

Atomic susceptibilities for collision-induced magnetization, and variation of dispersion interaction in a magnetic field

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(Submitted 19 November 1991)

Zh. Eksp. Teor. Fiz. **102**, 26–35 (July 1992)

Collision-induced magnetization and dispersion interaction of atoms in a magnetic field are determined by an energy correction $\Delta E(\mathbf{R}, \mathbf{B})$, which depends simultaneously on the interatomic distance \mathbf{R} and on the magnetic-field induction \mathbf{B} . We determine the structure of the susceptibility tensor $D_6^{(2)}$ which is a coefficient of the principal term of the series $\Delta E(\mathbf{R}, \mathbf{B})$

$= -\sum_n \sum_m D_m^{(n)} (\alpha B)^n / R^m$ (α is a constant of a thin structure). A procedure for a quantitative calculation is developed and the numerical values of the components of the tensor $D_6^{(2)}$ are determined for diatomic systems of hydrogen, alkali-metal, and inert-gas atoms.

1. INTRODUCTION

The solutions of the classical quantum-mechanics problems involving magnetization of a solitary atom and the dispersion interaction between atoms have already been treated in sufficient detail in the literature (see, e.g., Ref. 1). The energy of a diamagnetic atom was calculated not only in a purely magnetic field, but also in crossed magnetic and electric or optical fields.² The structures of the asymptotic series for binary and nonadditive three-atom energy were investigated and methods were found for their solution.^{3–5} The influence of electric and optical fields on the dispersive interaction of atoms was determined.^{6,7} The problem of the influence of the magnetic field on the dispersion interaction of atoms is still unsolved. Mention can be made only of one study⁸ in which the energy of a two-atom system was observed to contain a term corresponding to interaction of electric quadrupole moments induced by a magnetic field in the atoms. The existence of astrophysical objects with ultrastrong magnetic fields calls for an exhaustive study of the influence of magnetic fields on interatomic forces, and this may yield additional information on the properties of these objects.

We study in the present paper the structure of the asymptotic series for the dispersion energy of atoms in a magnetic field, and propose a procedure for calculating the diatomic susceptibilities that determine the first nonvanishing terms of this series.

Just as in the case of an electric field, the dispersion-interaction energy ΔE of atoms A_1 and A_2 (see Fig. 1) separated by a distance $R \gg a$ ($\mathbf{R} = R\mathbf{n}$, a is the linear dimension of the atom) in a magnetic field with an induction $\mathbf{B} = B\mathbf{b}$ (\mathbf{b} is a unit vector) can be represented in the form of a dual series in powers of the small parameters B/B_0 and a/R , where B_0 is the induction of the intra-atomic magnetic field (we use throughout the atomic system of units $e = \hbar = m = a = B_0 = 1$):

$$\Delta E = - \sum_m \sum_n D_m^{(n)} \frac{(\alpha B)^n}{R^m}. \quad (1)$$

Here $\alpha = 1/137$ is the fine-structure constant. The susceptibility tensor $D_m^{(n)}$ is defined both by the mutual orientation

of the vectors \mathbf{R} and \mathbf{B} and by the internal structure of the atoms A_1 and A_2 (we assume for simplicity that the atoms are in spherically symmetric S -states). Obviously, the series (1) includes the series for purely diamagnetic energy ($m = 0$) and for purely dispersive interaction ($n = 0$). In this case $D_m^{(0)} = C_m$, where C_m is the dispersion-interaction constant, the first nonvanishing one being the Van der Waals constant C_6 ; $\alpha^{(n)} D_0^{(n)} = \chi_n$ is the diamagnetic susceptibility of n th order, the first nonvanishing one being

$$\chi_2 = -1/6 \alpha^2 [\langle r_1^2 \rangle + \langle r_2^2 \rangle] \quad (2)$$

or the total susceptibility of the atoms A_1 and A_2 . It is obvious from symmetry considerations that the values of the index n in (1) can be only even. The values of m corresponding to nonzero susceptibilities $D_m^{(n)}$ can be even or odd. For $n = 0$ and $n = 2$, in particular, the first nonvanishing terms of the series correspond to $m = 6, 8$, and 10 , and at $m > 10$ nonzero $D_m^{(n)}$ correspond to m of either parity. For $n = 4$, the first nonvanishing susceptibility is $D_5^{(4)}$, and the subscripts $m > 5$ can be even or odd.

The symmetry properties, as well as the numerical values of the tensor components $D_m^{(n)}$, can be obtained by perturbation theory (PT) from the interactions of the atoms with one another and with the magnetic field. In Sec. 2 we describe a PT procedure for calculation and expansion into the irreducible parts of the tensor $D_m^{(n)}$. In Sec. 3 we obtain analytic expressions for the components of the tensor $D_6^{(2)}$ in terms of diatomic matrix elements, and present computation equations using a Sturm expansion for single-atom Green's

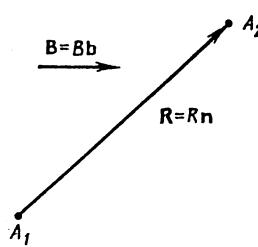


FIG. 1.

functions. In Sec. 4 we describe a procedure for an approximate calculation of two-atom matrix elements in terms of single-atom quantities. The numerical values of the components of the tensor $D_6^{(2)}$ are tabulated.

2. PERTURBATION THEORY FOR A TWO-ATOM SYSTEM IN A MAGNETIC FIELD

The perturbation operator in a system of two atoms A_1 and A_2 , separated by a large distance \mathbf{R} and located in a magnetic field \mathbf{B} , are given by

$$V = V_{12}(\mathbf{R}) + V_B, \quad (3)$$

where

$$\begin{aligned} V_{12}(\mathbf{R}) &= \sum_{l_1 l_2=1}^{\infty} \frac{v_{l_1 l_2}(\mathbf{n})}{R^{l_1+l_2+1}}, \\ v_{l_1 l_2}(\mathbf{n}) &= (-1)^{l_2} \left[\frac{(2l_1+2l_2)!}{2l_1! 2l_2!} \right]^{1/2} (C_{l_1+l_2})(\mathbf{n}) \{Q_{l_1} \otimes Q_{l_2}\}_{l_1+l_2} \end{aligned} \quad (4)$$

is the interatomic-interaction operator, $C_{lm} = \sqrt{4\pi(2l+1)} Y_{lm}$ is a modified spherical function, and Q_l is the 2^l -pole electric moment of the atom. We represent the operator of interaction with the magnetic field in standard form

$$V_B = V_\mu + V_d, \quad (5)$$

where

$$V_\mu = -\mathbf{B}(\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2) \quad (6)$$

takes into account the magnetodipole interaction,

$$\boldsymbol{\mu}_i = -i/2\alpha(\mathbf{J}_i + \mathbf{S}_i), \quad i=1, 2,$$

is the magnetodipole moment operator,

$$V_d = i/8\alpha^2([Br_1]^2 + [Br_2]^2) \quad (7)$$

is the diamagnetic-interaction operator, and \mathbf{r} is the radius vector of the valence electron relative to the atomic nucleus (the contribution of the inner-shell electrons is of no importance in our problem, and for multivalent atoms it is necessary to take into account the contributions of all the valence electrons).

For atoms in spherically symmetric S states with zero values of the total and spin quantum numbers J and S , the operator V_μ can contribute only in the higher perturbation-theory orders if the corresponding matrix elements contain intermediate states with nonzero J .

Let us take into account the correction introduced into the system energy by interaction (3), accurate to terms of second order in the interatomic interaction V_{12} and in the magnetic-field induction B . To this end it suffices to calculate the terms of the PT series in V up to fourth order inclusive.

The first-order correction differs from zero only for a diamagnetic interaction V_d and determines the first nonvanishing term for the diamagnetic energy:

$$\Delta E^{(1)} = \langle 0 | V_d | 0 \rangle = -i/2\chi_2 B^2, \quad (8)$$

where χ_2 is the diamagnetic susceptibility (2). Here $|0\rangle$ is

the wave function of the system of noninteracting ions, so that the mean value of the operator r^2 in (2) can be calculated for an isolated atom.

Nonzero contributions in second-order perturbation theory are made by the operators V_d and V_{12} . The corresponding corrections determine the terms of fourth order in the field and the dispersion-interaction energy which is independent of B :

$$\Delta E^{(2)} = -\frac{1}{4!} \chi_4 B^4 + E_{disp}^{(2)}, \quad (9)$$

where

$$\chi_4 = 3/8\alpha^4 \langle 0 | \{[Br_1]^2 + [Br_2]^2\} G \{[Br_1]^2 + [Br_2]^2\} | 0 \rangle \quad (10)$$

is the nonlinear diamagnetic susceptibility that determines the correction, quadratic in B , to the diamagnetic susceptibility (2),

$$E_{disp}^{(2)} = -\langle 0 | V_{12} G V_{12} | 0 \rangle = -\sum_{m=0}^{\infty} \frac{C_{2m}^{(2)}}{R^{2m}} \quad (11)$$

is the energy of the second-order dispersion interatomic interaction, and $C_{2m}^{(2)}$ are the corresponding dispersion constants; $C_6^{(2)}$, in particular, is the Van der Waals force (G is the Green's function of the two-atom system).

In third-order perturbation theory, nonzero contributions are made only by the operators V_{12} and V_d . Beside the terms that determine only the interaction with the field \mathbf{B} and only the dispersion term, there appear crossover terms that depend also on the magnetic induction and on the interatomic distance \mathbf{R} simultaneously:

$$\begin{aligned} \Delta E^{(3)} &= -\frac{1}{6!} \chi_6 B^6 + E_{disp}^{(3)} \\ &+ 6 \frac{Q_2^2 Q_2^2}{R^5} P_4(\mathbf{bn}) - \sum_{m=3}^{\infty} D_{2m}^{(2)} \frac{(\alpha B)^2}{2R^{2m}}. \end{aligned} \quad (12)$$

Here

$$\begin{aligned} \chi_6 &= \frac{45}{32} \alpha^6 \{ \langle 0 | [Br_1]^2 + [Br_2]^2 | 0 \rangle \langle 0 | \{[Br_1]^2 + [Br_2]^2\} \\ &\times G \{[Br_1]^2 + [Br_2]^2\} | 0 \rangle - \langle 0 | \{[Br_1]^2 + [Br_2]^2\} G \{[Br_1]^2 \\ &+ [Br_2]^2\} G \{[Br_1]^2 + [Br_2]^2\} | 0 \rangle \} \end{aligned} \quad (13)$$

is the nonlinear magnetic susceptibility of the order that follows (10)

$$E_{disp}^{(3)} = \langle 0 | V_{12} G V_{12} G V_{12} | 0 \rangle = -\sum_{m=5}^{\infty} \frac{C_{2m+1}^{(3)}}{R^{2m+1}} \quad (14)$$

is the dispersion energy of third order and determines the dispersion constants $C_{2m+1}^{(3)}$ with odd indices, corresponding to the series terms with odd powers of the parameter $1/R$ (Ref. 3).

The third term in (12) is the interaction energy of the electroquadrupole moments induced in the atoms by the magnetic field:

$$Q_2^i = i/12 (\alpha B)^2 \alpha_2^i, \quad (15)$$

where $\alpha_i^i = 2 \langle 0 | r_i^i P_i(\cos\theta_i) G r_i^i P_i(\cos\theta_i) | 0 \rangle$ is the 2^i -pole polarizability of the atom A_i ($i = 1, 2$), and $P_i(\cos\theta)$ is a

Legendre polynomial. Note that the third term in (12) alters the asymptotic dependence of the interatomic potential on the distance R : the principal term of the series for the atom interaction energy in a sufficiently strong magnetic field is proportional to R^{-5} rather than to R^{-6} . This circumstance was first noted for the potential of the hydrogen molecule in Ref. 8. A similar term corresponding to interaction of induced dipoles is contained also in the expression for the interatomic potential in an electric field:

$$E_{\text{dip}} = 2 \frac{Q_i^2 Q_j^2}{R^3} P_2(\mathbf{n}), \quad (16)$$

where

$$Q_i = F \alpha_i, \quad (17)$$

is the electric-dipole moment of the atom A_i , and $\mathbf{F} = F \mathbf{e}$ is the electric field-intensity vector.

Note that neither the dipole-dipole energy (16) nor the quadrupole-quadrupole energy in (12) vanishes when averaged over the orientations of the atoms (over the directions of the vector \mathbf{n}). They make therefore no contribution to the interatomic interaction in the atomic medium and do not manifest themselves in its macroscopic properties. An important role is assumed here by calculation of the terms that determine the change of the coefficients of the dispersion series (11) and (14) under the action of the field \mathbf{B} . As follows from (12), the expression for the energy of a diatomic system in a magnetic field acquires a series having the same dependence on the interatomic distance R as the dispersion series (11), with coefficients proportional to B^2 . This expression is formally manifested in the dependence of the dispersion-series coefficients on the induction of the magnetic field. Account must also be taken here of the contribution of the magnetodipole interaction V_μ , which yields in fourth-order perturbation theory a similar series with coefficients that depend quadratically on B :

$$\Delta E_\mu^{(4)} = -\langle 0 | V_{12} G V_\mu G V_\mu G V_{12} | 0 \rangle = - \sum_{m=3}^{\infty} D_{2m}^{(2)\prime\prime} \frac{(\alpha B)^2}{2R^{2m}}. \quad (18)$$

Combining this series with the last term of (12), we obtain for the correction to the dispersion energy, in second order in B :

$$\Delta E(\mathbf{R}, \mathbf{B}) = - \sum_{m=3}^{\infty} D_{2m}^{(2)} \frac{(\alpha B)^2}{2R^{2m}}, \quad (19)$$

where

$$\begin{aligned} D_{2m}^{(2)} &= D_{2m}^{(2)\prime} + D_{2m}^{(2)\prime\prime} = \frac{1}{6} [\langle r_1^2 \rangle + \langle r_2^2 \rangle] \langle 0 | v_{l_1 l_1}(\mathbf{n}) G^2 v_{l_1 l_1}(\mathbf{n}) | 0 \rangle \\ &- \frac{1}{4} \langle 0 | v_{l_1 l_1}(\mathbf{n}) G [(\mathbf{b} \mathbf{r}_1)^2 + (\mathbf{b} \mathbf{r}_2)^2] G v_{l_1' l_1'}(\mathbf{n}) | 0 \rangle \\ &- \frac{1}{2} \langle 0 | [(\mathbf{b} \mathbf{r}_1)^2 + (\mathbf{b} \mathbf{r}_2)^2] G v_{l_1 l_1}(\mathbf{n}) G v_{l_1' l_1'}(\mathbf{n}) | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | v_{l_1 l_1}(\mathbf{n}) G (\mathbf{b}(\mathbf{J}_1 + \mathbf{S}_1) + \mathbf{J}_2 + \mathbf{S}_2) G v_{l_1 l_1}(\mathbf{n}) | 0 \rangle. \end{aligned} \quad (20)$$

These quantities determine the correction quadratic in B to the coefficients of the dispersion series (11):

$$C_{2m}(\mathbf{B}) = C_{2m}^{(2)} + \frac{1}{2} (\alpha B)^2 D_{2m}^{(2)}(\mathbf{n}, \mathbf{b}). \quad (21)$$

On the other hand, the coefficients $D_{2m}^{(2)}$ are indicative of the

change introduced into the diamagnetic susceptibility by the interaction between the atoms:

$$\chi_2(\mathbf{R}) = \chi_2 + \alpha^2 \sum_{m=3}^{\infty} \frac{D_{2m}^{(2)}(\mathbf{n}, \mathbf{b})}{R^{2m}}. \quad (22)$$

It must be borne in mind, however, that in the fourth and fifth orders of perturbation theory, where account is taken of the corrections cubic in the interaction V_{12} between the atoms, there appear terms proportional to odd powers of $1/R$, starting with $(1/R)^{11}$ (Ref. 3); these, strictly speaking should be taken into account in the expression for $\chi_2(\mathbf{R})$. To find the corrections to the nonlinear susceptibilities χ_n ($n > 2$), and also corrections of higher degree in αB to the coefficients of the dispersion series (21), expressions of even higher orders of perturbation theory must be used.

3. IRREDUCIBLE PARTS OF THE TENSOR $D_{2m}^{(2)}(\mathbf{n}, \mathbf{b})$

After integrating over the angle variables in the expression (20) for atoms in S -states, we obtain:

$$D_{2m}^{(2)}(\mathbf{n}, \mathbf{b}) = D_{2m\perp}^{(2)} + \Delta D_{2m}^{(2)} \cos^2 \theta, \quad (23)$$

where $\cos \theta = \mathbf{b} \mathbf{n}$, and

$$\Delta D_{2m}^{(2)} = D_{2m\parallel}^{(2)} - D_{2m\perp}^{(2)} \quad (24)$$

is the anisotropy that determines the difference between the longitudinal $D_{2m\parallel}^{(2)}$ and the transverse $D_{2m\perp}^{(2)}$ components, which yield in turn the values of the coefficients $D_{2m}^{(2)}$ in (21) and (22) for $\mathbf{R} \parallel \mathbf{B}$ and $\mathbf{R} \perp \mathbf{B}$, respectively. In addition to the foregoing, one can introduce one more averaged characteristic, called the isotropic susceptibility:

$$\overline{D}_{2m}^{(2)} = \frac{1}{4\pi} \int D_{2m}^{(2)}(\mathbf{n}, \mathbf{b}) d\Omega_n = \frac{1}{3} D_{2m\parallel}^{(2)} + \frac{2}{3} D_{2m\perp}^{(2)}, \quad (25)$$

which yields the value of $D_{2m}^{(2)}$ averaged over the orientations of the vector \mathbf{n} .

All these quantities can be expressed in terms of linear combinations of radial diatomic matrix elements of third or fourth order. In particular,

$$\begin{aligned} D_{6\perp}^{(2)} &= \frac{1}{9} (\langle r_1^2 \rangle + \langle r_2^2 \rangle) \langle 0 | r_1 r_2 (g_{11})^2 r_1 r_2 | 0 \rangle \\ &- \frac{11}{90} \langle 0 | r_1 r_2 g_{11} (r_1^2 + r_2^2) g_{11} r_1 r_2 | 0 \rangle \\ &- \frac{2}{9} \langle 0 | [r_1^2 (g_0^{E_1} + \frac{1}{10} g_2^{E_1}) \\ &+ r_2^2 (g_0^{E_2} + \frac{1}{10} g_2^{E_2})] r_1 r_2 g_{11} r_1 r_2 | 0 \rangle \\ &+ \frac{1}{3} \langle 0 | r_1 r_2 (g_{11})^3 r_1 r_2 | 0 \rangle, \end{aligned} \quad (26)$$

$$\begin{aligned} \Delta D_{6\parallel}^{(2)} &= \frac{1}{30} \langle 0 | r_1 r_2 g_{11} (r_1^2 + r_2^2) g_{11} r_1 r_2 | 0 \rangle + \frac{1}{15} \langle 0 | (r_1^2 g_2^{E_1} \\ &+ r_2^2 g_2^{E_2}) r_1 r_2 g_{11} r_1 r_2 | 0 \rangle - \frac{1}{3} \langle 0 | r_1 r_2 (g_{11})^3 r_1 r_2 | 0 \rangle. \end{aligned} \quad (27)$$

Here $g_{l_i}^{E_i}$ is the radial Green's function of an individual i th atom with energy E_i in a subspace of states with angular momentum l_i , and $g_{l_1 l_2}$ is a two-atom radial Green's function in the subspace of states with angular momentum l_1 for atom A_1 and l_2 for atom A_2 . The matrix elements in (26) and (27) can be calculated by using for a diatomic Green's function an

integral representation, which makes it possible to factor out the variables of the atoms A_1 and A_2 (generalization of the known Casimir-Polder formula)

$$g_{l_1 l_2}(r_1 r_2, r_1' r_2') = \frac{2}{\pi} \int_0^\infty \text{Re } g_{l_1}^{E_1+i\omega}(r_1 r_1') \text{Re } g_{l_2}^{E_2+i\omega}(r_2 r_2') d\omega, \quad (28)$$

where $E_{1(2)}$ is the energy of the isolated atom A_1 (A_2). Using this generalization, the radial matrix elements in (26) and (27) are expressed in terms of integrals of products of single-atom matrix elements:

$$\begin{aligned} \langle 0 | r_1 r_2 (g_{11})^2 r_1 r_2 | 0 \rangle &= \frac{1}{\pi^2} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \text{Re}[\rho_{11}^{101}(i\omega_1, i\omega_2) \\ &+ \rho_{11}^{101}(i\omega_1, -i\omega_2)] \text{Re}[\rho_{11}^{101}(i\omega_1, i\omega_2) + \rho_{11}^{101}(i\omega_1, -i\omega_2)], \end{aligned} \quad (29a)$$

$$\begin{aligned} \langle 0 | r_1 r_2 g_{11} r_1^2 g_{11} r_1 r_2 | 0 \rangle &= \frac{1}{\pi^2} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \text{Re}[\rho_{11}^{121}(i\omega_1, i\omega_2) \\ &+ \rho_{11}^{121}(i\omega_1, -i\omega_2)] \text{Re}[\rho_{11}^{101}(i\omega_1, i\omega_2) + \rho_{11}^{101}(i\omega_1, -i\omega_2)], \end{aligned} \quad (29b)$$

$$\langle 0 | r_1^2 g_{11}^E r_1 r_2 g_{11} r_1 r_2 | 0 \rangle = \frac{2}{\pi} \int_0^\infty d\omega \text{Re}[\rho_{11}^{211}(0, i\omega) \text{Re}[\rho_{11}^{11}(i\omega)], \quad (29c)$$

$$\begin{aligned} \langle 0 | r_1 r_2 (g_{11})^3 r_1 r_2 | 0 \rangle &= \frac{1}{2\pi^3} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \int_0^\infty d\omega_3 \text{Re}[\rho_{111}^{1001}(i\omega_1, i\omega_2, i\omega_3) \\ &+ \rho_{111}^{1001}(i\omega_1, i\omega_2, -i\omega_3) + \rho_{111}^{1001}(i\omega_1, -i\omega_2, i\omega_3) \\ &+ \rho_{111}^{1001}(i\omega_1, -i\omega_2, -i\omega_3) + \rho_{111}^{1001}(-i\omega_1, i\omega_2, i\omega_3)] \\ &\quad \text{Re}[\rho_{111}^{1001}(i\omega_1, i\omega_2, i\omega_3) + \rho_{111}^{1001}(i\omega_1, i\omega_2, -i\omega_3) \\ &+ \rho_{111}^{1001}(i\omega_1, -i\omega_2, i\omega_3) + \rho_{111}^{1001}(-i\omega_1, i\omega_2, i\omega_3)], \end{aligned} \quad (29d)$$

where

$$\begin{aligned} \rho_{l_1 l_2 \dots l_N}^{n_1 n_2 \dots n_N+1}(\omega_1, \dots, \omega_N) \\ = \langle 0 | r^{n_1} g_{l_1}^{E_1+\omega_1} r^{n_2} \dots r^{n_N} g_{l_N}^{E_2+\omega_N} r^{n_{N+1}} | 0 \rangle \end{aligned}$$

is a single-atom radial matrix element of order N . Using the Sturm expansion for the single-atom Green's function $g_l^E(r, r')$, we can represent this matrix element in the form of an N -fold series of hypergeometric type, which converges rapidly enough in the range of those integration variables in expressions (29a-29d) which make the main contribution ($\omega_i \lesssim 10$). The speed and accuracy of calculation of the integrals (29) can be substantially increased by using the change of variables

$$\omega = t / (1-t)^{1/(2N-1)}, \quad 0 \leq t \leq 1,$$

where N is the order of the matrix element. To obtain numerical values of the integrals in (29) with a relative error not larger than 10^{-3} it suffices to use a Gaussian quadrature of seventh order for each of the integrals in the multiple integration. A calculation of hydrogen atoms in ground states yields

$$D_{6\perp}^{(2)} = -78.70, \quad \Delta D_6^{(2)} = 21.80.$$

Note that all these values are substantially lower (by about 2 orders) in absolute value than the components of the tensor A_6 which characterizes the variation of the Van der Waals constant in an electric field.^{6,7} In addition, $D_{6P}^{(2)}$ is always negative, whereas A_6 is positive, demonstrating that the electric magnetic fields exert opposite actions on the interatomic forces (increase by the electric field, decrease by the magnetic).

Notwithstanding the smallness of the corrections to the dispersion forces in the magnetic field, it is nonetheless important to know their values in view of the rapid decay (ionization) of the atom in a strong electric field, whereas in super-strong magnetic field the atom can remain stable.

4. APPROXIMATE CALCULATIONS OF DIATOMIC SUSCEPTIBILITIES USING MONATOMIC QUANTITIES

The variables of the atoms A_1 and A_2 in expressions (26) and (27) can also be separated by using the approximation of the effective excitation energy; this reduces to the substitution

$$g_{l_1 l_2}(r_1 r_2, r_1' r_2') = \delta(r_1 - r_1') \delta(r_2 - r_2') / (\omega_{l_1}^{(1)} + \omega_{l_2}^{(2)}), \quad (30)$$

where $\omega_{l_i}^{(i)}$ is the effective excitation energy of the levels of the atom A_i with angular momentum l_i . This value can be determined using a corresponding single-atom matrix element.³ Using (30), the elements (29) can be represented in the form

$$\langle 0 | r_1 r_2 (g_{11})^2 r_1 r_2 | 0 \rangle = \langle r_1^2 \rangle \langle r_2^2 \rangle / [\omega_{1(0)}^{(1)} + \omega_{1(0)}^{(2)}]^2, \quad (31a)$$

$$\langle 0 | r_1 r_2 g_{11} r_1^2 g_{11} r_1 r_2 | 0 \rangle = \langle r_1^4 \rangle \langle r_2^2 \rangle / [\omega_{1(2)}^{(1)} + \omega_{1(0)}^{(2)}]^2, \quad (31b)$$

$$\begin{aligned} \langle 0 | r_1^2 g_{11}^E r_1 r_2 g_{11} r_1 r_2 | 0 \rangle \\ = \langle r_1^4 \rangle \langle r_2^2 \rangle / [\omega_{1(l)}^{(1)} (\omega_{1(l)}^{(1)} + \omega_{1(l)}^{(2)})], \quad l=0, 2, \end{aligned} \quad (31c)$$

$$\langle 0 | r_1 r_2 (g_{11})^3 r_1 r_2 | 0 \rangle = \langle r_1^2 \rangle \langle r_2^2 \rangle / [\omega_{1(00)}^{(1)} + \omega_{1(00)}^{(2)}]^3. \quad (31d)$$

The excitation energies ω employed here are determined from the monatomic values as follows:

$$\begin{aligned} \omega_1^{(i)} &= \frac{\langle r_1^2 \rangle}{\rho_{11A_i}^{11}(0)}, \quad \omega_{1(l)}^{(i)} = \left[\frac{\langle r_1^{2+l} \rangle}{\rho_{11A_i}^{11}(0)} \right]^{1/2}, \\ \omega_l^{(i)} &= \frac{\langle r_1^4 \rangle}{\rho_{11A_i}^{211}(0) \omega_l^{(i)}}, \quad \omega_{1(00)}^{(i)} = \left[\frac{\langle r_1^2 \rangle}{\rho_{11A_i}^{1001}(0)} \right]^{1/3}. \end{aligned} \quad (32)$$

The mean values of the operators r^2 and r^4 in (32) and the monatomic radial matrix elements $\rho_{11A_i}^{..}$ for multielectron atoms can be calculated by the Fusse model-potential method.⁹ Within the framework of this method, the wave functions and the Green's functions are represented in simple

TABLE I. Numerical values of the parameters of the tensor $D_6^{(2)}$.

| atoms A_1-A_2 | $-D_{6\perp}^{(2)}$ | $\Delta D_6^{(2)}$ |
|--------------------|---------------------|--------------------|--------------------|---------------------|--------------------|--------------------|---------------------|--------------------|--------------------|---------------------|--------------------|
| H–H | 9.00(1) | 2.42(1) | He–Rb | 4.08(3) | 2.13(3) | Na–Na | 1.58(5) | 5.74(4) | Rb–Cs | 1.24(6) | 6.65(5) |
| H–He | 2.59(1) | 7.17 | He–Cs | 5.72(3) | 3.51(3) | Na–K | 3.29(5) | 1.36(5) | Rb–Ar | 3.75(4) | 1.99(4) |
| H–Li | 3.50(3) | 1.40(3) | He–Ar | 7.02(1) | 2.44(1) | Na–Rb | 3.96(5) | 1.74(5) | Rb–Kr | 5.24(4) | 2.79(4) |
| H–Na | 4.29(3) | 1.73(3) | He–Kr | 1.11(2) | 4.16(1) | Na–Cs | 5.32(5) | 2.71(5) | Rb–Xe | 7.91(4) | 4.25(4) |
| H–K | 9.60(3) | 4.58(3) | He–Xe | 1.95(2) | 7.99(1) | Na–Ar | 1.32(4) | 5.68(3) | Cs–Cs | 1.62(6) | 9.35(5) |
| H–Rb | 1.19(4) | 6.06(3) | Li–Li | 1.26(5) | 4.05(4) | Na–Kr | 1.85(4) | 8.05(3) | Cs–Ar | 5.25(4) | 3.25(4) |
| H–Cs | 1.66(4) | 9.91(3) | Li–Na | 1.43(5) | 4.95(4) | Na–Xe | 2.81(4) | 1.24(4) | Cs–Kr | 7.33(4) | 4.54(4) |
| H–Ar | 2.51(2) | 8.31(1) | Li–K | 3.04(5) | 1.22(5) | K–K | 6.67(5) | 2.95(5) | Cs–Xe | 1.11(5) | 6.88(4) |
| H–Kr | 3.68(2) | 1.30(2) | Li–Rb | 3.69(5) | 1.59(5) | K–Rb | 7.94(5) | 3.69(5) | Ar–Ar | 6.91(2) | 2.90(2) |
| H–Xe | 5.97(2) | 2.32(2) | Li–Cs | 5.03(5) | 2.56(5) | K–Cs | 1.05(6) | 5.48(5) | Ar–Kr | 1.04(3) | 4.57(2) |
| He–He | 5.95 | 1.54 | Li–Ar | 1.05(4) | 4.58(3) | K–Ar | 3.00(4) | 1.50(4) | Ar–Xe | 1.74(3) | 8.19(2) |
| He–Li | 1.13(3) | 4.78(2) | Li–Kr | 1.48(4) | 6.53(3) | K–Kr | 4.20(4) | 2.10(4) | Kr–Kr | 1.53(3) | 7.04(2) |
| He–Na | 1.43(3) | 6.00(2) | Li–Xe | 2.26(4) | 1.02(4) | K–Xe | 6.34(4) | 3.22(4) | Kr–Xe | 2.50(3) | 1.22(3) |
| He–K | 3.26(3) | 1.60(3) | | | | Rb–Rb | 9.42(5) | 4.56(5) | Xe–Xe | 3.98(3) | 2.05(3) |

Note. (n) = 10ⁿ

analytic form, so that the quantities in (31) are expressed in terms of Gamma functions and series of the hypergeometric type. In particular:

$$\langle r^L \rangle = (v_0/2)^L (2v_0+1)_L N_e N_0^2 \quad (L=1, 2, 3, \dots),$$

$$\omega_1 = \left\{ \frac{v_0^2}{2} \frac{[\Gamma(v_0+\lambda_1+3)]^2}{\Gamma(2v_0+3)\Gamma(2\lambda_1+2)(\lambda_1+1-v_0)} \right\}^{-1}.$$

$$\times {}_3F_2(\lambda_1-v_0-1, \lambda_1-v_0-1, \lambda_1-v_0+1; 2\lambda_1+2, \lambda_1-v_0+2; 1).$$

Here N_e is the number of valence electrons, N_0 is a factor that corrects the normalization of the ground state in accordance with the pseudopotential method, and v_0 and λ_k are parameters determined from the spectrum of the atom:⁹ $v_k = 1/\sqrt{-2E_k}$, $\lambda_k = v_k - 1$.

The table lists the numerical values of the components of the tensor $D_6^{(2)}$ for different pairs of atoms of hydrogen, alkali metals, and inert gases. It should be noted that the deviation of the tabulated approximate value for the hydrogen atom from the exact value obtained in the preceding section is about 10%, i.e., of the same order as the accuracy of the Fusse model potential used in the calculations for multielectron atoms.⁹ This allows us to regard the tabulated data as reliable enough. Just as for hydrogen, the component $D_{61}^{(2)}$ is negative and exceeds in absolute value the positive anisotropy $\Delta D_6^{(2)}$ of all pairs of atoms; this corresponds to a weakening of the dispersion interaction, which comes into play more strongly in transverse directions ($\mathbf{R} \perp \mathbf{B}$) than in longitudinal ones ($\mathbf{R} \parallel \mathbf{B}$).

We note in conclusion that the tabulated data can be used to obtain the asymptotic values of the diamagnetic sus-

ceptibility $\chi_2(R)$ of a diatomic molecule. We know at present of computations of $\chi_2(R)$ for the hydrogen molecules, obtained by perturbation theory on a variational basis, which take explicit account of interatomic correlation interactions.^{10–12} The numerical results for the H₂ molecule in the ground state¹⁰ in the asymptotic region $R \gg 1$ agree qualitatively with the analytic relation (22). The quantitative discrepancies are due in our opinion to inaccuracy of the calculations of Ref. 10 in the asymptotic region, in view of the large number of approximated variational parameters in the wave function of the molecule. Consequently expression (22) together with the numerical data in the table provide more reliable information on the $\chi_2(R)$ dependence in the region $R \gg 1$, where the exchange interaction between the atoms becomes negligible compared with the dispersion interaction, both for hydrogen and for other diatomic systems.

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Translated by J. G. Adashko