beta}_s^{(i)}$, i.e., separation from the entire series of only the diagrams that are compact with respect to the intermolecular interaction lines. The convergence of the series for the polarizability then becomes, generally speaking, better than the convergence of the series for the susceptibility.

## 5. HYPERPOLARIZABILITY OF FREE AND INTERACTING ATOMS OF INERT GASES

The diagram series for the susceptibility and polarizability of molecules in the DD interaction $\hat{H}_{int_2}$ in (9) have good convergence in the case of liquids and molecular crystals, in which the parameters of the expansion $\lambda = \alpha_0/(\bar{r})^3$ ($\alpha_0$ is the average polarizability of isolated particles and $\bar{r}$ is the average distance between the nearest neighbors) does not exceed 1/20. Such media are, in particular, liquefied inert gases. Taking the foregoing into account, we can confine ourselves in the calculation of the change of the polarizability of the particles due to dispersion forces having a DD character to compact diagrams of second order in $T^{(ij)}$.

To verify the method, we first calculate the static hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}^{(0)}$ of isolated inert-gas atoms, which is described by single-loop diagrams of third order in the interaction $\hat{H}_{int_1}$ with the external field. Recognizing that 0 → 0 dipole transitions are forbidden for nonpolar systems, we can easily obtain with the aid of the diagram rules formulated in Sec. 3 the following expression for the tensor $\hat{\gamma}^{(0)}$:

$$\gamma^{(0)}_{\alpha\beta\gamma\delta}=S(\alpha,\beta,\gamma,\delta)\Big[\sum_{\mu\neq0}\sum_{\nu\neq0}\sum_{\rho\neq0}\frac{(p_\alpha)_{0\mu}(p_\beta)_{\mu\nu}(p_\gamma)_{\nu\rho}(p_\delta)_{\rho0}}{\hbar^3\omega_{0\mu}\omega_{0\nu}\omega_{0\rho}}$$
$$-\sum_{\mu\neq0}\sum_{\nu\neq0}\frac{(p_\alpha)_{0\mu}(p_\beta)_{\mu0}(p_\gamma)_{0\nu}(p_\delta)_{\nu0}}{\hbar^3\omega_{0\mu}{}^2\omega_{0\nu}}\Big]. \qquad (19)$$

Here $S(\alpha, \beta, \gamma, \delta)$ is the operation of symmetrization over the corresponding indices, and $\hbar\omega_{0\mu} = W_0 - W_\mu$ is the difference between the energies of the ground and excited state of the atom.

Using the customarily employed[4,5] approximation of "equal energy denominators"

$$\hbar\omega_{0\mu}=\hbar\omega_{0\nu}=\hbar\omega_{0\rho}\approx U_0 \qquad (20)$$

($U_0$ is the average excitation energy of the atom, and is usually set equal to the first ionization potential) and recognizing that in the case of atoms only the following components of the tensor $\gamma^{(0)}_{\alpha\beta\gamma\delta}$ differ from zero:

$$\gamma^{(0)}_{xxxx}=\gamma^{(0)}_{yyyy}=\gamma^{(0)}_{zzzz}=3\gamma^{(0)}_{xxyy}=\ldots\equiv\gamma_0, \qquad (21)$$

we get from (19)

$$\gamma_0\approx\frac{24}{U_0{}^3}[(p_z{}^4)_{00}-2(p_z{}^2)^2_{00}]=\frac{6\alpha_0{}^2}{U_0}(\varkappa-2). \qquad (22)$$

In the considered equal-denominator approximation, the linear polarizability of the free atom is equal here, by definition, to

$$\alpha_0=2(p_z{}^2)_{00}/U_0 \qquad (23)$$

and we have introduced the notation

$$\varkappa=(p_z{}^4)_{00}/(p_z{}^2)_{00}{}^2. \qquad (24)$$

The parameter $\kappa$ in (24) was calculated with the aid of the wave functions of the ground state of the atoms, taken by the Hartree method in the form of products (without antisymmetrization) of single-electron wave functions:

$$\psi_0(r_1,\ldots,r_Z)=\varphi_1(r_1)\ldots\varphi_Z(r_Z), \qquad (25)$$

where Z is the number of electrons in the atom. As the single-electron functions we chose the Slater orbitals[10]

$$\varphi_{n^*,l,m}(r,\theta,\varphi)=r^{n^*-1}\exp\left(\frac{-Z^*r}{n^*}\right)Y_{l,m}(\theta,\varphi), \qquad (26)$$

where r is specified in atomic units, $n^*$ and $Z^*e$ are the effective values of the principal quantum number for the given orbital and of the charge of the atomic nucleus. These latter quantities were calculated by Slater's empirical rules[10] (see also[11]). We recall that the operator $\hat{p}_z$ is the dipole-moment operator of the entire atom, so that it is equal to the sum of the single-electron dipole-moment operators $\hat{p}^{(i)}_s$ (i = 1, ..., Z).

The results of the calculation of the parameter $\kappa$ and of the theoretical values of the hyperpolarizabilities $\gamma_0^{\text{theor}}$ of the free atoms are listed in the table. The experimental values $\gamma_0^{\text{exp}}$ were measured by Buckingham and Dunmur[13] at an incident-light wavelength 6328 Å and by Langhoff and co-workers[14] in a static electric field. As noted in[13] the variance of $\gamma_0$ cannot be large in the case of inert-gas atoms if the frequency of the incident light is much less than the frequencies of the electronic absorption of the atoms, which are in the ultraviolet. Therefore a comparison of the static value of $\gamma_0$ with measurements at optical frequencies in[13] is fully justified. As seen from the table, in spite of all the approximations made, the simple theoretical formula (22) describes well the experimental data for argon, krypton, and xenon. With respect to helium it must be noted that the value $\gamma_0^{\text{exp}}$ given in[14] seems more realistic than the value given in[13], since a rather accurate calculation of $\gamma_0$ for He, made by Buckingham and co-workers themselves[15] by a variational method, yields a value $\gamma_0 = 0.0157 \times 10^{-36}$ cgs esu, which agrees with the experiment in[14] and is close to the approximate value $0.0123 \times 10^{-36}$ obtained by us. In addition, as seen from (22), $\gamma_0 \sim \alpha_0^2$, as confirmed by relative measurements of $\gamma_0$ for He and Ne in[14] but not confirmed by the measurements of[13].

Hyperpolarizability of free and interacting atoms of inert gases

| Atom | $\alpha_0$, Å$^3$ [12] | $U_0\cdot10^{12}$, erg [12] | $\varkappa$ (24) | $\gamma_0^{\text{theor}}\cdot10^{36}$, cgs esu (22) | $\gamma_0^{\text{exp}}\cdot10^{36}$, cgs esu [13] | $\sum_{j\neq i}\langle r_{ij}^{-6}\rangle10^{-45}$, cm$^{-6}$ [17] | $\Delta\bar{\gamma}/\gamma_0$, % theory |
|---|---|---|---|---|---|---|---|
| He | 0.214 | 39.2 | 3.750 | 0.0123 | 0.0270±0.002 [13]<br>0.0157 [14] | 5.897 | 0.03 |
| Ne | 0.3966 | 34.4 | 2.956 | 0.0262 | 0.051±0.004 | 11.87 | 3 |
| Ar | 1.641 | 25.2 | 2.908 | 0.583 | 0.59±0.04 | 3.905 | 36 |
| Kr | 2.4825 | 22.4 | 2.889 | 1.467 | 1.4±0.1 | 2.43 | 59 |
| Xe | 4.0 | 19.44 | 2.878 | 4.336 | 3.9±0.3 | 1.27 | 87 |

The correction $\Delta\gamma_{\alpha\beta\gamma\delta}$ to the tensor $\gamma^{(0)}_{\alpha\beta\gamma\delta}$ of the hyperpolarizability of isolated atoms, necessitated by the dispersion forces in condensed phases of matter, is described by compact two-loop diagrams of second order, which are of third order in the interaction $\hat{H}_{\text{int}_1}$ with the external field $E_0$ and of second order in the interatomic interaction $\hat{H}_{\text{int}_2}$ in (9). The number of similar diagrams of fifth order turns out to be several hundred. It is clear that the use of a purely analytic method in which it is necessary to calculate before hand the wave functions $\Psi_0^{(5)}$ of fifth order in perturbation theory with an interaction Hamiltonian consisting of two parts would be practically impossible. On the other hand, the graphic method makes it possible to write down immediately, on the basis of the diagram rules formulated above, expressions for the diagonal matrix elements of the dipole moment, which describe each given diagram.

Summing all the diagrams described above, and carrying out in the obtained expression the previously described[16] statistical averaging of the interatomic interaction factors that are quadratic in $T^{(ij)}$, we obtain ultimately the following expression for the average change of the hyperpolarizability of the atoms:

$$\Delta\bar{\gamma}=\frac{6}{U_0{}^5}\sum_{j\neq i}\langle r_{ij}^{-6}\rangle[64.5(p_z{}^2)_{00}(p_x{}^2p_z{}^4)_{00}+73.35(p_x{}^2p_z{}^2)^2_{00}$$
$$+16.3(p_z{}^4)_{00}(p_x{}^2p_z{}^2)_{00}+32.25(p_z{}^2)_{00}(p_z{}^6)_{00}+32.6(p_z{}^4)^2_{00}+108.05(p_z{}^2)^4_{00} \qquad (27)$$
$$-139.75(p_z{}^2)^2_{00}(p_z{}^4)_{00}-99(p_z{}^2)^2_{00}(p_x{}^2p_z{}^2)_{00}].$$

The calculation of the matrix elements in (27) by the method given above, but under the simplifying assumption that all the atom electrons are on a single orbital with $n^* = 1$, yields

$$\Delta\bar{\gamma}=\frac{\alpha_0{}^4}{16U_0}\sum_{j\neq i}\langle r_{ij}^{-6}\rangle(3322.2-3704.85Z^{-1}-4334.94Z^{-2}). \qquad (28)$$

The values of the relative change $\Delta\bar{\gamma}/\gamma_0$ of the hyperpolarizability of inert gases on going to the liquid phase, calculated from (28), are given in the last column of the table. The factor $\sum_{j\neq i}\langle r_{ij}^{-6}\rangle$ was calculated from the data of[17] for a radial distribution function in the corresponding liquids. The calculated values of $\Delta\bar{\gamma}/\gamma_0$ tentatively describe also atomic crystals of inert gases, since the latter retain also the density and the isotropic packing of the atoms when the liquids solidify.

The change of the atom hyperpolarizability reaches several dozen percent, whereas the linear polarizability is changed in liquids by the same dispersion forces by only one or two per cent. This occurs primarily because the nonlinear effects receive contributions from hundreds of diagrams, the number of which is larger by an order of magnitude than in the linear (in the external field) case. In this connection, the relative role of the intermolecular interactions, as already noted in[16], increases in the region of the nonlinear electro-optical phenomena. Consequently, measurements of the nonlinear susceptibilities of the liquids and crystals can yield information on the nonlinear properties of the corresponding molecules only after substantial corrections for the intermolecular interactions are introduced, and this is frequently a nontrivial problem.[9,8]

We note in conclusion the following useful circumstance: the corrections to the polarizabilities of particles interacting in dense media can be expressed in terms of the polarizabilities of free particles of the same order and of higher orders in the field. This is seen when the two-loop diagrams for the change $\Delta\hat{\alpha}_2$ of the tensor of the linear polarizability of the molecules, due to the DD forces, are compared with the single-loop diagrams for the tensors $\hat{\gamma}^{(0)} \equiv \hat{\alpha}_4^{(0)}$ of the hyperpolarizability and $\hat{\alpha}_2^{(0)}$ of the linear polarizability of free molecules. It is easy to show that in a nonstationary external field there is an integral relation between the three indicated tensors:

$$\Delta\alpha_{\alpha\beta}^{(i)}(\omega) = \frac{1}{6}\int \gamma_{\alpha\beta\gamma\delta}^{(0)(i)}(-\omega, \omega, -\omega', \omega')\, T_{\gamma\mu}^{(ij)}\, T_{\delta\nu}^{(ji)}\, \alpha_{\mu\nu}^{(0)(j)}(-\omega', \omega')\, d\omega'. \tag{29}$$

Analogously, the correction $\Delta\hat{\gamma} \equiv \Delta\hat{\alpha}_4$ to the hyperpolarizability tensor is expressed in terms of the free-molecule tensors $\hat{\alpha}_2^{(0)}$, $\hat{\alpha}_4^{(0)}$, and $\hat{\alpha}_6^{(0)}$. It is interesting to note that in a system of harmonic oscillators for which all the nonlinear polarizabilities $\hat{\alpha}_4^{(0)}, \alpha_6^{(0)}, \ldots$ are equal to zero the change $\Delta\hat{\alpha}_2$ of the linear polarizability also vanishes in accord with (29), as is confirmed by direct analysis[4] of the perturbation-theory formulas for $\Delta\alpha_2$. Thus, the diagram technique developed here leads automatically to relations that connect the higher and lower correlation functions of the electron density in the interacting molecules, and the molecule polarizabilities of corresponding order are expressed in terms of these functions.

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