Regularities in the behavior of dipole moment functions of diatomic molecules at very small internuclear separations

M. A. Buldakov,1 E. V. Koryukina,2 V. N. Cherepanov,2 and Yu. N. Kalugina2

1Institute of Monitoring of Climatic and Ecological Systems SB RAS, Akademicheski Avenue 10/3, Tomsk, 634055, Russia
2Tomsk State University, Lenin Avenue 36, Tomsk, 634050, Russia

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A theoretical approach to calculating the dipole moment function of a diatomic molecule at very small internuclear separations has been suggested. The approach is based on the united-atom model and the LS-coupling approximation. Regularities in the behavior of the dipole moments as functions of the internuclear separation, electronic state, and nuclear charge of the molecule have been found. Within the approach, the dipole moment functions of some diatomic molecules, whose united atoms are in groups II, IV, V, VII, and VIII of periods 1–4 of the periodic table, were calculated.

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I. INTRODUCTION

The electrical properties of a molecule are characterized by its multipole moments, with the dipole moment being the first and most practically significant one. In the adiabatic approximation, there arises the concept of the dipole moment function, defined as the dipole moment operator averaged over the electronic coordinates of a molecule. In this approximation, the dipole moment of a molecule is a coordinate function of its nuclei; in particular, for a diatomic molecule the dipole moment is a function of the internuclear separation $R$. Such a dipole moment function $\mu(R)$ is continuous and smooth throughout the entire internuclear separation range of a diatomic molecule and most completely reproduces electrical molecular properties in comparison with the dipole moment of a molecule at the equilibrium internuclear distance $R_e$. Knowledge of the function $\mu(R)$ in the entire range of values $R \in [0, \infty)$ is mainly of theoretical importance to form correct concepts relating to the dipole moment function for all internuclear separations of a molecule. In addition, the method of divergent series summation based on the generalized Euler transformation requires knowledge of the whole function [1].

Two approaches based on \textit{ab initio} and semiempirical calculation methods exist for description of the dipole moment function of diatomic molecules. At present, existing computer codes based on \textit{ab initio} methods are widely used in the calculations of dipole moment functions of many-electron molecules for internuclear separations exceeding $\sim 0.8R_e$ (for example, recent works in this field [2–12]). Unfortunately, these code packages in principle do not allow us to calculate the dipole moment functions of many-electron molecules at small internuclear separations. An exception to this rule is one-electron diatomic molecules, for which \textit{ab initio} calculations of the dipole moment functions at arbitrary internuclear distances including small $R$ are possible [13,14], because the wave functions for these molecular ions can be calculated with high precision. In contrast to \textit{ab initio} methods, semiempirical methods allow us to obtain the dipole moment functions of any diatomic molecules for the total internuclear separation range $R \in [0, \infty)$. Semiempirical dipole moment functions given as exponential forms [15–18], Padé approximations [19–21], or piecewise continuous functions [22–27] coincide with the experimental dipole moment function in the vicinity of the equilibrium position of the molecular nuclei and, as a rule, have physically correct asymptotic behavior at $R \to \infty$ and $R \to 0$. However, such dipole moment functions require verification by \textit{ab initio} calculations, especially in the small internuclear separation range.

It is reasonable to perform \textit{ab initio} calculations of properties of many-electron molecules in the very small internuclear separation range within the united-atom model, because at $R \to 0$ the molecule is rather an atom than a molecule. The united-atom model suggested in [28] was shown to be highly efficient for calculations of electronic energies of diatomic molecules as functions of the internuclear separation. The united-atom model is most completely developed in [29–31]; however, the dipole moment functions were not considered in these works. For the first time, the idea of calculations of the dipole moment functions at very small internuclear separations in the framework of the united-atom model was stated in [32]. Further, the behavior of the function $\mu(R)$ at $R \to 0$ was investigated in [33]. It was shown that $\mu(R)$ is a power function of $R$ tending to zero as $R^3$ for the united atom in the $S$ and $P$ states and as $R^5$ for the united atom in the $D$ and $F$ states. Note that the author of [33] restricted himself to qualitative estimations alone, giving neither calculation schemes nor results for the function $\mu(R)$ at very small internuclear separations for any diatomic molecules. Nevertheless, these regularities are generally used to construct semiempirical dipole moment functions for the entire range of $R$ (see, for instance, [19–22]). However, Goodisman’s results [33] need to be carefully verified, because in this work the author took into account only the case of $L=1$ in Bingel’s expansion [see Eq. (18) in [29]].

In this work, a quantum-mechanics approach based on the united-atom model and the formalism of irreducible tensor operators is developed for calculating the dipole moment function of diatomic molecules at very small internuclear separations. The approach allows us to derive exact formulas for calculation of the dipole moment functions in the first-order perturbation theory and, on the basis of these formulas, to find regularities in the behavior of $\mu(R)$ at very small
very small internuclear separations for any diatomic molecules. The approach was applied to the calculation of the dipole moment functions of the alkali-metal hydrides LiH, KH, and NaH, hydrogen halides HF, HCl, and HBr, the radical OH, the molecules CO and NO, and other diatomic heteronuclear molecules having the same united atoms.

II. CALCULATION METHOD

In the nonrelativistic approximation, the electronic Hamiltonian of a diatomic molecule (without the nuclear repulsion energy), with the A and B nuclei being at the distance \( R \), has the form

\[
H = H_U + V,
\]

where the Hamiltonian of the unperturbed system (the united atom) has the form

\[
H_U = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{ai}} - \frac{Z_B}{r_{bi}} \right) + \sum_{i<j} \frac{1}{r_{ij}},
\]

and the perturbation operator is

\[
V = \sum_{i=1}^{N} \left[ Z_a \left( \frac{1}{r_i} - \frac{1}{r_{ai}} \right) + Z_b \left( \frac{1}{r_i} - \frac{1}{r_{bi}} \right) \right] + \sum_{i=1}^{N} \left( \begin{array}{c} Z_U - Z_a - Z_b \\ Z_U - Z_a - Z_b \\ Z_U - Z_a - Z_b \end{array} \right).
\]

Here \( r_i \) is the distance between the \( i \)th electron and the united-atom nucleus, and \( r_{ai} \) and \( r_{bi} \) are the distances between the \( i \)th electron and the A and B nuclei, respectively. The wave functions and energies of the united atom are found by solving the Schrödinger equation

\[
H_U \Psi_U = E_U \Psi_U.
\]

Then the wave function of a certain electronic state (hereinafter, this state will be denoted by the index "0") of a molecule with accuracy to the first order of perturbation theory takes the form

\[
\Psi_0 = \psi_0^{(a)} + \sum_j \frac{V_{0j}}{E_{0}^{(a)} - E_{j}^{(a)}} \psi_j^{(a)},
\]

where \( \psi_0^{(a)} \), \( \psi_j^{(a)} \), and \( E_0^{(a)} \), \( E_j^{(a)} \) are the wave functions and total energies of the initial and final states of the united atom, and \( V_{0j} = \langle \psi_0^{(a)} | V | \psi_j^{(a)} \rangle \) are the matrix elements of the perturbation operator.

The dipole moment function \( \mu(R) \) of a molecule in the adiabatic approximation is the average dipole moment operator

\[
\mu = -\sum_{i=1}^{N} \mathbf{r}_i + \sum_{\alpha=1}^{\nu} Z_{\alpha} \mathbf{R}_{\alpha}.
\]

In first-order perturbation theory, the dipole moment function can be written as [34]

\[
\mu(R) = \langle \psi_0^{(a)} | \mu(R) | \psi_0^{(a)} \rangle = 2 \sum_j \frac{V_{0j} \mu_j}{E^{(a)} - E_j},
\]

where \( \mu_j = \langle \psi_j^{(a)} | \mu_j | \psi_0^{(a)} \rangle \) [the z axis coincides with that of the molecule and is directed from the A atom to the B atom, and the origin of coordinates is placed at the charge center (see Fig. 1)].

It is convenient to calculate the matrix elements \( V_{0j} \) and \( \mu_j \) in Eq. (8) using the formalism of irreducible tensor operators, because the perturbation operator \( V \) and dipole moment operator \( \mu \) are one-electron operators, which can be represented as irreducible spherical tensor operators. To represent the perturbation operator \( V \) as an irreducible spherical tensor, we use the standard expansion [29,35]

\[
\sum \frac{1}{r_{ai}} = \frac{1}{|\mathbf{R}_{a}|} = \sum_k f_k(r_a, R_b) P_k[\cos(\theta_a - \pi)],
\]

(9)

\[
\sum \frac{1}{r_{bi}} = \frac{1}{|\mathbf{R}_{b}|} = \sum_k f_k(r_b, R_a) P_k[\cos(\theta_b)],
\]

(10)

where \( R_a = R Z_a / Z_{\alpha} \), \( R_b = R Z_a / Z_{\alpha} \) and the function \( f_k \) is written as

\[
f_k(r, R) = \left\{ \begin{array}{ll}
\frac{r^k}{R^{k+1}}, & r < R, \\
\frac{R^k}{r^{k+1}}, & r \geq R.
\end{array} \right.
\]

In Eqs. (9) and (10), it is convenient to express the Legendre polynomials \( P_k[\cos(\theta)] \) in terms of the spherical functions \( Y_{\ell \ell}(\theta, \varphi) \) as

\[
P_k(\cos \theta) = C_0^{(k)}(\theta, \varphi) = \sqrt{\frac{4\pi}{2k+1}} Y_{0 \ell}(\theta, \varphi).
\]

Hence, taking into account Eqs. (9)–(12), the perturbation operator takes the following form:
where

\[ V = V_0^{(0)} - \sum_k V_0^{(k)}, \]  

(13)

and

\[ V_0^{(k)} = \sum_{i=1}^N \frac{Z_{e_i}}{r_i} \]

(14)

The dipole moment operator can be represented as a first-order spherical tensor operator [36]

\[ \mu_z = \mu_0^{(1)} = -\sum_{i=1}^N r_i C_0^{(1)} (\theta_i, \varphi)_i. \]  

(15)

In this work, the matrix elements \( \mu_{0j} \) and \( V_{0j} \) in Eq. (8) are calculated for the most widely used type of atomic transitions \( n^p_{\alpha} \rightarrow n^p_{\alpha'} n' l' \), where \( n \) and \( n' l' \) are the principal and orbital quantum numbers of an electron in the initial and final states, and \( n_i \) is the number of electrons in the \( n^p_i \) shell. We will consider the united-state wave functions in the \( S_{L M_L} M_L \) representation. Where necessary, the foregoing algorithm can be easily extended to other transition types. In the case of the \( p^1 \alpha S_{L M_L} \rightarrow p^1 \alpha'[\alpha_1 S_{L_1} L_{1}'] l' S' L'M_{S'M_{L'}} \) transitions, the wave functions of the initial and final states become

\[ |p^1 \alpha S_{L M_L}\rangle = \sum_{\alpha_1 S_{L_1} L_{1}'} G^{\alpha S_{L L_1}}_{\alpha_1 S_{L_1} L_{1}'} \sum_{M_{S M_{S}} m_{M_{S}} m_{M_{L}}} C^{M_{S} M_{L}}_{L_{1} M_{1}} \times C^{S_{L} S_{S} M_{S} M_{S}}_{L_{1} M_{1} L_{1}} |p^1 \alpha S_{L_2 L_{2} M_{S_2} M_{L_2}}\rangle |m_{M_{S}} m_{M_{L}}\rangle, \]  

(16)

\[ |p^1 \alpha'_1 S_{L_1} L_{1}'\rangle = \sum_{M_{S_1} M_{L_1} m_{M_{S_1}} m_{M_{L_1}}} C^{L_1}_{M_{S_1} M_{L_1} M_{L}} \times C^{S'M'}_{S_{S_1} L_{1} M_{S_1} M_{L_1}} |p^1 \alpha_1 S_{L_1} L_1 M_{S_1} M_{L_1}\rangle |l' m'_{M_{S}} m'_{M_{L}}\rangle, \]  

(17)

where \( |p^1 \alpha S_{L_2 L_2} M_{S} M_{L_2}\rangle \) and \( |p^1 \alpha S_{L_1} L_1 M_{S_1} M_{L_1}\rangle \), and \( \{m_{M_{S}} m_{M_{L}}\} \) are the wave functions of the core and the electron involved in the transition in the initial and final states, \( G^{\alpha S_{L L_1}}_{\alpha_1 S_{L_1} L_{1}'} \) are the fractional parentage coefficients, and \( C^{L}_{M_{S} M_{L} M_{L}} \) are the Clebsch-Gordan coefficients. Taking into account the Wigner-Eckart theorem, the matrix elements of the dipole moment operator \( \mu_{0j} \) can be written as [36]

\[ \langle P^1 \alpha S_{L M_L} M_{L} | \mu_0^{(1)} | P^1 \alpha S_{L_1} L_1 M_{L_1} \rangle = \delta_{S S'} \delta_{M M_{S}} \langle -1 \rangle^{L L_{1} - M \cdot L_{1}} \times \langle P^1 \alpha S_{L M_L} | \mu_0^{(1)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle, \]  

(18)

where

\[ \langle P^1 \alpha S_{L M_L} | \mu_0^{(1)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle = \sqrt{n_{1}} G^{\alpha S_{L L_1}}_{\alpha_1 S_{L_1} L_{1}} \langle -1 \rangle^{L_{1} L_{1} + L \cdot L} \sqrt{2L + 1}(2L' + 1) \times \langle R_{nl} | F_{k}(r, R) | R_{nl'} \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle. \]  

(19)

The matrix elements of the perturbation operator are calculated in a similar way:

\[ \langle P^1 \alpha S_{L M_L} M_{L} | \sum_k V_0^{(k)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle = \delta_{S S'} \delta_{M M_{S}} \langle -1 \rangle^{L L_{1} - M \cdot L_{1}} \times \langle P^1 \alpha S_{L M_L} | V^{(k)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle, \]  

(20)

In Eqs. (19) and (21), we designate

\[ \langle \alpha' S' L'M_{S'} M_{L'} \rangle = \langle -1 \rangle^{L_{1} L_{1} + L \cdot L} \langle \alpha' S' L'M_{S'} M_{L'} \rangle, \]

(22)

and \( R_{nl}(r) \) is the radial function of the \( nl \) electron. It should be noted that, in consequence of Eqs. (20) and (22), \( k \) takes on odd values in the range between 1 and \( \min(l + l', L + L') \). The matrix elements of the operator \( V^{(k)} \) are proportional to \( \delta_{\alpha \alpha'} \), and make no contribution to the dipole moment function \( \mu(R) \).

The final expression for calculation of the dipole moment function of diatomic molecules in the \( 2^{3}S_{1/2} A \) states results from averaging \( \mu(R) \) from Eq. (8) over the quantum numbers \( M_{S_1} M_{L} \) with allowance for the correlation rules [37] between the united atom and molecular terms (\( \Lambda = |M_{L}| \); the spin value \( S \) coincides with the spin value of the corresponding united-atom state). As a result, the dipole moment function of a diatomic molecule in the \( 2S_{1/2} A \) state becomes

\[ \mu_{\Lambda S}(R) = -2 \sum_{\alpha_1 L_1 S_1 \alpha' L'} \sum_k \langle P^1 \alpha S_{L M_L} | V^{(k)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle \langle P^1 \alpha S_{L M_L} | \mu_0^{(1)} | P^1 \alpha S_{L_1} L_1 \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle \langle \alpha' S' L'M_{S'} M_{L'} \rangle. \]  

(23)
Equation (23) allows us to obtain the dipole moment function of a diatomic molecule at very small internuclear separations in a numeric form. It is of interest to analyze this expression to reveal analytical regularities in the behavior of the function $\mu_{\Lambda S}(R)$ of a diatomic molecule in the given range $R$.

The behavior of the dipole moment function depending on the internuclear separation of a molecule is completely determined by the integral $I = \langle R_{nl} \mid F_{nl}(r, R) \mid R_{nl} \rangle$, where integration is taken over the range $r \in [0, \infty)$. To calculate this integral, it is convenient to divide the range of integration into two parts $r \in [0, R_b]$ and $r \in [R_b, \infty)$, assuming, for definiteness, $R_a < R_b$. Then, using Eq. (11), we get

$$I_1 = \int_0^{R_b} R_{nl}(r) R_{nl}(r) r^{k+1} dr + \int_{R_b}^{\infty} R_{nl}(r) R_{nl}(r) r^{k+1} dr$$

$$I_2 = \int_0^{R_b} R_{nl}(r) R_{nl}(r) r^{k+1} dr = \int_{R_b}^{\infty} R_{nl}(r) R_{nl}(r) r^{k+1} dr$$

where $I_1 + I_2 = I$.

Calculating the integral $I_1$ in the range $r \in [0, R_b]$, we write the radial functions as

$$R_{nl}(r) = r^l (A_{nl} B_{nl} r + \cdots)$$

$$R_{nl}(r) = r^l (A_{nl} B_{nl} r + \cdots)$$

where $A_{nl}$, $B_{nl}$, $A_{nl}'$, and $B_{nl}'$ are parameters independent of $r$. Hence, we get the following relation for the integral $I_1$:

$$I_1 = R^{k+1} A_{nl} B_{nl} Z_{nl}(1-t) \times \left( \frac{(1-t)^{l+1} - l + 1}{l + 1 + k + 3} - \frac{(1-t)^{l+1} - l + 1}{l + 1 - k + 2} \right)$$

$$- R^{k+1} A_{nl} B_{nl} Z_{nl}(1-t) \times \left( \frac{(1-t)^{l+1} - l + 1}{l + 1 + k + 4} - \frac{(1-t)^{l+1} - l + 1}{l + 1 - k + 3} \right)$$

where the parameter $t = Z_b / Z_{nl}$.

To calculate the integral $I_2$ in the range $r \in [R_b, \infty)$, the radial functions are conveniently written as

$$R_{nl}(r) = r^l \exp(-\alpha r)(A_{nl} + D_{nl} r + \cdots), \quad \alpha > 0$$

$$R_{nl}(r) = r^l \exp(-\beta r)(A_{nl} + D_{nl} r + \cdots), \quad \beta > 0$$

where $D_{nl}$ and $D_{nl}'$ are some parameters independent of $r$. Substituting the radial functions from Eq. (28) into Eq. (25), we get

$$I_2 = R^{k+1} C_{nl}(1-t)[(1-t)^{l+1} - l + 1]$$

$$- \int_{l+1}^{\infty} \frac{1}{l + 1 + l'' - k + 2} Z_{nl}(1-t)^{l+1} dr$$

$$\times [(1-t)^{l+1} - l + 1]$$

where the parameter $C_{nl}$ does not depend on $R$ and $t$. It should be noted that the exponent of $R$ in the integral $I_2$ depends only on $l+l''$, whereas in the integral $I_1$ it also depends on $k$.

Let us analyze Eq. (23) with allowance for Eqs. (27) and (29) in order to find the dependences of the dipole moment functions on $R$, $t$, and $\Lambda$.

$R$ dependence. Let us consider the situations most essential for the LS-coupling scheme.

(a) $l=0$ (the $s \rightarrow p$ transitions are allowable). In this case, $k=1$ for any state $L$ of the united atom, and, since $I_2=0$, only the integral $I_1$ makes a contribution to the dipole moment, and therefore the dependence of the dipole moment function at very small internuclear separations on $R$ is written as follows:

$$\mu_{\Lambda S}(R) = A_{\Lambda S} R^3 + B_{\Lambda S} R^3 + \cdots$$

(b) $l=1$ (the $p \rightarrow s$ and $p \rightarrow d$ transitions are allowable). The contribution from the $p \rightarrow s$ transitions ($k=1$) to $\mu_{\Lambda S}(R)$ leads to Eq. (30) irrespective of the contribution from the $p \rightarrow d$ transitions. It is valid for any value of $L$ of the united atom, if the $p \rightarrow s$ transitions are not forbidden by additional selection rules. In the case where the $p \rightarrow s$ transitions are forbidden, the function $\mu_{\Lambda S}(R)$ at very small $R$ has the form

$$\mu_{\Lambda S}(R) = A_{\Lambda S} R^3 + B_{\Lambda S} R^5$$

(c) $l=2$ (the $d \rightarrow p$ and $d \rightarrow f$ transitions are allowable). In this case, the $k$ can take on the values $1, 2, 3$ with allowance for the limitation $k \leq \min(l+l''+L+L')$. Let us consider the following cases.

(i) $L=0$ ($k=1$). Here $I_1 - R^5$, and $I_2 = 0$. As a result, the dipole moment function of a molecule at very small internuclear separations is derived as

$$\mu_{\Lambda S}(R) = A_{\Lambda S} R^3 + B_{\Lambda S} R^5 + \cdots$$

(ii) $L=1$ ($k=1, 3$). As in the previous case, $I_1 - R^5$, and $I_2 = 0$ at $k=1$, and $I_2 - R^5$ at $k=3$. Thus, the function $\mu_{\Lambda S}(R)$ at very small $R$ is determined by Eq. (31).

(iii) $L \geq 2$. In this case, there are terms with $k=3$ in Eq. (23), which determine the dependence of the dipole moment function of a molecule [see Eqs. (25) and (29)] on $R$ in the form of Eq. (31) at very small internuclear separations.

A similar analysis can also be easily performed for the case $l>2$; however, this case is not typical of the LS-coupling scheme. It should also be noted that the $A_{\Lambda S}$ and $B_{\Lambda S}$ coefficients in Eqs. (30) and (32) have opposite signs.

Thus, in the framework of the developed model of the LS-coupling scheme and for atomic transitions of the $nl_{nl} \rightarrow ml_{nl}$ type, the dipole moment function of a diatomic molecule at very small internuclear separations exhibits the asymptotic behavior $\mu_{\Lambda S}(R) \rightarrow A_{\Lambda S} R^3$ for all united-atom states except for the cases where the conditions $l \geq 2$ and $L$
is obvious that the change their signs at a transition through the point

\[ t \] dependence. This dependence shows the behavior of the dipole moment function versus \( t = \frac{Z_b}{Z_u} \), when a diatomic molecule with nuclear charges \( Z_u \) and \( Z_b \) is formed from a united atom with the charge \( Z_u \). Let us consider the dependence of the \( A_{AS} \) and \( B_{AS} \) parameters on \( t \) (\( 0 \leq t \leq 1 \)), which is determined by the function

\[ w_n(t) = t(1-t)[(1-t)^n - r^n]. \quad (33) \]

(a) The function \( \mu_{AS}(t) \) is determined by Eq. (30). In this case, the dependence of the \( A_{AS} \) and \( B_{AS} \) parameters on \( t \) is written as

\[ A_{AS}(t) = \bar{A}_{AS}w_2(t), \quad B_{AS}(t) = \bar{B}_{AS}w_3(t). \quad (34) \]

(b) The function \( \mu_{AS}(t) \) is determined by Eq. (31). In this case, the \( A_{AS}(t) \) and \( B_{AS}(t) \) parameters take on the form

\[ A_{AS}(t) = \bar{A}_{AS}w_2(t), \quad B_{AS}(t) = \bar{B}_{AS}w_3(t). \quad (35) \]

(c) The function \( \mu_{AS}(t) \) is determined by Eq. (32). In this case, the \( A_{AS}(t) \) and \( B_{AS}(t) \) parameters have the form

\[ A_{AS}(t) = \bar{A}_{AS}w_4(t), \quad B_{AS}(t) = \bar{B}_{AS}w_5(t). \quad (36) \]

Thus, the coefficient \( A_{AS}(t) \) has form of Eq. (34) for all united-state atoms, except for the cases where \( t \geq 2 \) and \( L = 0 \) at the same time. For these cases, the leading coefficient \( A_{AS}(t) \) is determined as

\[ A_{AS}(t) = \bar{A}_{AS}w_{4t+1}(t). \quad (37) \]

The quantities \( w_n(t) \), which are the \( t \) dependencies of the \( A_{AS}(t) \) and \( B_{AS}(t) \) coefficients, are shown in Fig. 2. Analysis of the obtained \( t \) dependencies shows that they have characteristic features. These functions are zero for \( t \leq 0, 1/2, 1 \). The points \( t = 0, 1 \) correspond to a united atom, and the point \( t = 1/2 \) corresponds to a diatomic homonuclear molecule. Moreover, these functions have a single maximum in the \( t < 1/2 \) range, a single minimum in the \( t > 1/2 \) range, and change their signs at a transition through the point \( t = 1/2 \). It is obvious that the \( t \) dependencies of the \( A_{AS}(t) \) and \( B_{AS}(t) \) coefficients at \( t > 1/2 \) carry no new information as compared with the range \( t < 1/2 \), since they correspond to a simple replacement of the \( A \) atom by the \( B \) atom in the \( AB \) molecule. The replacement leads only to a change to the opposite sign in the dipole moment of the molecule.

It should be noted that the dependence of the coefficient \( A_{AS} \) on \( t \) from Eq. (34) coincides with a similar dependence for one-electron molecular ions, for which exact calculation of the dipole moment function at small internuclear separations can be performed [14].

A dependence. It follows from Eq. (23) that the dipole moment function depends on the quantum number \( \Lambda \). Based on this formula, it is difficult to obtain the explicit form of the dependence of the dipole moment function on \( \Lambda \); however, this dependence can be easily calculated numerically for a particular united-atom state with \( L \geq 1 \). Such calculations will be presented in the following section.

Note that the use of higher-order perturbation theory in calculations of the dipole moment functions neither breaks revealed regularities nor changes the \( A_{AS} \) and \( B_{AS} \) coefficients in Eqs. (30)–(37), since the contributions from the first and \( n \)th orders of perturbation theory are related as \( \mu_{AS}(t) \sim R^{2n-2}\mu_{AS}(R) \). It is of interest to estimate the range of internuclear separations where the calculated function \( \mu_{AS}(t) \) adequately describes the dipole moment of a molecule, and thereby determine the range of applicability of the foregoing calculation method. We suppose that the calculation of the dipole moment function gives reasonable values in the range of internuclear separations \( R \) where the contribution from the second term to the dipole moment function [see Eqs. (30)–(32)] does not exceed 50% of the contribution from the first term. Hence, the calculated functions \( \mu_{AS}(R) \) are acceptable in the range \( R \in [0, R_0(t)] \), where \( R_0(t) \) is determined using the formulas

\[ R_0(t) = \frac{A_{AS}(t)}{2B_{AS}(t)} = \frac{\bar{A}_{AS}}{2\bar{B}_{AS}}h_1(t), \quad h_1(t) = \frac{w_2(t)}{w_3(t)} \quad (38) \]

for the \( R \) dependence in the form of Eq. (30) and

\[ R_0(t) = \sqrt{\frac{A_{AS}(t)}{2B_{AS}(t)}} = \sqrt{\frac{\bar{A}_{AS}}{2\bar{B}_{AS}}}h_2(t), \quad h_2(t) = \frac{w_4(t)}{w_5(t)} \quad (39) \]

for the \( R \) dependence in the form of Eq. (31). Provided the values of the \( \bar{A}_{AS} \) and \( \bar{B}_{AS} \) coefficients are fixed, which corresponds to a family of molecules formed from one united atom, the boundary value \( R_0(t) \) monotonically increases with \( t \). In particular, \( h_1(t) \) changes from 1 to 1.33 when \( t \) changes from 0 to 0.5.

In the following section, direct numerical calculations of the dipole moment functions at very small internuclear separations are performed on the basis of Eq. (23) for a number of diatomic molecules. The purpose of the calculations is to verify the analytical regularities (30)–(37) and to determine numerical values of the \( A_{AS} \) and \( B_{AS} \) parameters of the dipole moment functions.

III. RESULTS AND DISCUSSION

The theoretical approach was applied to the calculation of the dipole moment functions of diatomic molecules with the
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moment functions for these molecules. The most interesting small internuclear separations increase with increase in the about 1% =/H20851/H20849, provided convergence of series (23) with an accuracy within about 1% [24,26]. In this work, the sign of the dipole moment of the diatomic molecule AB is positive for the polarity A−B+. For definiteness, in our calculations, we always assumed that the charge of the A atom is greater than that of the B atom (Za ≥ Zb), keeping the standard sequence of notation of symbols in chemical formulas.

A. Molecules with the united atoms Be, Mg, and Ca: Alkali-metal hydrides LiH, KH, and NaH

In this section, molecules with the united atoms Be, Mg, and Ca in the 1S ground state are considered. In accordance with the correlation rules [37], molecules in the 1Σ+ electronic states alone are formed from this united-atom state. It is obvious that there are no Λ dependencies of the dipole moment functions for these molecules. The most interesting representatives of the given class of molecules are the LiH, KH, and NaH molecules in the ground electronic state.

From the 1S states of the Be, Mg, and Ca atoms, only transitions of the type ns2(1S) → ns3(lS)n′p(lP) with k = 1 are possible, where n = 2, 3, 4, respectively. In this case, the dipole moment function (23) takes on a simple form

\[ \mu(R) = \frac{4}{3} \sum_{n'} \frac{(R_{ns}|r| R_{n'p})(R_{n'p}|F_1(r,R)|R_{ns})}{E_{ns} - E_{n'p}}. \]  (40)

The indices Λ and S of the function \( \mu_\Lambda S(R) \), and, correspondingly, of the \( A_{\Lambda S} \) and \( B_{\Lambda S} \) coefficients, are omitted, because, in this case, they have single values. Equation (40) was used to calculate the dipole moment functions of molecules with the united atoms Be, Mg, and Ca. The calculation shows that the dipole moment functions of these molecules are negative, which corresponds to the A−B+ polarity at Za ≥ Zb. As an illustration, the calculated dipole moment functions of the LiH, KH, and NaH molecules in the ground states are shown in Fig. 3. An analysis of the results allows us to reveal the following regularities.

1. The dipole moment functions at \( R \rightarrow 0 \) are governed by the \( \mu(R)=AR^3 \) regularity, which is in good agreement with Eq. (30). The deviation of the function \( \mu(R) \) from the cubic dependence with an increase in \( R \) is caused by the opposite sign (with respect to the coefficient \( A \)) of the coefficient \( B \) in Eq. (30).

2. The range of internuclear separations \( R \) where the dipole moment functions have the form \( \mu(R)=AR^3 \) is diminished as the united-atom charge increases.

3. The dipole moment functions in the range of very small internuclear separations increase with increase in the united-atom charge.

The regularities found are also valid for other diatomic molecules with the united atoms Be, Mg, and Ca in the 1S state.

To obtain the \( t \) dependencies of the \( A \) and \( B \) coefficients in Eq. (34), use was made of the calculation results of the dipole moment functions of the NaH, HeNe, LiF, BeO, and BN molecules (the Mg united atom), and the KH, HeAr, LiCl, BeS, BP, SiSe, AlN, MgO, and NaF molecules (the Ca united atom). It should be noted, that the Be united atom forms only one diatomic homonuclear molecule LiH, so that there are no \( t \) dependencies of the \( A \) and \( B \) coefficients. The calculated functions \( \mu(R) \) for these molecules allowed us to find the values of the \( A \) and \( B \) coefficients, which are presented in the normalized form (\( A^N=A/A \) and \( B^N=B/B \)) in Fig. 4. For comparison, the theoretical \( t \) dependencies of these coefficients are also shown in this figure [see Eq. (34)]. It is seen that the \( t \) dependencies of the \( A \) and \( B \) coefficients obtained from direct numerical calculations are in good agreement with the theoretical dependencies. Note that at fixed \( R \), in a family of molecules with a shared united atom, the molecule with \( t = Z_a/Z_u \) closest to \( t_0 = (3 - \sqrt{3})/6 = 0.21 \) (where the \( A \) coefficient as a function of \( t \) reaches the maximal value) has the maximal dipole moment. In particular, for the Mg united atom the LiF (\( t = 0.25 \)) molecule has the maximal dipole moment, and for the Ca united atom the BeS (\( t = 0.20 \)) molecule does.

In accordance with the chosen criterion (37), the calculated functions \( \mu(R) \) are correct for \( R \in [0,R_0(t)] \), where \( R_0(t=1/4) = 0.2 \) a.u. for the LiH molecule; in the molecule family of the Mg united atom, \( R_0(t) \) changes from 0.06 a.u. for NaH (\( t=1/12 \)) to 0.07 a.u. for BN (\( t=5/12 \)); and in the molecule family of the Ca united atom, \( R_0(t) \) changes from 0.03 a.u. for KH (\( t=1/20 \)) to 0.04 a.u. for NaF (\( t=9/20 \)). These estimations demonstrate that \( R_0(t) \) decreases with an increase in the united-atom nuclear charge \( Z_u \).

B. Molecules with the united atoms Ne, Ar, and Kr: Hydrogen halides HF, HCl, HBr

In this section, molecules with rare-gas Ne, Ar, and Kr atoms as united atoms in the 1S ground state are considered.
As in the previous section, these united atoms produce diatomic molecules only in the states with $\Lambda=0$, and, consequently, there are no $\Lambda$ dependencies of the dipole moment functions for these molecules. The best known representatives of molecules with Ne, Ar, and Kr united atoms are the HF, HCl, and HBr hydrogen halide molecules in the $X^1\Sigma^+$ electronic states.

For the $1S$ states of Ne, Ar, and Kr atoms the $np^6(1S)\rightarrow np^5(2P)n^2(1S)$ and $np^6(1S)\rightarrow np^5(2P)n^4d(1P)$ one-electron transitions with $k=1$ are allowable, where $n=2,3,4$, respectively. In this case, Eq. (23) for the dipole moment function is transformed into

$$\mu(R) = \sum_{\ell'} \sum_{n'} c_{\ell} \left\langle R_{np} | r | R_{n'\ell'} \right\rangle \left\langle R_{n'\ell'} | F_1(r, R) | R_{np} \right\rangle / E_{np} - E_{n'\ell'},$$

(41)

where $c_{\ell}=4/3$ and $c_{\ell'}=8/3$ for the one-electron $np\rightarrow n's$ and $np\rightarrow n'd$ transitions, respectively. The use of the $LS$ coupling instead of the $Jl$ coupling typical for the excited states of inert atoms leaves the dipole moment function almost unaffected. Indeed, if one neglects small corrections to the atomic energy in the denominator of Eq. (23) induced by the interaction between electrons and takes into account the orthonormality of the Racah coefficients relating atomic functions for the $LS$ and $Jl$ couplings of the angular moments, the function $\mu(R)$ will not depend on the type of coupling.

Equation (41) was used for calculation of the dipole moment functions of molecules with Ne, Ar, and Kr united atoms. The calculation results show that the dipole moment functions of these molecules are positive (the $A^*\rightarrow B^*$ polarity at $Z_A \gg Z_B$) and are basically formed by the $np\rightarrow n's$ transitions, whose contribution to the functions $\mu(R)$ is several orders of magnitude higher than the contribution of the $np\rightarrow n'd$ transitions. As an illustration, the dipole moment functions calculated for very small internuclear separations for the HF, HCl, and HBr molecules in the ground states are given in Fig. 5. It is seen that the functions $\mu(R)$ of both hydrogen halides and alkali-metal atom hydrides satisfy the asymptotic behavior $\mu(R)=AR^3$ and increase with the united-atom charge. The calculations also suggest that such asymptotic behavior is determined by the contribution of the $np\rightarrow n's$ transitions alone, because the contribution of the $np\rightarrow n'd$ transitions with $k=1$ to the function $\mu(R)$ is small and proportional to $R^5$, which is in good agreement with Eq. (27).

The calculated results of the dipole moment functions of the HF, HeO, LiN, and BeC molecules (the Ne united atom), the HCl, HeS, LiP, BeSi, BAl, MgC, NaN, and NeO molecules (the Ar united atom), and the HBr, HeSe, LiAs, BeGe, BGa, ZnC, CuN, NiO, CoF, FeNe, NaMg, MgCr, AlV, SiTi, ScF, CaS, and KCl molecules (the Kr united atom) were used to obtain the $t$ dependencies of the $A$ and $B$ coefficients in Eq. (34). The numerical values of the normalized $A^n$ and $B^n$ coefficients and their theoretical $t$ dependencies are shown in Fig. 6. As seen from the figure, they are in good agreement. Small deviations of the $B^n$ coefficients from the theoretical $t$ dependence are induced by a higher uncertainty as compared with the $A^n$ coefficients. Moreover, the uncertainty of the $B^n$ coefficients noticeably increases with $Z_U$ because of reduction of the range of true values of the $\mu(R)$ function. Note that the maximal dipole moments will be observed for the molecules HeO (the Ne united atom, $t=0.20$), BeSi (the Ar united atom, $t=0.22$), and NiO (the Kr united atom, $t=0.22$).

In accordance with the chosen criterion (37), the calculated functions $\mu(R)$ can be considered to be satisfactory at $R \leq R_0(t)$, where $R_0(t)$ in the molecule family of the Ne united atom changes from 0.07 a.u. for HF ($t=1/10$) to 0.08 a.u. for BeC ($t=4/10$); in the molecule family of the Ar united atom from 0.04 a.u. for HCl ($t=1/18$) to 0.05 a.u. for NeO ($t=8/18$); and in the molecule family of the Kr united atom from 0.02 a.u. for HBr ($t=1/36$) to 0.03 a.u. for KCl ($t=17/36$). As in the previous section, the range of $R$ where the calculated functions $\mu(R)$ have correct values also decreases with increase of $Z_U$.

C. Molecules with the F united atom: OH radical

In this section, molecules with the F united atom in the $2P$ ground state are considered. The F atom in the $2P$ ground state corresponds to diatomic molecules OH, HeN, LiC, and BeB in states with $\Lambda=0$ and 1. In this case, the calculation...
formula for the dipole moment function is written as

$$\mu_{\Lambda}(R) = \sum_{i,k} c_{ik}^{(\Lambda)} \sum_{n'} \frac{(R_{np}|p|E_{n'})_{\Lambda}(R_{np}|F_{2}(r,R)|R_{np})}{(E_{np} - E_{n'n'})}.$$  \hspace{1cm} (42)

where $n=2$, and $R_{np}^{(0)}$ and $E_{n'n'}^{(0)}$ are the wave functions and excited-state energies of the F atom, respectively, for each $i$th allowed one-electron transition. The calculated values of the coefficients $c_{ik}^{(\Lambda)} (k=1,3)$ for all allowed dipole transitions $2p^5(^2P) \rightarrow 2p^4[5s+L_1]n'p'(2L')$ of the F atom are listed in Table I.

Using Eq. (42), the dipole moment functions of the OH radical, HeN, HeC, and BeB molecules in the lowest $^2\Sigma^+$ and $^3\Pi$ states were calculated. The calculations show that the dipole moment functions of these molecules are positive (the $A^rB^u$ polarity at $Z_{\mu} \approx Z_{\lambda}$) for the $^2\Sigma^+$ and $^3\Pi$ states. The calculated dipole moment functions of the OH radical for these states are given in Fig. 7. It shows that the functions $\mu_{\Lambda}(R)$ of the OH radical obey the law $\mu_{\Lambda}(R) = A_{\Lambda}^r R^3$ both for the $^2\Sigma^+$ and for the $^3\Pi$ states. Figure 8 shows the $R$ dependencies of the contributions of the $2p^5(^2P) \rightarrow 2p^4[3P]n's(^2P)$ transitions with $k=1$ and the $2p^5(^2P) \rightarrow 2p^4[3P]n'd(^2D)$ transitions with $k=1$ and 3 (summed over $n'$) to the dipole moment function of the OH radical in the $^3\Pi$ state. It is clearly seen that at very small internuclear separations the contributions of the $2p\rightarrow n's$ and $2p\rightarrow n'd$ transitions ($k=3$) are proportional to $R^3$, and the contribution of the $2p\rightarrow n'd$ transitions ($k=1$) is proportional to $R^5$, which is in close agreement with Eqs. (27) and (29). It is also seen that the $2p\rightarrow n's$ transitions make the determining contribution to the function $\mu_{\Lambda}(R)$ of the OH radical. It should be noted that the contributions of the $2p\rightarrow n's$ and $2p\rightarrow n'd$ transitions ($k=1$) are positive, whereas the contributions of the $2p\rightarrow n'd$ transitions ($k=3$) are negative.

The calculated normalized $A_{\Lambda}^r = A_{\Lambda}^{r}/\tilde{A}_{\Lambda}$ and $B_{\Lambda}^r = B_{\Lambda}^{r}/\tilde{B}_{\Lambda}$ coefficients for the OH, HeN, HeC, and BeB molecules in the lowest $^2\Sigma^+$ and $^3\Pi$ states are given in Fig. 7. The values are in good agreement with the theoretical $t$ dependencies (34) for both the $^2\Sigma^+$ and $^3\Pi$ states. Among these molecules, the molecule HeN ($t=0.22$) has the maximal dipole moment at very small $R$.

As the $np\rightarrow n's$ transitions make the major contribution to the dipole moment function, it is possible to approximately estimate the $\Lambda$ dependence of the function $\mu_{\Lambda}(R)$. Restricting ourselves to these transitions alone, we can write Eq. (23) as

| Table I. Coefficients $c_{ik}^{(\Lambda)}$ for allowed dipole transitions of the F ($^2P$) atom. |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| $i$                          | $2p^5(^2P) \rightarrow 2p^4[2s+L_1]n'l(^2L')$ | $c_{ij}^{(0)}$ | $c_{ij}^{(0)}$ | $c_{ij}^{(1)}$ | $c_{ij}^{(1)}$ |
| 1                            | $2p^5(^2P) \rightarrow 2p^4[1s]n's(^2S)$       | 2/9            | 0              | 0              | 0              |
| 2                            | $2p^5(^2P) \rightarrow 2p^4[2s]n'd(^2D)$       | 8/45           | 4/35           | 2/15           | –2/35          |
| 3                            | $2p^5(^2P) \rightarrow 2p^4[3s]n's(^2P)$       | 0              | 0              | 1              | 0              |
| 4                            | $2p^5(^2P) \rightarrow 2p^4[3p]n'd(^2D)$       | 0              | 0              | 1/2            | 0              |
| 5                            | $2p^5(^2P) \rightarrow 2p^4[3p]n's(^2P)$       | 6/5            | –18/35         | 9/10           | 9/35           |
| 6                            | $2p^5(^2P) \rightarrow 2p^4[3d]n'd(^2S)$       | 4/9            | 0              | 0              | 0              |
| 7                            | $2p^5(^2P) \rightarrow 2p^4[3d]n's(^2D)$       | 4/9            | 0              | 1/3            | 0              |
| 8                            | $2p^5(^2P) \rightarrow 2p^4[4d]n'd(^2D)$       | 0              | 0              | 1/2            | 0              |
| 9                            | $2p^5(^2P) \rightarrow 2p^4[4d]n's(^2D)$       | 14/45          | 2/35           | 7/30           | –1/35          |
FIG. 8. Contributions of individual transitions to the dipole moment function of the OH radical in the \( ^1\Pi \) state (all values are in a.u.). Curve 1, the \( 2p^2(\Pi) \rightarrow 2p^2[\Pi]p'\Pi' \) transition with \( k=1 \); curve 2, the \( 2p^2(\Pi) \rightarrow 2p^1[\Pi]n'd(\Pi) \) transition with \( k=3 \); curve 3, the \( 2p^3(\Pi) \rightarrow 2p^3[\Pi]n'd(\Pi) \) transition with \( k=1 \).

\[
\mu_\Lambda(R) = \frac{2}{3} n_1(2L + 1) g(R) g_L(\Lambda),
\]

where

\[
g(R) = \sum_{n'} \frac{(R_{np}|R_{n'p}) (R_{np}), R_{n'p})}{E_{np} - E_{n'p}},
\]

\[
g_L(\Lambda) = \sum_{L'} (G_{SL,L'}(\Lambda))^2 \frac{1}{2} \left[ L 1 L' \Lambda 0 - \Lambda \right].
\]

In Eq. (44), the summation over the quantum number \( S_1 \) is absent for \( g_L(\Lambda) \), because for the \( p \) electrons there is a unique connection between the \( S_1 \) and \( L_1 \) quantum numbers, and \( L_1 = L' \). In the case of molecules with the F united atom, the function \( g_L(\Lambda) \) becomes \( g_F(\Lambda) = (2 + \delta_{00} + 4\Lambda^2)/45 \). Then we get \( \mu_\Lambda(R)/\mu_\Sigma(\Lambda) \approx g_F(\Lambda=1)/g_F(\Lambda=0)=2 \) from Eq. (43), which is in good agreement with the quantity 2.18 obtained by direct calculations. Note that \( g_F(\Lambda=1)/g_F(\Lambda=0)=\Sigma_{e_{11}}(\Lambda) \Sigma_{e_{11}}(\Lambda) = \Sigma_{c_{11}}^2 + \Sigma_{c_{11}}^2 \), where summation of the \( c_{ik} \) coefficients from Table I is performed only for the \( p \rightarrow s \) transitions.

The calculated functions \( \mu_\Lambda(R) \) can be considered to be satisfactory at \( R=R_0(i) \), where \( R_0(i) \) is independent of \( \Lambda \) and changes from 0.08 a.u. for OH (\( i=1/9 \)) to 0.09 a.u. for BeB (\( i=4/9 \)).

D. Molecules with the Si united atom: CO molecule

In this section, molecules with the Si united atom in the \( ^1D \) state of the ground configuration are considered. According to the correlation rules, the Si atom in this state corresponds to the diatomic molecules AlH, MgHe, NaLi, BeNe, BF, and CO in the lower singlet states with \( \Lambda=1 \). The calculation of the dipole moment functions of these molecules was performed using Eq. (42), where \( n=3 \), and \( R_{n'n'}(\Lambda) \) and \( E_{n'n'}(\Lambda) \) are the wave functions and excited-state energies of the Si atom for each \( \Lambda \) allowed one-electron transition, respectively. The coefficients \( c_{ik}^{(\Lambda)}(k=1, 3) \) for all allowed dipole transitions \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]n'l'(\Pi') \) of the Si atom are listed in Table II.

The calculations show that the dipole moment functions of the molecules under consideration are positive (the \( A^+B^+ \) polarity at \( Z_a \geq Z_b \)) for the \( ^1\Sigma^+ \) and \( ^1\Pi \) states and negative (the \( A^+B^- \) polarity) for the \( ^1\Delta \) states. The calculated dipole moment functions of the CO molecule in the lowest \( ^1\Sigma^+ \), \( ^1\Pi \), and \( ^1\Delta \) states are shown in Fig. 10. As seen from this figure, at very small internuclear separations the functions \( \mu_{\Lambda}(R) \) of the CO molecule obey the asymptotic law \( \mu_{\Lambda}(R) \approx A_{\Lambda}R^3 \) for all these states. The \( 3p \rightarrow n's \) transitions make the determining contribution to the function \( \mu_{\Lambda}(R) \) for the \( ^1\Sigma^+ \) and \( ^1\Pi \) states of the CO molecule, and hence the \( R \) dependencies of \( \mu_{\Lambda}(R) \) for these states are described by Eq. (30). In the case of the \( ^1\Delta \) state, the dipole moment function of the CO molecule is formed only by the \( 3p \rightarrow n'd \) transitions and described by Eq. (31). The absence of contribution from the \( 3p \rightarrow n's \) transitions to the dipole moment function of the \( ^1\Delta \) state of the CO molecule leads to the fact that the function \( \mu_{\Lambda}(R) \) is much less in absolute magnitude than \( \mu_{2S}(R) \) and \( \mu_{2\Sigma}(R) \). The \( \mu_{2S}(R) \) and \( \mu_{2\Sigma}(R) \) functions are well described by Eq. (43) with \( g_{1\Sigma}(\Lambda)=(4-\Lambda^2)/30 \); in doing so, we have with a high precision \( \mu_{2S}(R)/\mu_{2\Sigma}(R)=3/4 \). It should be noted,

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\( i \) & \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]n'l'(\Pi') \) & \( c_{00}^{(0)} \) & \( c_{00}^{(0)} \) & \( c_{01}^{(1)} \) & \( c_{10}^{(1)} \) & \( c_{10}^{(0)} \) & \( c_{10}^{(0)} \) \\
\hline
1 & \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]p's(\Pi) \) & 8/9 & 0 & 2/3 & 0 & 0 & 0 \\
2 & \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]p'd(\Pi) \) & 4/225 & 12/175 & 1/75 & -6/175 & 0 & 0 \\
3 & \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]n'd(\Pi) \) & 0 & 0 & 1/15 & 4/35 & 4/15 & -4/35 \\
4 & \( 3p^3(\Pi) \rightarrow 3p^3[\Pi]p'd(\Pi) \) & 24/25 & 48/175 & 64/75 & 16/175 & 8/15 & -8/35 \\
\hline
\end{tabular}
\caption{Coefficients \( c_{ik}^{(\Lambda)} \) for allowed dipole transitions of the Si \( ^1D \) atom.}
\end{table}
that Eq. (43) is not applicable to the function $\mu_{\lambda}(R)$ because in this case $g_{\lambda}(\lambda=2)=0$. The conclusions drawn are valid for other diatomic molecules under study in this section.

The calculated normalized $A_{\lambda}^N$ and $B_{\lambda}^N$ coefficients for the AlH, MgHe, NaLi, BeNe, BF, and CO molecules in the lowest $1\Sigma^+$, $1\Pi$, and $1\Delta$ states are shown in Fig. 11. These values are in good agreement with the theoretical $t$ dependencies (34). In each of these states, the LiNu molecule has the dipole moment maximal in absolute magnitude at very small $R$.

The calculated functions $\mu_{\lambda}(R)$ can be considered satisfactory at $R\approx R_0(t)$, where $R_0(t)$ for the $1\Sigma^+$ and $1\Pi$ states changes from 0.05 a.u. for AlH ($t=1/14$) to 0.06 a.u. for CO ($t=6/14$), and for the $1\Delta$ states it changes from 0.22 a.u. to 0.28 a.u. The values $R_0(t)$ for the $1\Sigma^+$ and $1\Pi$ states were calculated using Eq. (38), and for the $1\Delta$ states using Eq. (39).

E. Molecules with the P united atom: NO molecule

In this section, molecules with the P united atom in the $2D$ state of the ground configuration are considered. In accordance with the correlation rules, the P atom in this state corresponds to diatomic molecules SiH, AlHe, LiMg, NaBe, BNe, CF, and NO in the lower $1\Sigma^+$, $3\Pi$, and $3\Delta$ states. The calculations of the dipole moment functions of these molecules were performed using Eq. (42), where $n=3$, and $R_{n'i'}^t$.

![FIG. 10. Dipole moment functions of the CO molecule for the lowest $1\Sigma^+$, $1\Pi$, and $1\Delta$ states (all values are in a.u.) Solid lines, ab initio calculation, dashed lines, calculation using asymptotic formula $\mu_{\lambda}(R)=A_{\lambda}R^{3}$, where $A_{\Sigma}=58.6$ a.u., $A_{\Pi}=44.0$ a.u., and $A_{\Delta}=-0.155$ a.u.](image)

![FIG. 11. Coefficients $A_{\lambda}^N=\overline{A}_{\lambda}/\overline{A}_{\lambda}$ (1) with $\lambda=0$, $2$, $B_{\lambda}^N=\overline{B}_{\lambda}/\overline{B}_{\lambda}$, (2) with $\lambda=0,1$, and $B_{\lambda}^N=\overline{B}_{\lambda}/\overline{B}_{\lambda}^N$, and (3) with $\lambda=2$ for molecules with the Si united atom. Solid lines, $w_3(t)$, $w_3(t)$, and $w_3(t)$; boxes, ab initio calculation for molecules in the $1\Sigma$ states ($\overline{A}_{\Sigma}=1.67\times10^3$ a.u., $\overline{B}_{\Sigma}=1.82\times10^4$ a.u.); triangles, ab initio calculation for molecules in the $1\Pi$ states ($\overline{A}_{\Pi}=1.25\times10^3$ a.u., $\overline{B}_{\Pi}=-1.37\times10^4$ a.u.), triangles, ab initio calculation for molecules in the $1\Delta$ states ($\overline{A}_{\Delta}=-4.41$ a.u., $\overline{B}_{\Delta}=55.5$ a.u.).](image)

$\overline{E}_{n'i'}^{i}$ are the wave functions and excited-state energies of the P atom for each $i$th allowed one-electron transition, respectively. The coefficients $c_{i'i'}^{(k)}$ ($k=1,3$) for all allowed dipole transitions $3p^n(2D)\rightarrow 3p^n(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$ of the P atom are listed in Table III.

The calculations show that the dipole moment functions of the molecules are positive (the $A'$-$B'$ polarity at $Z_a=Z_b$) for the $1\Sigma^+$, $3\Pi$, and $3\Delta$ states. Figure 12 depicts the calculated dipole moment functions of the NO molecule in the lowest $1\Sigma^+$, $3\Pi$, and $3\Delta$ states. It is clearly seen that the functions $\mu_{\lambda}(R)$ in these states almost coincide and obey the asymptotic law $\mu_{\lambda}(R)=A_{\lambda}R^{3}$. For the considered states of the NO molecule, the $3p\rightarrow n's$ transitions make the determining contribution to the function $\mu_{\lambda}(R)$; therefore the $R$ dependencies of $\mu_{\lambda}(R)$ of these states are described by Eq. (30). In this case, the function $g_{\lambda}(\lambda)$ does not depend on $L$ ($g_{\lambda}=1/15$), which accounts for the weak dependence of the functions $\mu_{\lambda}(R)$ on $\Lambda$. A negligible difference due to different contributions of weak $3p\rightarrow n'd$ transitions arises between the functions $\mu_{\lambda}(R)$. A similar behavior of the dipole moment functions is observed for the SiH, AlHe, LiMg, NaBe, BNe, CF, and NO molecules.

The calculated normalized $A_{\lambda}^N$ and $B_{\lambda}^N$ coefficients and the theoretical $t$ dependencies (34) for all molecules in the low-

<table>
<thead>
<tr>
<th>$i$</th>
<th>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</th>
<th>$c_{i'i'}^{(0)}$</th>
<th>$c_{i'i'}^{(0)}$</th>
<th>$c_{i'i'}^{(1)}$</th>
<th>$c_{i'i'}^{(1)}$</th>
<th>$c_{i'i'}^{(1)}$</th>
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<td>0</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>2</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>1/75</td>
<td>9/175</td>
<td>1/100</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>0</td>
<td>0</td>
<td>1/20</td>
<td>3/35</td>
<td>1/5</td>
<td>-3/35</td>
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<tr>
<td>4</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>18/25</td>
<td>36/175</td>
<td>16/25</td>
<td>12/175</td>
<td>2/5</td>
<td>-6/35</td>
</tr>
<tr>
<td>5</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>0</td>
<td>0</td>
<td>1/6</td>
<td>0</td>
<td>2/3</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>3/25</td>
<td>-9/175</td>
<td>9/100</td>
<td>9/350</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>0</td>
<td>0</td>
<td>7/60</td>
<td>-3/35</td>
<td>7/15</td>
<td>3/35</td>
</tr>
<tr>
<td>8</td>
<td>$3p^3(2D)\rightarrow 3p^3(2S)^{i'+1}L_{n}^{i'}L_{n}^{i'}$</td>
<td>12/25</td>
<td>-36/175</td>
<td>32/75</td>
<td>-12/175</td>
<td>4/15</td>
<td>6/35</td>
</tr>
</tbody>
</table>
ab initio has the dipole moment maximal in the absolute magnitude at Fig. 13. It is seen from the figure that they are in good agreement. In each of these states, the LiMg formula leads to the revealed regularities in the behavior of the dipole moment function.

Thus, the results under consideration in Sec. III show that the regularities in the behavior of the dipole moment functions of diatomic molecules at very small internuclear separations [Eqs. (30)–(35)] are completely supported by direct numerical calculations. As was expected, the range of applicability of the developed method is limited to very small internuclear separations ($R \leq 0.1$ a.u.), which is due to the nature of the united-atom model [33].

The calculations also show that the dipole moment functions of diatomic molecules under consideration can have opposite signs at very small internuclear separations. The sign of the dipole moment function of a molecule with any $\Lambda$ is determined by the $p \rightarrow s$ transitions of the united atom, because it is these transitions that make the determining contribution to the dipole moment function. The $AB$ molecules with $Z_a \neq Z_b$, where the $p \rightarrow s$ transitions make the determining contribution to $\mu(R)$, have the dipole moment function of the positive sign (the polarity $A^+B^-$). However, the molecules where the determining contribution to the $\mu(R)$ is made by the $s \rightarrow p$ transitions have a dipole moment function of negative sign (the polarity $A^-B^-$). If the $p \rightarrow s$ transitions are forbidden by the selection rules, the rule of signs takes on a more complicated form (see the case of the CO molecule with $\Lambda=2$). The polarity of diatomic molecules in the vicinity of the united atom was also considered in [40], where the polarity of the CO and BF molecules was determined as C$^+O^-$ and B$^+F^-$, which is in agreement with our calculations for the states with $\Lambda=0$.

Note that in a number of cases our results for the $R$ dependence of the dipole moment function differ from those predicted in theoretical work [33]. Thus, in Secs. III C and III D, where the Si and P united atoms in the $^1D$ and $^2D$ states were considered, $R^3$ asymptotic behavior of the dipole moment function was obtained, while it was asserted in [33] that the dipole moment function should exhibit $R^5$ behavior. These discrepancies are due to missing in [33] the terms with $L=3$ (here the index $L$ corresponds to $k$ in the present work) in Bingen’s expansion [see Eq. (18) in [29]].

IV. CONCLUSION

In this work, a theoretical approach to calculation of the dipole moment function of a diatomic molecule at very small internuclear separations was developed in the framework of the $LS$-coupling approximation. The approach is based on the united-atom model. The proposed calculation method allowed us to find regularities in the behavior of the dipole moments as functions of the internuclear separation $R$, electronic state $\Lambda$, and the parameter $Z_a/Z_b$ for the united atom with charge $Z$. Within the approach, the dipole moment functions of 61 diatomic molecules, whose united atoms are in the groups II, IV, V, VII, and VIII of periods 1–4 of the periodic table, were calculated. By virtue of the universality of the method developed, it should be expected that the revealed regularities will be valid for diatomic molecules whose united atoms are in other groups of the first three periods of the periodic table.

In calculations of dipole moment functions for molecules with heavy united atoms or united atoms in highly excited states, for which the applicability conditions of the one-electron and $LS$-coupling approximations are broken, it is necessary to modify the developed calculation scheme. The transition to other types of angular moment coupling will cause the appearance of the Racah coefficients in Eq. (23), but will not affect the $R$ dependence of the dipole moment function. Nor does the influence of other electronic configurations of the united atom break the $R^3$ asymptotic dependence of the dipole moment function, which is practically always observed. Moreover, if one takes into account weak transitions from inner atomic shells, the $p \rightarrow s$ transitions will make contributions to the dipole moment, which always leads to the $R^3$ asymptotic dependence of the dipole moment.


