Electronic polarizability of the N_2 and O_2 molecules: the role of exchange interactions

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A semiempirical method is proposed to describe the polarizability function for diatomic homonuclear molecules taking into account exchange interatomic interactions. The exchange interactions are described in the analytical form within the framework of the asymptotic method. The polarizability functions are represented in the form of piecewise-continuous functions, which have a physically true behavior at small and large internuclear separations and describe correctly the polarizability near the equilibrium position of molecular nuclei. The polarizability functions for the N_2 and O_2 molecules are calculated in the internuclear separation range [0, ∞).

Introduction

The concept of electronic polarizability of molecules appears in the polarizability theory as a result of application of the adiabatic approximation and neglect of the rotational-vibrational structure of electronic energy levels. The electronic polarizability is a second-rank tensor, whose components are functions of coordinates of molecular nuclei and the frequency ω of the external electric field. For diatomic molecules, the tensor of electronic polarizability has only two independent components (polarizability functions)

$$\alpha_{zz}(\omega,R) \text{ and } \alpha_{xx}(\omega,R) = \alpha_{yy}(\omega,R),$$

where R is the internuclear separation, and the axis z coincides with the molecular axis. The frequency dependence of the polarizability functions becomes noticeable only when the frequency of the external electric field approaches the frequencies of electronic transitions in the molecule.

At present, the polarizability functions of diatomic molecules are calculated using quantum-chemistry and semiempirical methods. The former methods are applied to relatively small parts of internuclear separations in the vicinity of the equilibrium position R_e, and only for the H_2 molecule such calculations have been carried out for the entire range of R variability.[1,2] Semiempirical methods are used for calculation of polarizability functions of diatomic molecules all over the range of internuclear separations in the case that the *ab initio* methods fail to give the reliable values of the polarizability functions. Only a few semiempirical polarizability functions of diatomic molecules are known,[3–6] but the models used for construction of these functions have some methodical disadvantages. Thus, the polarizability functions determined in Refs. 4 and 5 do not satisfy their known asymptotic dependences at large[4] and small[4,5] R values. In addition, the polarizability functions in Ref. 5 are constructed based on the empirical regularities found in that paper, but their universality is under question. The polarizability functions in Refs. 3 and 6 are free of these disadvantages, but the neglect of exchange interactions leads to their underestimation in the range of medium internuclear separations.

This paper presents a further development of the semiempirical method proposed in Refs. 3 and 6. This development consists in refinement of the behavior of polarizability functions in the range of medium R values through consideration of exchange interactions between the approaching atoms. The method is applied to determination of polarizability functions for N_2 and O_2 molecules in the entire interval $R \in [0, \infty)$.

Contribution of exchange interatomic interactions to polarizability functions of homonuclear molecules

Polarizability of a molecule at long internuclear separations can be described based on the idea about interactions between the atoms forming this molecule. Two types of the interatomic interactions can be distinguished: multipole (long-range) and exchange ones, for which the polarizability function of a molecule can be described analytically. Each of these interactions is decisive in its own range of internuclear separations: multipole one at $R \to \infty$ and exchange one at shorter R.

To take into account the exchange interaction between electrons of two atoms, it is possible to use asymptotic methods,[7] which are applicable at the internuclear separations characterized by slight overlapping of the valence electrons of interacting atoms. In this range, the exchange interaction of atoms can be approximately considered as an exchange interaction of two valence electrons (by one from each atom).

Consider the interaction of two valence *s*-electrons. In this case, the asymptotic radial wave function of a valence electron of a neutral atom is determined by the following equation[7]:

$$\varphi(r) = Ar^{1/\beta-1}e^{-r\beta}, \qquad (1)$$

where $\beta^2/2$ is the atom ionization potential, and the value of the asymptotic coefficient A depends on the electron distribution in the internal zone of the atom. Then the two-electron (one electron from atom a and one from atom b) molecular wave function of the state n can be written in the form

$$\Psi_n(r_1,r_2,R) = c_n^{(1)}\psi_n^{(1)}(r_1,r_2,R) + c_n^{(2)}\psi_n^{(2)}(r_1,r_2,R), \qquad (2)$$

where

$$\psi_n^{(1)}(r_1,r_2,R) = \left[\varphi^{(a)}(r_1,R)\varphi^{(b)}(r_2,R)\chi_{\text{I}}(r_1,r_2,R)\right]_n,$$

$$\psi_n^{(2)}(r_1,r_2,R) = \left[\varphi^{(a)}(r_2,R)\varphi^{(b)}(r_1,R)\chi_{\text{II}}(r_1,r_2,R)\right]_n.$$

Here $\varphi^{(a)}(r_1,R)$, $\varphi^{(b)}(r_1,R)$ and $\varphi^{(a)}(r_2,R)$, $\varphi^{(b)}(r_2,R)$ are asymptotic wave functions of the first and second electrons located largely near the corresponding atomic cores. Equations (2) and (3) are written in the molecular coordinate system, in which the interacting atoms are located on the axis z, and the center of the interatomic separation is taken as the origin of coordinates. In this coordinate system, r_1 and r_2 are the coordinates of the first and second electrons. The explicit form of the functions $\chi_{\text{I}}(r_1, r_2, R)$ and $\chi_{\text{II}}(r_1, r_2, R)$ accounting for the interaction of electrons with each other and with foreign nuclei is given in Ref. 7.

For calculation of the static polarizability tensor of a diatomic molecule in the electronic state n, we use the quantum-mechanical equation for components of the electronic polarizability tensor

$$\alpha_{ii}^{(n)}(R) = 2\sum_{m\neq n}\frac{\left|\langle n(R)\left|d_i\right|m(R)\rangle\right|^2}{E_m(R)-E_n(R)}. \qquad (4)$$

In the calculation of the molecular polarizability, the exchange interaction shows itself through its contribution to the matrix element of the dipole moment of the electronic transition $\langle n(R)|d_i|m(R)\rangle$ and the difference between the electronic energy levels of the molecule $E_m(R)-E_n(R)$; and the contribution to the matrix element of the dipole moment of the electronic transition is decisive. The contribution of the exchange interaction to the ith component of the dipole moment calculated by Eqs. (2) and (3) for a homonuclear molecule can be represented in the form

$$\langle n(R)\left|d_i\right|m(R)\rangle \quad \langle\Psi_n^{(1)}(r_1,r_2,R)\left|d_i\right|\Psi_m^{(2)}(r_1,r_2,R)\rangle =$$

$$= A_{nm}^{i}(\beta_n,\beta_m,R)R^{\delta_i}\exp[-(3\beta_n+\beta_m)R/2], \qquad (5)$$

where $A_{nm}^{i}(\beta_n,\beta_m,R)$ is the function weakly depending on R in the range of slight overlapping of electron shells of atoms; $\beta_n^2/2$ and $\beta_m^2/2$ are ionization potentials of the atoms in the ground and excited states, respectively, and

$$\delta_z = \frac{11}{4\beta_n}+\frac{1}{\beta_m}-\frac{1}{2(\beta_n+\beta_m)}+1,$$

$$\delta_{x,y} = \frac{11}{4\beta_n}+\frac{1}{\beta_m}-\frac{1}{2(\beta_n+\beta_m)}+\frac{1}{2}. \qquad (6)$$

Then, after substitution of Eq. (5) into the equation for the components of the electronic polarizability tensor (4) and substitution of some effective parameter $\bar\beta$ for β_m, the equation for the contribution of the exchange interaction to the molecular polarizability takes the form

$$\alpha_{ii}^{(n)}(R) = B_i(\beta_n,\bar\beta,R)R^{2\delta_i}\exp\left[-(3\beta_n+\bar\beta)R\right]. \qquad (7)$$

Here $B_i(\beta_n,\bar\beta,R)$ also weakly depends on R and is assumed a parameter B_i in what follows.

The result obtained can also be applied in case that the interacting electrons have nonzero orbital moments l. This is connected with the fact that the exchange interaction occurs in the range of electron coordinates near the axis z, where the wave angular functions of the electrons vary slightly, therefore, they can be replaced by the values on the axis z with the zero projection of the orbital moment. As a consequence, the problem of exchange interaction of the valence l-electrons reduces to the problem considered above with the only difference that the coefficient A in Eq. (1) should be multiplied by $\sqrt{2l+1}$ [Ref. 8].

Method for construction of polarizability functions

The semiempirical method[3,6] for construction of the polarizability functions of diatomic molecules in the ground electronic state (hereinafter the subscript n of the molecular parameters is omitted) implies that the following three conditions are met.

1. The polarizability functions $\alpha_{zz}(R)$ and $\alpha_{xx}(R) = \alpha_{yy}(R)$ of the molecule in the range of small R are described by the following polynomials[9]:

$$\alpha_{ii}(R) = \alpha_{ii}^{(0)} + a_i^{(2)}R^2 + a_i^{(3)}R^3 + a_i^{(4)}R^4 + \cdots, \qquad (8)$$

where $\alpha_{ii}^{(0)}$ are the components of polarizability of the "joint" atom, and the constants $a_i^{(k)}$ ($k \geq 2$) are proposed to be determined using the known values of the polarizability functions and their derivatives at the point R_e. Polynomials (8) with the determined coefficients $a_i^{(k)}$ describe the molecular polarizability functions in the range of small R, including the vicinity of the equilibrium internuclear separation.

2. Polarizability functions of a molecule in the range of large R can be presented as sums of

contributions from the multipole[3] and exchange interactions:

$$\alpha_{zz}(R) = 2\alpha_{zz}^{0} + 4(\alpha_{zz}^{0})^{2}\frac{1}{R^{3}} + \left[8(\alpha_{zz}^{0})^{3} + \frac{7\gamma C_6}{9\alpha_0}\right]\frac{1}{R^{6}} + $$
$$+18\alpha_0^{3}\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^{2}}{R^{8}} + 16(\alpha_{zz}^{0})^{4}\frac{1}{R^{9}} + $$
$$+32\alpha_0^{3}\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^{4}}{R^{10}} + B_z R^{2\delta_z}\exp\left[-(3\beta_0+\bar{\beta})R\right] \qquad (9)$$

and

$$\alpha_{xx}(R) \equiv \alpha_{yy}(R) = 2\alpha_{xx}^{0} - 2\left(\alpha_{xx}^{0}\right)^{2}\frac{1}{R^{3}} + $$
$$+\left[2\left(\alpha_{xx}^{0}\right)^{3} + \frac{4\gamma C_6}{9\alpha_0}\right]\frac{1}{R^{6}} + 6\alpha_0^{3}\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^{2}}{R^{8}} - $$
$$-2\left(\alpha_{xx}^{0}\right)^{4}\frac{1}{R^{9}} + 12\alpha_0^{3}\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^{4}}{R^{10}} + $$
$$+B_x R^{2\delta_x}\exp\left[-(3\beta_0+\bar{\beta})R\right]. \qquad (10)$$

Here α_{ii}^{0} are the components of the atomic polarizability tensor; r_0 is the Van-der-Waals radius of the interacting atoms; α_0 is the mean polarizability of the atom; C_6 is the coefficient of the Van-der-Waals interaction between atoms; γ is the mean second hyperpolarizability of the atom, and the effective permittivity ε of the atom is determined from the equation

$$\alpha_0 = \frac{\varepsilon-1}{\varepsilon+2}r_0^{3}. \qquad (11)$$

In this paper, B_i are determined by fitting $\alpha_{ii}(R)$ to the *ab initio* data for the H_2 molecule[2] in the range of slight overlapping of electron shells of H atoms. Then, taking into account the scaling factor reflecting the size of the electron shells of the atoms, they are extended to other homonuclear molecules.

3. The polarizability functions of the molecule in the intermediate range of the internuclear separations are determined by the method of sewing together the polarizability functions at small and large R and described by the fifth-order polynomials in terms of R:

$$\alpha_{ii}(R) = \sum_{j=0}^{5} b_i^{(j)}R^{j}, \qquad (12)$$

the coefficients $b_i^{(j)}$ are determined from the sewing conditions accurate to the second derivatives inclusive. In this paper, the sewing points R_1 and R_2 are chosen as: $R_1 \approx R_e$, $R_2 \approx 2r_0$. Such a choice accepts some arbitrariness, which does not significantly change the form of the polarizability functions.

Polarizability functions of N_2 and O_2 molecules

We have calculated the polarizability functions of the H_2, N_2, and O_2 homonuclear molecules; and the reliable *ab initio* values of the polarizability functions of the H_2 molecule[2] were used to test the proposed model and to find the unknown B_i in Eqs. (9) and (10). The values of atomic and molecular constants, as well as ε, B_i, $\bar{\beta}$, R_1, and R_2 used in the calculation are tabulated below. The coefficients B_i ($\equiv B_i^{(H)}$) of the exchange interaction of the H atoms were determined by the least-square method from the data of the *ab initio* calculation of the polarizability functions $\alpha_{ii}(R)$ [Ref. 2] at the internuclear separations $2.4 \le R < 4.0$ Å. The coefficients B_i for the atoms N and O were calculated by the equation $B_i^{(\mathrm{N,O})} = 9B_i^{(\mathrm{H})}A_{(\mathrm{N,O})}^{i}/\ A_{(\mathrm{H})}^{6}$, where $A_{(\mathrm{N,O})}$ is the parameter of the asymptotic radial wave function of the valence *p*-electron of, respectively, N and O atoms, and $A_{(\mathrm{H})}$ is the parameter of the asymptotic radial wave function of the valence *s*-electron of the H atom. The parameter $\bar{\beta}$ was estimated based on the probabilities of radiative transitions in H, N, and O atoms.

Figure 1 depicts the polarizability functions of the H_2 molecule calculated taking into account and neglecting the exchange interactions between the H atoms.

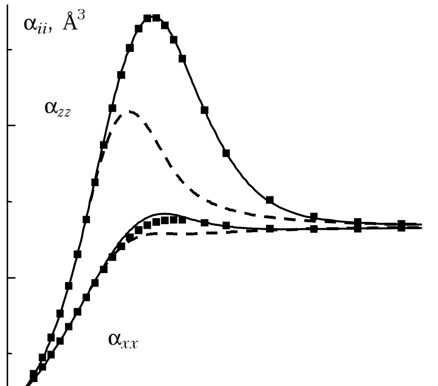

Fig. 1. Polarizability function of the H_2 molecule: this work (solid curves), this work neglecting the exchange interaction (dashed curves), *ab initio* calculation[2] (squares).

It is clearly seen that accounting for the contribution of these interactions into $\alpha_{ii}(R)$ allows a close agreement with the *ab initio* data[2] in the entire range of the internuclear separations. The use of a single fitting parameter B_i is indicative of the physical correctness of the description of the contribution from the exchange interactions to $\alpha_{ii}(R)$.

Parameters for calculation of the polarizability functions of H_2, N_2, and O_2 molecules

Molecule Term	H_2 $^1\Sigma_g^+$	N_2 $^1\Sigma_g^+$	O_2 $^3\Sigma_g^-$	
$(\alpha_{xx})_e$, Å^3	0.679[a]	1.53 [Ref. 10]	1.25 [Ref. 10]	
$(\alpha'_{xx})_e$, Å^3	0.669[a]	1.12 [Ref. 10]	0.70 [Ref. 10]	
$(\alpha''_{xx})_e$, Å^3	0.121[a]	0.33 [Ref. 10]	0.80[b]	
$(\alpha_{zz})_e$, Å^3	0.947[a]	2.24 [Ref. 10]	2.33 [Ref. 10]	
$(\alpha'_{zz})_e$, Å^3	1.372[a]	3.35 [Ref. 10]	3.89 [Ref. 10]	
$(\alpha''_{zz})_e$, Å^3	1.221[a]	2.93 [Ref. 10]	8.60[b]	
"Joint" atom	He	Si	S	
Term	^{1}S	^{1}D ($M_L = 0$)	^{3}P (M_L=0)	
$\alpha^{(0)}_{xx}$, Å^3	0.205 [Ref. 11]	5.62 [Ref. 12]	2.68 [Ref. 12]	
$\alpha^{(0)}_{zz}$, Å^3	0.205 [Ref. 11]	7.50 [Ref. 12]	3.35 [Ref. 12]	
Isolated atom	H	N	O	
Term	^{1}S	^{4}S	^{3}P (M_L= 0)	^{3}P (M_L= ±1)
α^0_{xx}, Å^3	0.6668 [Ref. 11]	1.101[c]	0.755[c]	0.825[c]
α^0_{zz}, Å^3	0.6668 [Ref. 11]	1.101[c]	0.895[c]	0.755[c]
α_0, Å^3	0.6668	1.101	0.802	
r_0, Å^3	1.1 [Ref. 13]	1.5 [Ref. 13]	1.4 [Ref. 13]	
ε	4.01[d]	2.45 [d]	2.24[d]	
$\gamma\, C_6$, Å^{12}	4.18[e]	10.51 [e]	5.03[e]	
β_0, a.u.	1.000 [Ref. 8]	1.033 [Ref. 8]	1.000 [Ref. 8]	
$\bar{\beta}$, a.u.	0.41	0.31	0.31	
A, a.u.	2.00 [Ref. 8]	1.49 [Ref. 8]	1.32 [Ref. 8]	
B_x, Å$^{(3-2\delta)}$	32.60	50.16	24.25	
B_z, Å$^{(3-2\delta)}$	108.81	167.44	80.94	
R_1, Å	0.9	1.1	1.2	
R_2, Å	2.2	3.0	2.8	

[a] Calculated from the data of Ref. 2; [b] the values refined in this work as compared to Ref. 10; [c] borrowed from the Table in Ref. 6; [d] calculated by Eq. (11); [e] the values of γ and C_6 for H are borrowed from Ref. 14, γ for N and O is borrowed from Ref. 15, C_6 for N and O is taken from Ref. 16.

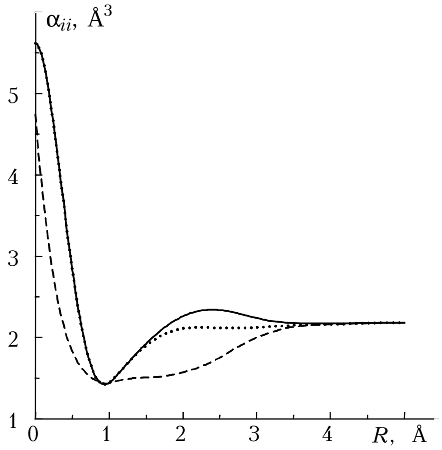

Fig. 2. Polarizability function $\alpha_{xx}(R)$ of the N_2 molecule: this work (solid curve), our calculation neglecting the exchange interaction (dotted curve), calculation in Ref. 5 (dashed curve).

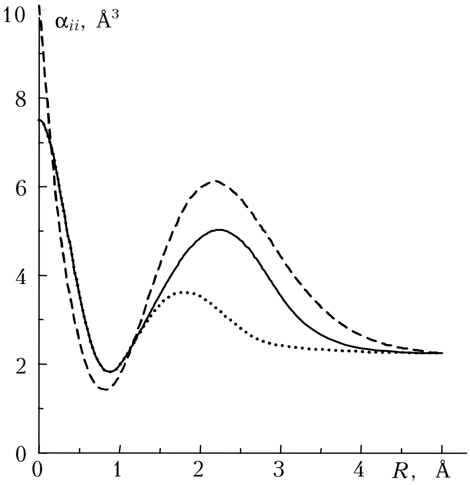

Fig. 3. Polarizability function $\alpha_{zz}(R)$ of the N_2 molecule: this work (solid curve), our calculation neglecting the exchange interaction (dotted curve), calculation in Ref. 5 (dashed curve).

The proposed method of the polarizability function calculation was applied to N_2 and O_2, and for O_2 the both channels of its decomposition were considered (Figs. 2–5).

It is clearly seen that, as for the H_2 molecule, the allowance for the exchange interactions between atoms leads to an increase of the polarizability functions for N_2 and O_2 molecules in the 1 to 3 Å range of the internuclear separations. Note that the calculated polarizability functions for N_2 and O_2 should be considered as approximate, because B_i and $\bar{\beta}$ for N_2 and O_2 are only estimating parameters. Nevertheless, we guess that the polarizability functions for N_2 and O_2 obtained by us are more accurate than those from Refs. 3–6.

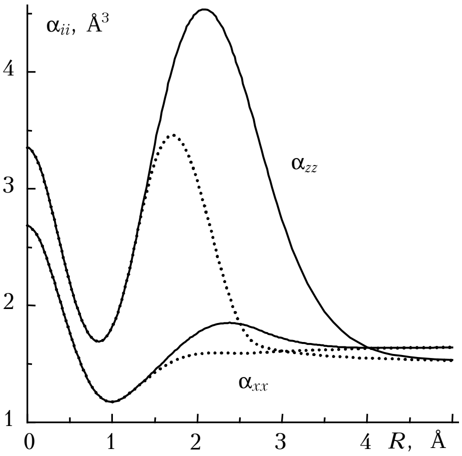

Fig. 4. Polarizability functions of O_2 (the O atoms at the states with $|M_L| = 1$): this work (solid curves), this work neglecting the exchange interactions (dotted curves).

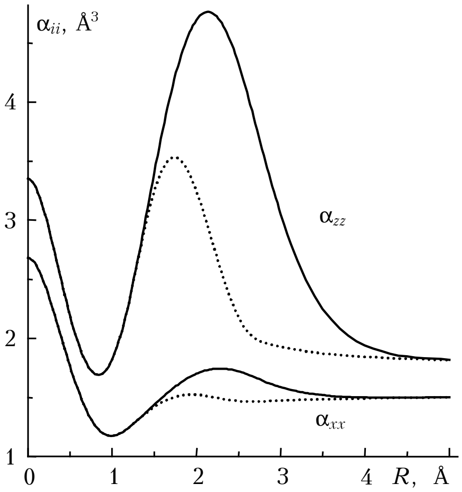

Fig. 5. Polarizability functions of O_2 (the O atoms at the states with $|M_L| = 0$): this work (solid curves), this work neglecting the exchange interactions (dotted curves).

It is interesting to compare the obtained polarizability functions of N_2 with the functions calculated by an alternative method, which tried to take into account the exchange interactions through the found correlations.[5] Apart from some differences in the polarizability functions in the range of small R connected with different choice of $\alpha_{xx}^{(0)}$ and $\alpha_{zz}^{(0)}$ values for Si atom, noteworthy is the unjustified underestimation of $\alpha_{xx}(R)$ for $R \approx 1–3$ Å (see Fig. 2). This is caused, in our opinion, by unjustified extension to the nitrogen molecule of the correlations found for the molecules mostly consisting of atoms belonging to the first group of the Periodic Table.

Conclusion

The semiempirical approach considered by us allows the polarizability functions of diatomic homonuclear molecules to be obtained in the analytical form for the whole range of the internuclear separations. It is shown that the allowance for the exchange interatomic interactions considerably improves the polarizability functions in the range of medium R values. Despite the disadvantages inherent in semiempirical methods, this approach gives a correct idea about physical mechanisms of formation of the polarizability functions of diatomic molecules.

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