Atomic susceptibilities for the collision-induced polarizability and the corrections to the dispersion forces in the field of a light wave

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(Submitted 26 October 1981; resubmitted 25 December 1981)
Zh. Eksp. Teor. Fiz. **82**, 1749–1761 (June 1982)

A method of calculating the diatomic susceptibility $A_6(\omega)$ that determines the change that occurs in the polarizability of atoms as a result of their binary interactions, as well as the corrections to the van der Waals forces in an electromagnetic field, is proposed. Simple formulas are derived for approximate calculations in the resonance and nonresonance cases. Numerical values of $A_6(\omega)$ are determined for specific pairs of atoms in electrostatic and pulsed-laser fields. The general properties, the resonance characteristics, the feasibility of an experimental measurement of the diatomic susceptibilities, and the practical use of the data obtained are discussed.

PACS numbers: 33.90. + h, 34.20.Fi

§1. INTRODUCTION

The theory of the higher-order interactions of high-power light beams with individual atoms is fairly well developed at present, and is quite satisfactorily corroborated by experiments performed, as a rule, in very tenuous atomic media (see, for example, Refs. 1–3). But a collisionless atomic medium is only an approximate model for the gaseous media used in practice, and the interatomic interaction leads, generally speaking, to quantitative and qualitative discrepancies between the results of such a theory and experiment. In particular, the presence in an atomic-gas spectrum of lines with frequency equal to the sum of, or difference between, the natural frequencies of the individual atoms[4] can only explain the interaction of the atoms in the course of their collision.[5] Another experimental confirmation of the dependence of the properties of an atomic medium on the interatomic forces is the fluorescence under the action of a high-power light wave of alkali-metal vapors of sufficiently high density.[6] The presence in this radiation of a number of lines that do not occur in the spectrum of the individual atoms and the nonlinear character of the dependence of their intensities on the power of the pump field indicate that this radiation is of cooperative origin, which stems from the collisional interaction of the atoms in the course of the stimulated scattering of the light.

The enumerated phenomena are the subject of investigation of a presently well formulated field of science: the physics of radiative collisions. Definite advances have been made in the theoretical description of these processes, as in the experimental investigation of them.[3,7] But there are still a number of difficulties here, due, in particular, to the fact that there is no method for a consistent quantum-mechanical computation of the microscopic quantities that enter in the theory namely the atomic susceptibilities that determine both the diatomic-transition cross sections and the change in the interatomic interaction in the presence of an electromagnetic wave (below we shall assume that the interatomic interactions in the gas are determined by the van der Waals dispersion forces).

Besides the radiative collisions, the collision-induced effects in light-beam scattering by an atomic medium, which lead, in particular, to the depolarization and broadening of the Rayleigh scattering studied in recent years in the inert gases (see Ref. 8 and the references cited therein), as well as to cooperative nonlinear optical phenomena,[2] are of great interest. A consistent theoretical description of these processes requires the computation of the dynamic susceptibility of the diatomic system. This same quantity determines the corrections to the van der Waals forces in the field of a light wave, and, consequently, is of particular importance in connection with the determination of the effect of high-power radiation on the thermodynamic properties of an atomic gas.

It should be noted that the above-indicated effects are effects of order higher than that of, and therefore contain information about, the radiative collisions. In particular, the dispersion relation for the diataomic susceptibility has resonance poles at the locations of the diatomic lines emitted (absorbed) by the atoms in the course of their collisions. The residue at such a pole is equal to the square of the matrix element of the corresponding collision-induced radiative transition. In view of this, it is essential that we develop a consistent method of calculating the optical susceptibilities of polyatomic systems that can be used in the problem of the effect of laser radiation on the van der Waals forces, in the problem of the cooperative effects in light scattering by atomic gases, and in the theory of radiative collisions.

Of greatest practical interest for a system of two spherically symmetric atoms is the dipolar susceptibility A_6, which determines the long-range correction to the polarizability of the diatomic quasimolecule,[9] as well as the change that occurs in the van der Waals forces under the action of the external field.[10] At present, the components of this tensor have been calculated only for the case of electrostatic fields. The exact solution of the problem of the corrections to the van der Waals forces has been obtained for hydrogen[10] and an approximate computation of the quantity A_6 has

0038-5646/82/061010-07$04.00

been carried out with the use of the stochastic-dipole model for the inert gases[9] in this case. For variable fields, these data can be used only in the low-frequency limit $\omega \ll \omega_n$, where the ω_n are the natural frequencies of the atoms. Such a situation obtains for the inert gases in the optical region of electromagnetic-wave frequencies ω. But for other gaseous media, in particular for metal vapors, which are the most interesting objects of modern nonlinear spectroscopy,[3] at optical frequencies $\omega \approx \omega_n$, and the use of the static values of $A_6(\omega) = A_6(0)$ is not justified here. Therefore, a consistent quantum-mechanical computation of the susceptibilities $A_6(\omega)$ for arbitrary external-field frequencies is necessary.

In the present paper we propose a calculation method based on the application of the perturbation theory for quasienergy states[11] to a system of two interacting atoms in a monochromatic-radiation field. The general expressions determining the susceptibility $A_6(\omega)$ (§§2 and 3) are reduced to a form suitable for approximate calculations in situations that are of greatest interest from the practical standpoint (§4). The resonance characteristics of the quantities $A_6(\omega)$ are studied, and the feasibility of their experimental observation in specific situations is discussed (§5). Among these characteristics must be noted the resonances at the combination diatomic lines $\omega = \omega_{nA} + \omega_{nB}$, which do not occur in the frequency dependences of the monatomic susceptibilities. Numerical calculations are carried out for specific pairs of atoms A and B (Tables I and II). The model-potential method is used to find the numerical values of the composite matrix elements of the higher-order perturbation theory that determine $A_6(\omega)$.

§2. THE QUASIENERGY OF A DIATOMIC SYSTEM IN THE FIELD OF A LIGHT WAVE

In a sufficiently rarefied gas of density $n \ll a_0^{-3}$, where $a_0 \approx 10^{-8}$ cm is the linear dimension of the atom, the major role in the collision processes is played by the long-range forces, which make the dominant contribution to the characteristics of the processes occurring at large interatomic distances $R \gg a_0$. In this case we can retain in the multipole expansion of the A–B interaction operator $\hat{v}_{AB}$ only the dipole–dipole term determining the van der Waals interaction[12]:

$$\hat{v}_{AB} = -\frac{\sqrt{6}}{R^3}(C_2(\mathbf{n})\{\hat{\mathbf{d}}^A \otimes \hat{\mathbf{d}}^B\}_2). \tag{1}$$

Here $C_{lm}(\theta, \varphi)$ is a modified spherical function, $\mathbf{n} = \mathbf{R}/R$ is the unit vector along the line joining the atoms, and $\hat{\mathbf{d}}$ is the dipole moment operator.

The operator representing the interaction of the diatomic system AB with an electromagnetic wave of intensity

$$\vec{\mathscr{F}}(t) = F\,\mathrm{Re}\{\mathbf{e}\exp[i(kz - \omega t)]\},$$

where F is the amplitude and $\mathbf{e}$ is the unit polarization vector (the wave propagates along the z axis), has, in the dipole approximation, the form

$$\hat{v}_F = -F\,\mathrm{Re}\{(\mathbf{e}(\hat{\mathbf{d}}^A + \hat{\mathbf{d}}^B))e^{-i\omega t}\}. \tag{2}$$

Assuming that the atoms are in spherically-symmetric S states, we can represent the correction, arising from the interactions (1) and (2), to the quasienergy of the diatomic system AB up to terms of the order of F^2/R^6 (in the atomic system of units, $R \gg 1$ and $F \ll 1$) in the form[1)]

$$\Delta E_{AB} = -\frac{F^2}{4}[\alpha^A(\omega) + \alpha^B(\omega)] - \frac{C_6}{R^6} - \frac{F^2}{2R^3}\alpha^A(\omega)\alpha^B(\omega)[3|\mathbf{ne}|^2 - 1]$$
$$-\frac{F^2}{4R^6}[A_6^{\perp}(\omega) + (A_6^{\parallel}(\omega) - A_6^{\perp}(\omega))|\mathbf{ne}|^2]. \tag{3}$$

In the case of unpolarized radiation we must set here

$$|\mathbf{ne}|^2 = {}^1/_2(n_x^2 + n_y^2).$$

The first two terms in (3) are the second-order correction due to the separate interactions of the atoms A and B with the electromagnetic-wave field, and determined by the total polarizability $\alpha^A(\omega) + \alpha^B(\omega)$ of the atoms and their dispersion interaction with each other with the van der Waals constant C_6. The third term, which corresponds to the third-order correction (second in $\hat{v}_F$ and first in $\hat{v}_{AB}$), determines the interaction energy for the atomic dipoles induced by the external field. This term vanishes on being averaged over the mutual orientations of the atoms (i.e., over the directions of the vector $\mathbf{n}$), so that the third-order correction makes no contribution to the energy of the atomic medium.

In view of this, the last term in (3), which is the fourth-order (second-order in $\hat{v}_F$ and second-order in $\hat{v}_{AB}$) perturbation-theory correction in the approximation being considered by us (we neglect the corrections of order F^4 and $1/R^{12}$, which arise respectively in the fourth-order perturbation theories in terms of $\hat{v}_F$ and $\hat{v}_{AB}$) acquire especial significance. This quantity is determined by two linearly independent—the longitudinal $A_6^{\parallel}(\omega)$ and transverse $A_6^{\perp}(\omega)$—components of the diatomic susceptibility tensor:

$$A_6(\omega, \mathbf{n}) = A_6^{\perp}(\omega) + [A_6^{\parallel}(\omega) - A_6^{\perp}(\omega)]|\mathbf{ne}|^2, \tag{4}$$

which, like the van der Waals constant C_6, is a characteristic of the entire diatomic system AB. It is easy to verify that this quantity averaged over the orientations has the nonzero value:

$$\overline{A_6(\omega)} = \int A_6(\omega, \mathbf{n})\frac{d\Omega_{\mathbf{n}}}{4\pi} = \frac{1}{3}A_6^{\parallel}(\omega) + \frac{2}{3}A_6^{\perp}(\omega). \tag{5}$$

Let us note that it is sometimes convenient to use the averaged value (5) and the anisotropy $\Delta A_6(\omega) = A_6^{\parallel} - A_6^{\perp}$ as the linearly independent components of the tensor $A_6(\omega, \mathbf{n})$, instead of the longitudinal and transverse components. As can hence be seen, the correction in question, which describes the interaction of the virtual atomic dipoles with the external field and with each other simultaneously, makes a nonzero contribution to the change in the energy of the entire atomic medium in the external field $\mathscr{F}(t)$. Using (3), we can represent the expression for the collision-induced polarizability of the diatomic system in the form

$$\alpha^{\mathrm{col}}(\omega, \mathbf{R}) = \frac{2\alpha^A(\omega)\alpha^B(\omega)}{R^3}[3|\mathbf{ne}|^2 - 1] + \frac{A_6(\omega, \mathbf{n})}{R^6}. \tag{6}$$

Similarly, for the van der Waals constant in the external field we obtain the expression

$$C_6(\mathscr{F})=C_6+{}^1/_4F^2A_6(\omega,\,\mathbf{n}). \tag{7}$$

Thus, the interaction of the atoms induces an anisotropic correction to the polarizability of the spherically symmetric atoms, which causes depolarization in the scattering of the light by the monatomic gas,[8] while the action of the light field leads to a change in the van der Waals constant, which also becomes anisotropic. In this case, in the region of frequencies far from the atomic lines the polarizability anisotropy

$$\Delta\alpha^{\mathrm{col}}(\omega,\,R)=\alpha^{\|}(\omega,\,R)-\alpha^{\perp}(\omega,\,R)=6\alpha^A(\omega)\alpha^B(\omega)/R^3+\Delta A_6(\omega)/R^6 \tag{8a}$$

is characterized largely by the term $\sim 1/R^3$, which is determined by the polarizabilities of the individual atoms. But in a number of situations the role of the second term in (8a) can be significantly more important. In particular, there exist frequencies at which $\alpha(\omega)\approx 0$ (Ref. 1): the contribution of the term $\sim 1/R^3$ is then small, and the collision-induced polarizability, like the change in the van der Waals interaction of the atoms in the field, is determined by the susceptibility $A_6(\omega, n)$.

In the nonresonance region for rarefied gases the isotropic part

$$\overline{\alpha^{\mathrm{col}}(\omega,\,R)}=\overline{A_6(\omega)}/R^6 \tag{8b}$$

plays an unimportant role in comparison with the anisotropic part (8a). This explains, in particular, the fact that the Rayleigh line wing (RLW) for light scattered in inert gases is virtually completely depolarized.[8] In the vicinity of a resonance, where the anisotropy $\Delta\alpha^{\mathrm{col}}$, like $\overline{\alpha^{\mathrm{col}}}$, is determined by the terms $\sim 1/R^6$, the degree of depolarization of the RLW should be significantly lower (see §5). The shape of the RLW in this case practically does not differ from the shape in the nonresonance region.[13]

§3. GENERAL FORMULAS FOR THE SUSCEPTIBILITY $A_6(\omega)$

Using the expression for the correction that is of fourth order in the perturbation $\hat{V}=\hat{v}_F+\hat{v}_{AB}$, we can represent the components of the tensor A_6 in the form of a linear combination of composite matrix elements:

$$\begin{aligned}A_6^{\|(\perp)}(\omega)={}&K^{\|(\perp)}[2q_z^1+2q_z^2+q_z^3+q_z^4]+(6-K^{\|(\perp)})[2q_x^1+2q_x^2\\&+q_x^3+q_x^4]-C_6[\beta^A(\omega)+\beta^B(\omega)]-B_6[\alpha^A(\omega)+\alpha^B(\omega)],\end{aligned} \tag{9}$$

where

$$q_t^1=\langle 0|(d_z^A+d_z^B)(G_{E_0+\omega}+G_{E_0-\omega})(d_z^A+d_z^B)G_{E_0}d_t^Ad_t^BG_{E_0}d_t^Ad_t^B|0\rangle;$$

$$\begin{aligned}q_t^2=\langle 0|(d_z^A+d_z^B)&(G_{E_0+\omega}d_t^Ad_t^BG_{E_0+\omega}\\&+G_{E_0-\omega}d_t^Ad_t^BG_{E_0-\omega})(d_z^A+d_z^B)G_{E_0}d_t^Ad_t^B|0\rangle;\end{aligned}$$

$$\begin{aligned}q_t^3=\langle 0|(d_z^A+d_z^B)&(G_{E_0+\omega}d_t^Ad_t^BG_{E_0+\omega}d_t^Ad_t^BG_{E_0+\omega}\\&+G_{E_0-\omega}d_t^Ad_t^BG_{E_0-\omega}d_t^Ad_t^BG_{E_0-\omega})(d_z^A+d_z^B)|0\rangle;\end{aligned}$$

$$q_t^4=\langle 0|d_t^Ad_t^BG_{E_0}(d_z^A+d_z^B)(G_{E_0+\omega}+G_{E_0-\omega})(d_z^A+d_z^B)G_{E_0}d_t^Ad_t^B|0\rangle;$$

$$B_6=6\langle 0|d_z^Ad_z^BG_{E_0}G_{E_0}d_z^Ad_z^B|0\rangle;$$

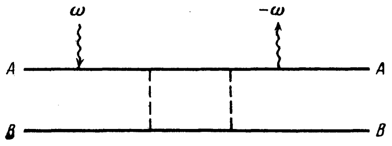
$$\beta(\omega)=\langle 0|d_z(G_{E_0+\omega}G_{E_0+\omega}+G_{E_0-\omega}G_{E_0-\omega})d_z|0\rangle.$$

Here $t=x$ or z, $K^{\|}=4$, $K^{\perp}=1$, and $E_0=E_{0A}+E_{0B}$ is the energy of the system in the absence of the perturbation $\hat{V}$ (we have, for simplicity, dropped the sign ^ above the operators in the matrix elements).

The expressions obtained are similar to the formulas for the fourth-order susceptibilities (i.e., the hyperpolarizabilities) of isolated atoms.[1,11] But there is an important difference, namely, the composite matrix elements in (9) contain the diatomic Green function, which is determined by a double series and a double integral over the states of the discrete and continuous spectrum of the system:

$$G_E=\sum_{n_An_B}{}'\frac{\langle\mathbf{r}_A|n_A\rangle\langle n_A|\mathbf{r}_A'\rangle\langle\mathbf{r}_B|n_B\rangle\langle n_B|\mathbf{r}_B'\rangle}{E_{n_A}+E_{n_B}-E}. \tag{10}$$

Here E_n is the energy and $\langle \mathrm{r}|n\rangle$ is a state vector for the isolated atom. The quantities q_t in (9) correspond to Feynman diagrams of the type



with all possible permutations of the photon and interatomic lines. The terms with C_6 and B_6 are the standard normalization terms that arise in higher-order perturbation theory. The object in these expressions that is most complicated from the computational point of view is the diatomic Green function standing between two interatomic lines.

Actually, the variables of the atoms A and B in (10) are separated, but the common energy denominator does not allow us to write the expansion of G_E in a form similar to the Sturm expansion for the monatomic Green function, in which there would be no integration over the continuous spectrum.[1] Nevertheless, the computations of the composite matrix elements can be significantly simplified by factorizing the denominator of the expression (10) with the aid of the identity

$$\frac{1}{a+b}=\frac{2}{\pi}\int_0^\infty\frac{ab\,dx}{(a^2+x^2)(b^2+x^2)},$$

which leads, in particular, to the representation of C_6 in terms of an integral of imaginary-frequency-dependent polarizabilities (see, for example, Ref. 12) of the interacting atoms. In this case

$$\begin{aligned}G_{E_0}={}&G_{E_{0A}}\langle\mathbf{r}_B|0_B\rangle\langle 0_B|\mathbf{r}_B'\rangle+\langle\mathbf{r}_A|0_A\rangle\langle 0_A|\mathbf{r}_A'\rangle\\&+\frac{2}{\pi}\int_0^\infty\mathrm{Re}\,G_{E_{0A}+ix}\cdot\mathrm{Re}\,G_{E_{0B}+ix}\,dx,\end{aligned} \tag{11}$$

where $G_{E_{0A(B)}}$ is the Green function of the isolated A(B) atom, and the diatomic composite matrix elements in (9) are represented in the form of integrals of products of monatomic matrix elements with complex energies in the intermediate states. A method of computing such quantities with the use of a model potential for the description of the states of a valence electron is developed in Ref. 14, but the representation of the quantities q_t with the aid of (11) is inexpedient, since it then becomes necessary to evaluate a double integral for q_t^2 and a triple integral for q_t^4. Nevertheless, we can propose on the basis of the expression (11) a fairly simple approximate method of determining the numerical values of the composite matrix elements in (9), as shown in the following section.

The most convenient representation for the numerical computations of the susceptibilities A_6 with the aid of (9) is a representation of the form

$$G_E=\sum_{n_B}\langle \mathbf{r}_B|n_B\rangle\langle n_B|\mathbf{r}_B'\rangle G_{E-\omega_{nB}}(\mathbf{r}_A,\mathbf{r}_A')$$

$$=\sum_{n_A}\langle \mathbf{r}_A|n_A\rangle\langle n_A|\mathbf{r}_A'\rangle G_{E-\omega_{nA}}(\mathbf{r}_B,\mathbf{r}_B'). \qquad (12)$$

We can derive with the aid of this expression a representation of the diatomic quantities q_t in the form of spectral sums of products of the simple $\rho_n=\langle 0|r|n\rangle$ and composite

$$\rho_{l_1l_2l_3}(\omega_1,\ \omega_2,\ \omega_3)=\langle 0|rg_{l_1}(E_0+\omega_1)rg_{l_2}(E_0+\omega_2)rg_{l_3}(E_0+\omega_3)r|0\rangle \qquad (13)$$

monatomic (radial) matrix elements, the procedure for numerically computing which is described in detail in Ref. 15. In particular,

$$q_t^1=\frac{1}{27}\sum_{n_B}\{\overset{A}{\rho}_{101}(\omega,0,-\omega_{n_B})+\overset{A}{\rho}_{101}(-\omega,0,-\omega_{n_B})$$

$$+\frac{2}{5}(3\delta_{t2}-1)[\overset{A}{\rho}_{121}(\omega,0,-\omega_{n_B})+\overset{A}{\rho}_{121}(-\omega,0,-\omega_{n_B})]\Big\}|\rho_{n_B}|^2+(A\rightleftharpoons B).$$

Analysis of these sums in the static (i.e., $\omega=0$) case shows that the series over the discrete states $|n\rangle$ converges like $\Sigma_n n^{-3}$, and to find its numerical value to within 10^{-4} we must take about 100 terms into account. To evaluate the integral over the continuous spectrum with the same degree of accuracy, it is sufficient to use, for example, the Gaussian quadrature of the twelfth order. The values $A_6^{\parallel}=2556$ and $A_6^{\perp}=1270$ a.u. obtained in this way for hydrogen atoms in the ground states coincide within the limits of the indicated error with the results of the variational calculations.[9,10]

§4. SIMPLIFIED FORMULAS FOR APPROXIMATE CALCULATIONS

The slow convergence of the series (13) leads to error accumulation, and, consequently, to the necessity of a very exact computation of the monatomic matrix elements, which complicates significantly with increasing ω_{nB}. Therefore, the computation of q_t with the aid of expressions of the type (13) is as laborious and the result as unstable as when the representation (11) is used. There arises the need for the derivation of fairly simple approximate formulas for determining the quantities A_6. Below we obtain such formulas, i.e., formulas suitable for approximate calculations in various situations encountered in practice.

1. *In a low-frequency (i.e., $\omega \ll \omega_n$) field* we can use the representation (11) and the following approximate relation for the monatomic Green functions:

$$\operatorname{Re} G_{E+ix}\approx G_E\bar{\omega}/(\bar{\omega}^2+x^2), \qquad (14)$$

where $\bar{\omega}$ is an energy parameter that can be determined, using the well-known values of the oscillator-strength (f_n) sums

$$S_{-k}=\sum_n \frac{f_n}{\omega_n^{k}},$$

which are connected with each other by the relation

$$S_{-k-1}=S_{-k}/\bar{\omega}.$$

TABLE I. Numerical values of the static parameters of $A_6(0)$ in a.u.; $(n)=10^n$.

A—B	$\bar{A}_6$	ΔA_6	A—B	$\bar{A}_6$	ΔA_6
H–He	3.4(2)	4.1(2)	Li–Kr	1.54(6)	6.69(5)
–Li	3.6(5)	1.61(5)	–Xe	2.11(6)	9.53(5)
–Na	4.37(5)	1.54(5)	Na–Na	1.4(7)	1.24(7)
–K	1.45(6)	3.75(5)	–K	3.86(7)	2.49(7)
–Rb	1.92(6)	4.0(5)	–Rb	4.92(7)	2.87(7)
–Cs	3.13(6)	3.52(5)	–Cs	7.88(7)	3.71(7)
–Ar	4.29(3)	3.04(3)	–Ar	1.28(6)	4.08(5)
–Kr	6.38(3)	4.52(3)	–Kr	1.87(6)	6.3(5)
–Xe	1.07(4)	7.08(3)	–Xe	2.55(6)	9.12(5)
He–He	5.69(2)	3.75(2)	K–K	7.41(7)	6.35(7)
–Li	1.23(5)	4.86(4)	–Rb	9.11(7)	7.15(7)
–Na	1.49(5)	4.37(4)	–Cs	1.4(8)	9.09(7)
–K	4.91(5)	1.03(5)	–Ar	4.25(6)	9.69(5)
–Rb	6.51(5)	1.03(5)	–Kr	6.2(6)	1.51(6)
–Cs	1.06(6)	6.8(5)	–Xe	8.47(6)	2.2(6)
–Ar	8.94(2)	4.18(2)	Rb–Rb	1.05(8)	8.81(7)
–Kr	1.37(3)	6.75(2)	–Cs	1.56(8)	1.11(8)
–Xe	2.78(3)	1.21(3)	–Ar	5.63(6)	9.96(5)
Li–Li	1.11(7)	1.04(7)	–Kr	8.22(6)	1.59(6)
–Na	1.26(7)	1.12(7)	–Xe	1.12(7)	2.33(6)
–K	3.58(7)	2.33(7)	Cs–Cs	2.04(8)	1.88(8)
–Rb	4.6(7)	2.7(7)	–Ar	9.2(6)	7.5(5)
–Cs	7.44(7)	3.54(7)	–Kr	1.34(7)	1.3(6)
–Ar	1.06(6)	4.42(5)	–Xe	1.84(7)	2.03(6)

It can be verified, in particular, that for hydrogen and alkali-metal atoms in the ground states $E_1<\bar{\omega}<E_2$, where $E_{1(2)}$ is the energy of the first (second) P state of the atom. For the inert gases $\bar{\omega}$ roughly coincides with the ionization potential $|E_0|$. In this case $\bar{\omega}$ practically does not depend on the order k of the S_{-k} sums (the relative difference between the sums for $k=1$ and $k=2$ is about 5–7%). Using (14) and (11), we can express the quantity q_t in terms of the monatomic matrix elements and the effective excitation energy $\bar{\omega}$. In particular,

$$q_t^1=[\overset{A}{T}_{zztt}\alpha^B(0)+\overset{B}{T}_{zztt}\alpha^A(0)]\bar{\omega}^A\bar{\omega}^B/2(\bar{\omega}^A+\bar{\omega}^B). \qquad (15)$$

Here

$$T_{ijkl}=\langle 0|d_iG_{E_0}d_jG_{E_0}d_kG_{E_0}d_l|0\rangle$$

is the composite fourth-order matrix element, which determines, for example, the hyperpolarizability tensor for an isolated atom.[1,11]

As an example, in Table I we give the numerical values obtained by means of the proposed method for the quantities $\bar{A}_6$ and ΔA_6 in the static ($\omega=0$) case. For comparison we give the values $\bar{A}_6=1812$ and $\Delta A_6=1214$ computed by the above-expounded method for hydrogen atoms. These values differ from the exact values $\bar{A}_6=1698$ and $\Delta A_6=1290$ (Refs. 9 and 10) by less than 8%. This accuracy is not worse than the accuracy of the method used here in the calculations of the monatomic quantities.[1]

TABLE II. Susceptibilities $A_6(\omega)$ (in a.u.) for atoms with greatly differing ionization potentials.

A—B	$\bar{A}_6(\omega_N)$	$\Delta A_6(\omega_N)$	$\bar{A}_6(\omega_R)$	$\Delta A_6(\omega_R)$
H–Li	8.47(5)	8.80(5)	6.94(7)	8.07(7)
–Na	7.16(5)	6.64(5)	4.46(6)	4.42(6)
–K	4.45(6)	4.56(6)	2.21(7)	2.42(7)
–Rb	5.96(6)	6.01(6)	2.18(7)	2.33(7)
–Cs	1.54(7)	1.58(7)	9.21(6)	1.01(7)
He–Li	2.71(5)	2.81(5)	2.30(7)	2.67(7)
–Na	2.26(5)	2.09(5)	1.47(6)	1.45(6)
–K	1.46(6)	1.49(6)	7.22(6)	7.99(6)
–Rb	1.96(6)	1.96(6)	7.11(6)	7.69(6)
–Cs	5.11(6)	5.20(6)	2.96(6)	3.32(6)

2. *For atoms with greatly differing ionization potentials* (i.e., for $|E_{0A}| \gg |E_{0B}|$) the dominant contribution to the diatomic composite matrix elements is made by those terms of the series (10) for which the inequality $\omega_{nA} \gg \omega_{nB}$, which allows us to neglect the quantities ω_{nB} in comparison with ω_{nA} and $\omega_{nA} \pm \omega$, is fulfilled. Then

$$G_E \approx G_E(\mathbf{r}_A, \mathbf{r}_A')\delta(\mathbf{r}_B - \mathbf{r}_B') + \langle \mathbf{r}_A | 0_A \rangle \langle 0_A | \mathbf{r}_A' \rangle G_E(\mathbf{r}_B, \mathbf{r}_B'). \tag{16}$$

Using this expression, we find, in particular, that

$$q_t^1 \approx 2\langle 0_A | d_z^A G_{E_{0A}} d_z^A G_{E_{0A}} d_t^A G_{E_{0A}} d_t^A | 0_A \rangle \langle 0_B | (d_t^B)^2 | 0_B \rangle + \langle 0_A | d_t^A G_{E_{0A}} d_t^A | 0_A \rangle \langle 0_B | d_z^B (G_{E_{0B}+\omega} + G_{E_{0B}-\omega}) d_z^B G_{E_{0B}} (d_t^B)^2 | 0_B \rangle. \tag{17}$$

Similarly,

$$C_6 \approx \alpha^A(0) \langle 0_B | r_B^2 | 0_B \rangle, \quad B_6 \approx \beta^A(0) \langle 0_B | r_B^2 | 0_B \rangle. \tag{18}$$

Similar expressions with the composite matrix elements factorized into monatomic matrix elements can be derived for the remaining quantities q_t in (9).

In Table II we present numerical $\bar{A}_6(\omega)$ and $\Delta A_6(\omega)$ values obtained by the present method. These values determine the interaction of hydrogen and helium atoms with alkali-metal atoms in the fields of neodymium ($\omega_N = 9440$ cm^{-1}) and rubidium ($\omega_R = 14400$ cm^{-1}) lasers.

3. *In the case of resonances at the lines of the isolated atoms*, i.e., at $\omega = \omega_{nA} - \Delta$, where $|\Delta| \ll \omega$, all the quantities in (3) that are proportional to F^2 increase resonantly. Then in the neighborhood of the resonance on the P state $\alpha^A(\omega) \sim 1/\Delta$ and $A_6(\omega) \sim 1/\Delta^2$, so that for nonidentical atoms A and B the last term can, in the present situation, predominate over the remaining terms. Taking only the resonance terms of the order of $1/\Delta^2$ into account in $A_6(\omega)$, we can write

$$A_6^{\parallel(\perp)}(\omega) = 2(1+\delta_{AB}) \frac{|\langle 0_A | d_z | nP_A \rangle|^2}{\Lambda^2} [C_6^{\parallel(\perp)} - C_6], \tag{19}$$

where δ_{AB} is the Kronecker symbol and $C_6^{\parallel(\perp)}$ is the longitudinal (transverse) component of the van der Waals constant, which determines the interaction of the atom A resonantly excited into the $|nP_A\rangle$ state with zero angular-momentum component with the atom B. Notice that the expression (19) is applicable only when there is no saturation, i.e., when the population of the excited level can be neglected. A necessary condition for this is clearly the condition that $\Delta \gg \gamma$, where γ is the total width of the resonance levels (with allowance for the effect of the external field). Results valid for $\Delta \lesssim \gamma$ are obtained in the two-level approximation in Ref. 16, and have a form similar to that of (19) for the $\Delta \gg \gamma$ case, with the difference that in Ref. 16 the interaction of the atoms is assumed to be isotropic in all the states, i.e., it is assumed that $C_6^{\parallel} = C_6^{\perp}$, which is incorrect in the case of atoms in states with nonzero angular momenta. In the case of resonance with a highly-excited nP state $C_6^{\parallel(\perp)} \gg C_6$, and the relative anisotropy of the collision-induced susceptibility tends to a fixed limit:

$$\Delta\alpha^{\text{col}}/\bar{\alpha}^{\text{col}} \approx \Delta A_6(\omega)/\bar{A}_6(\omega) \approx (C_6^{\parallel} - C_6^{\perp})/({}^1/{}_3 C_6^{\parallel} + {}^2/{}_3 C_6^{\perp}) = {}^3/{}_5. \tag{20}$$

This relation can be uniquely related with the coefficient of depolarization of the collision-induced scattering of the RLW and, thus, be verified experimentally. It should be borne in mind here that experiment in the resonance region in atomic gases is substantially facilitated by the fact that the intensity of the RLW in the vicinity of a resonance increases rapidly as the detuning Δ decreases.

4. *In the vicinity of the resonance with the diatomic lines* $\omega = \omega_{nA} + \omega_{nB} - \Delta$, $|\Delta| \ll \omega$, the components of the tensor $A_6(\omega)$ are proportional to $1/\Delta$. The susceptibilities of the isolated atoms in this case remain nonresonant. Consequently, the contribution of the corrections in the expressions (3), (6), and (7), which are determined by the tensor $A_6(\omega)$, is higher at these frequencies. Furthermore, in contrast to resonance at the 1 lines of the isolated atoms, the parameters of $A_6(\omega)$ change sign when the sign of the detuning Δ is changed, which allows us to change the sign of the corrections to the polarizability (6) and the van der Waals constant (7) through the retuning of the frequency of the light radiation. Notice that, according to the dipole selection rules, one of the states, $|n_A\rangle$ or $|n_B\rangle$, in the case under consideration is a P state, while the other is an S or a D state. Taking only the resonance terms in (9) into account, we can write the expression for $A_6(\omega)$ in the form

$$A_6^{\parallel(\perp)}(\omega) \approx \varkappa_l^{\parallel(\perp)} (1+\delta_{AB}) \frac{|\langle 0_A | d_z | nP_A | \rangle^2}{\Delta} [\rho_{0,n_B}(\omega) + \rho_{0,n_B}(-\omega_{nPA})]^2, \tag{21}$$

where $\varkappa_0^{\parallel} = \frac{4}{9}$, $\varkappa_0^{\perp} = \frac{1}{9}$ for the resonance S state and $\varkappa_2^{\parallel} = \frac{22}{45}$, $\varkappa_2^{\perp} = \frac{19}{45}$ for resonance at the D state. Here

$$\rho_{ab}(\omega) = \langle a | r g_1 (E_a + \omega) r | b \rangle$$

is the radial composite matrix element for the atomic transition between the states $|a\rangle$ and $|b\rangle$.

Let us note that the substitution $\Delta \to \Delta + i\gamma$, where γ is the total width of the resonance levels, should be made in the expression (21) in the immediate neighborhood of the resonance, i.e., in the region where $\Delta \lesssim \gamma$. Then, according to the optical theorem, the imaginary part of A_6 determines the cross section σ for absorption of the resonance photons by the diatomic system for a fixed distance R between the atoms:

$$\sigma = 4\pi\alpha\omega \operatorname{Im} A_6(\omega, \mathbf{n})/R^6,$$

where $\alpha = \frac{1}{137}$ is the fine structure constant. This expression can be used to determine the optical characteristics of the static wing of the line. For this purpose it should be averaged over the interatomic distances R, bearing in mind that the detuning Δ also depends on R. The correct formulas giving the connection between the atomic parameters and the optical characteristics of the medium in broad Δ and light-field-intensity (F) ranges are given in Ref. 5. The quantity B_3 used in Ref. 5 is connected with A_6 by the simple relation $|B_3|^2 = \frac{1}{4}\Delta\bar{A}_6(\omega)$.

§5. RESULTS AND DISCUSSIONS

As can be seen from the specific calculations carried out above, the numerical values of the quantities $A_6(\omega)$ are fairly high (see Tables I and II), so that even at nonresonance frequencies the corrections determined by these parameters can make an appreciable contribution (3) to the quasienergy of the atom. In particular, the relative change that occurs in the static polarizability of cesium atoms as a result of their interaction with each other is equal to 20% for $R \approx 10$ a.u. The same amount of change is induced in the van der Waals constant C_6 for these atoms by a field of intensity $F = 5 \times 10^6$ V/cm.

It can be seen from Table II that the indicated effects are even more important in variable fields, the most significant changes in the polarizability and the van der Waals forces being attainable in the vinicity of resonances. The substantial increase that occurs in the corrections to the polarizability of the atoms in this neighborhood can simplify the experimental observation of the collision-induced scattering of the RLW. whose intensity is proportional to the square of $\alpha^{\mathrm{col}}(\omega, R)$. For this reason, in particular, the scattering of the RLW can be relatively easily detected in the vapors of the alkali metals, the values of the susceptibilities $A_6(\omega)$ in the optical frequency region for these metals being five–seven orders of magnitude higher than the susceptibilities of the inert gases.

As noted above (§4), the quantity $\alpha^{\mathrm{col}}(\omega, R)$ [Eq. (6)] has poles in the vicinities of the resonances at the lines of the isolated atoms: the terms $\sim 1/R^6$ have a second-order pole, while the terms $\sim 1/R^3$ have a second-order pole for identical atoms and a first-order pole for different atoms A and B. As an example, let us give the expression for the collision-induced correction to the polarizability of cesium atoms at the frequency $\omega = \omega_{6PJ} - \Delta_J (J = \frac{1}{2}, \frac{3}{2})$:

$$\alpha^{\mathrm{col}}(\omega, R) \approx \frac{107}{R^3}\left[\frac{1}{\Delta_{1/2}} + \frac{2}{\Delta_{3/2}}\right]^2 [3|\mathbf{ne}|^2 - 1] + \frac{2.24 \cdot 10^5}{R^6}\left\{\frac{1}{\Delta_{1/2}^2} + \frac{1.71}{\Delta_{3/2}^2}\left[1 + \frac{|\mathbf{ne}|^2}{2}\right]\right\}. \tag{22}$$

As can be seen from (22), when $R > 15$ a.u. the dominant role is, generally speaking, played by the corrections $\sim 1/R^3$, which are due to the interaction of the external-field-induced atomic dipoles: the dispersion interaction of the virtual dipoles (the term $\sim 1/R^6$) makes, for $R = 15$ a.u., a contribution ~20–30%. Therefore, the interatomic interaction leads at these frequencies largely to the appearance of an anisotropy in the polarizability of the atoms, and, consequently, as in the resonance case,[8] the collision-induced RLW will be completely depolarized. But the term $\sim 1/R^3$ in (22) vanishes when $\Delta_{1/2} = -0.5\Delta_{3/2} \approx -185$ cm^{-1} ($\omega \approx 11363$ cm^{-1}), and the contribution of the isotropic correction, which is proportional to $1/R^6$, is then appreciably greater. This should lead to the decrease of the experimentally observed degree of depolarization of the RLW as ω approaches the indicated frequency.

By using the well-known relations connecting the degree of depolarization of light scattered by an axisymmetric molecule to the molecule's polarizability tensor components—the anisotropy and the averaged polarizability—given by the expressions (8a) and (8b) (we consider only the quantity responsible for the scattering of the RLW),[17] we can verify that in the nonresonance case, when the major role in α^{col} is played by the term $\sim 1/R^3$ and $|\Delta\alpha^{\mathrm{col}}| \gg |\overline{\alpha^{\mathrm{col}}}|$, the degree of vertical depolarization $D_v = \frac{3}{4}$. The coefficient D_v is significantly smaller in the case when the major role is played by terms $\sim 1/R^6$. As is easy to verify with the aid of (22), for the example considered $D_v = 1.36 \times 10^{-3}$ when $\omega \approx 11363$ cm^{-1}, i.e., the RLW at the given frequency should be practically completely polarized.

The dependence of the van der Waals constant on the intensity of the light field for the system under consideration can be represented in the form

$$C_6(\vec{\mathscr{F}}) = 6500\left\{1 + \frac{11.9}{\Delta_{1/2}^2} I + \frac{20.4}{\Delta_{3/2}^2} I\left[1 + \frac{|\mathbf{ne}|^2}{2}\right]\right\}. \tag{23}$$

Here I is in MW/cm^2 and Δ is in cm^{-1}. In particular, in a neodymium laser field of intensity $I = 10^4$ MW/cm^2 the correction to $C_6^{\mathrm{Cs-Cs}}$ attains a value of 10%.

Under resonance conditions the role of the corrections $\sim 1/R^6$ in α^{col} is more important in collisions of different atoms A and B, since in this case the correction $\sim 1/R^3$ in (6) has a first-order resonance pole, while the pole singularity in $A_6(\omega)$ is of second order, as in the case of identical atoms. In particular, for the pair of atoms Cs–Xe at the same frequency as the one in the above-considered example,

$$\alpha^{\mathrm{col}}_{\mathrm{Cs-Xe}}(\omega, \mathbf{R}) = \frac{409}{R^3}\left(\frac{1}{\Delta_{1/2}} + \frac{2}{\Delta_{3/2}}\right)[3|\mathbf{ne}|^2 - 1] + \frac{1.06 \cdot 10^4}{R^6}\left\{\frac{1}{\Delta_{1/2}^2} + \frac{1.31}{\Delta_{3/2}^2}[1 + 1.16|\mathbf{ne}|^2]\right\}.$$

It can be seen from this expression that the role of the corrections $\sim 1/R^6$ becomes increasingly important not only as $\Delta_{1/2} \to -0.5\Delta_{3/2} = -185$ cm^{-1}, but also as $\Delta_{1/2}$, $\Delta_{3/2} \to 0$. The minimum value of the degree of depolarization of the RLW (at $\omega \approx 11363$ cm^{-1}) is $D_v = 4.46 \times 10^{-3}$, i.e., as in pure cesium vapor, the RLW at the frequency in question is practically completely polarized.

For the van der Waals constant here we obtain, similarly to (23), the expression

$$C_6^{\mathrm{Cs-Xe}}(\vec{\mathscr{F}}) = 785\left\{1 + \frac{4.65}{\Delta_{1/2}^2} I + \frac{6.11}{\Delta_{3/2}^2} I[1 + 1.16|\mathbf{ne}|^2]\right\}.$$

From this it follows that the correction to the van der Waals constant in a neodymium laser field of intensity $I = 10^4$ MW/cm^2 is ~3%.

In the case of resonance at the diatomic lines, the individual susceptibilities of the atoms remain nonresonant in all orders and for any multipolarity, so that only the collision-induced effects undergo resonance amplification. Neglecting the nonresonance corrections, we can determine with the aid of the expression (21) the numerical values for the depolarization coefficient: $D_v = \frac{1}{8}$ in the case of resonance on the S state and $D_v = \frac{1}{668}$ for resonance with the D level.

As an example, let us give the expression for the van der Waals constant for two cesium atom in a field of frequency $\omega = \omega_{6P1/2} + \omega_{5D3/2} - \Delta$:

$$C_6(\vec{\mathscr{F}}) \approx 6500 + \frac{I}{\Delta}\left[\frac{50.3}{31 + \Delta} - 0.366\right]^2\left[1 + \frac{3}{19}|\mathbf{ne}|^2\right]. \tag{24}$$

As can be seen from this expression, for $I = 10^4$ MW/cm^2 the van der Waals constant increases by 12%

when the detuning $\Delta = 10$ cm^{-1}, but decreases by ~60% when $\Delta = -10$ cm^{-1}. Thus, in the vicinities of the diatomic resonances, an external field can cause an increase or a decrease in C_6. Notice that in the above-considered case the transition matrix element $\rho_{6S,5D}(\omega)$ has a pole at the $8^2P_{1/2}$ level, that, in terms of frequency, lies 31 cm^{-1} away from the diatomic resonance and produces a second-order pole in the expression (24).

§6. CONCLUSION

The proposed method is, apparently, the first example of a consistent quantum-mechanical calculation of the diatomic susceptibilities determining the atomic collision processes in the field of light radiation.

The specific susceptibility [i.e., $A_6(\omega)$] calculations performed here allow us to conclude that it is necessary to allow for the effect of the long-range interatomic forces on the dynamic polarizabilities of the atoms in the medium, as well as for the action of the high-power light radiation on the van der Waals forces. In particular, the data obtained show that in the optical frequency region the collision-induced depolarized RLW scattering effect has the highest cross sections in the case of the alkali elements: therefore, it will be expedient to use alkali-metal vapors in an effective experimental investigation of it. The greatest contribution to the collision-induced polarizability from the term determined by a parameter of $A_6(\omega)$ can then be attained through the fine tuning of the frequency. Thus, the direct determination of the higher-order diatomic susceptibilities in experiments on RLW scattering in atomic gases is possible under resonance conditions.

The calculations performed also show that light radiation can, in certain situations, have a significant effect on the van der Waals forces. This fact is quite interesting from the practical standpoint, since there thus arises the possibility of controlling the rate of chemical reactions in gases with the aid of intense light radiation: This control will be most effective at the frequencies that are in resonance with the diatomic lines, in the vicinity of which we can either increase or decrease the van der Waals constant C_6, and thereby speed up or slow down the process in which the atoms stick together to form molecules. This effect can be detected, in particular, by measuring the change that occurs in the concentration of the molecular component in an alkali-metal vapor as a result of the action of laser radiation.

Furthermore, the experimental measurement of the parameters of $A_6(\omega)$ can also be performed by determining the dependence of thermodynamic quantities (e.g., the virial coefficients) of an atomic gas on the intensity of the light radiation acting on the gas.

The procedure, proposed here, for carrying out numerical computations can be generalized to the case of atoms in states with nonzero spins. The determination of the parameters of $A_6(\omega)$ for such states is important in view of the intensive investigation of the physical properties of the Rydberg levels of atoms.[18] In particular, knowledge of the numerical values of the components of the tensor $A_6(\omega)$ will allow us to elucidate the effect of the interatomic forces on the polarizabilities of excited atoms, which have recently been measured in a number of experiments (see, for example, Ref. 19 and the references cited therein).

By taking into account the terms of higher multipole orders in the interatomic interaction operator $\hat{v}_{AB}$ (Ref. 12), we can also generalize the present method to the case of corrections of higher orders in $1/R$, corrections which determine diatomic multipole effects similar to those considered here in the dipole approximation.[20]

The author is grateful to I. L. Fabelinskiĭ, V. S. Starunov, and S. I. Yakovlenko for useful discussions.

[1)] Generally speaking, the thermal motion of the atoms makes R dependent on the time, but we can neglect this dependence, assuming v_{AB} to be stationary. This approximation is valid when the velocities in the relative motion of the atoms $v \ll \omega_n R$. In the case of unexcited atoms this inequality is satisfied at normal temperatures if $R > a_0$.

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Translated by A. K. Agyei