

Dipole moment function of diatomic molecules: hydrogen halides

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A semiempirical method is proposed for construction of the dipole moment function for diatomic molecules in the whole range of internuclear separations. The dipole moment function is represented as a piecewise continuous function satisfying physically correct asymptotics at small and large internuclear separations and the values of dipole moment and its derivatives at the equilibrium configuration of the molecular nuclei. Asymptotic methods are used to take into account exchange interactions in the range of small overlapping of electron orbits of interacting atoms. The dipole moment functions for the HF, HCl, HBr, and HI molecules are obtained.

Introduction

In the last decades, the scientific literature actively discusses different approaches and methods for construction of the dipole moment function of diatomic molecules. These methods can be divided into two groups. One group incorporates the methods for description of the dipole moment function in a limited range of internuclear separations in a molecule, for example, near the equilibrium configuration¹⁻⁴ or in the range of large separations.^{5,6} Another group includes semiempirical methods describing the dipole moment function in the whole range of internuclear separations. To be noted among these methods are the Pade approximation⁶⁻⁸ and exponential representation.^{9,10} A disadvantage of the exponential representation of the dipole moment function is its incorrect asymptotic behavior within small and large internuclear separations, while the Pade approximation may lead to breaks in the function.

In this paper, a new approach is proposed for construction of the dipole moment function for the whole range of internuclear separations of a diatomic molecule. This approach is based on representation of the dipole moment function as a piecewise continuous function, and it is free of the above disadvantages. The new method is applied to hydrogen halides, which play an important role in chemical reactions in planetary atmospheres, in particular, in the ozone layer depletion in the Earth's atmosphere.

Asymptotic description of the dipole moment function

To find the molecular dipole moment function defined in the adiabatic approximation as a dipole moment operator averaged over electronic coordinates is a complicated problem that requires calculation of the molecular wave function for arbitrary values of the

internuclear separation R . Now it seems impossible to specify the wave function in the general form, but this problem can be solved for some ranges of R values. We can separate three characteristic subranges in the whole range of R values: large, medium, and small R values. In each of these subranges, the wave functions can be set analytically. These subranges, in their turn, can be divided into two parts depending on the type of the main interaction: multipole (at $R \rightarrow \infty$) and exchange (at smaller R). The methods for calculation of the wave function and the dipole moment function for each subrange are different.

Subrange of small R

For small internuclear separations ($R \rightarrow 0$), the molecular wave function can be calculated by perturbation methods with the wave functions of a "united" atom taken as zero approximation functions. Thus, in the first order of the perturbation theory, the molecular dipole function in the ground state can be represented as

$$\mu(R) = 2 \sum_m \frac{V_{0m}(R) \mu_{m0}}{E_0 - E_m}, \quad (1)$$

where E_k is the energy of the k th state of the united atom; μ_{m0} are the matrix elements of the dipole moment operator, and the matrix elements of the perturbation operator $V_{0m}(R)$ have the form^{7,11}:

$$V_{0m}(R) = A_{0m}R^3 + B_{0m}R^4 + C_{0m}R^5 + \dots \quad (2)$$

As a result, the dipole moment function in the subrange of small R can be written in the form

$$\mu(R) = \sum_{i=3} a_i R^i, \quad (3)$$

where the coefficients a_i are individual for each molecule.

Subrange of multipole interaction

In this subrange, the molecular wave function (wave function of two interacting atoms) can also be calculated by the perturbation methods, but now the products of the wave functions of atoms forming the molecule can be taken as zero-approximation functions. In this case, the molecular dipole function can be expressed through characteristics of individual atoms, just which determine its asymptotic behavior at $R \rightarrow \infty$. Thus, if the both atoms are in the S -state, then the first nonvanishing term of the dipole moment function appears in the second order of the perturbation theory and decreases as R^{-7} . If at least one of atoms has a quadrupole moment, then the dipole moment function decreases as R^{-4} , and the first nonvanishing term appears already in the first order of the perturbation theory.⁷

In accordance with the rules of correlation of electronic terms of molecules and atoms, into which the molecule decomposes at $R \rightarrow \infty$, the hydrogen halide molecules in the ground electronic state decompose into H atom in the S -state and halogen atom in the P -state with $M_L = 0$. Since the halogen atoms in the P -state have a quadrupole moment, the dipole moment function of the hydrogen halides takes the form similar to Eq. (1) with the corresponding re-definition of wave functions and zero-approximation energies. In this case, the decisive contribution to the dipole moment function is due to the dipole-quadrupole interaction operator

$$\hat{V}(R) = \frac{3}{2R^4} \hat{\mu}_z \hat{Q}_{zz}, \quad (4)$$

and, taking this into account, we can write the dipole moment function as

$$\mu(R) = \frac{3}{2R^4} \alpha Q_{zz}, \quad (5)$$

where α is the static polarizability of the hydrogen atom in the ground state; $Q_{zz} = 4e/5 \langle r^2 \rangle$ is a component of the quadrupole moment of the halogen atom¹² (the axis z coincides with the molecular axis), and $\langle r^2 \rangle$ is the mean value of the square separation of a valence electron from the nucleus.

Subrange of exchange interaction

This subrange is characterized by small overlap of electron shells of interacting atoms. The consequence is the exchange of valence electrons, one from each atom. In this case, asymptotic methods can be used to find the wave function of these electrons.¹³ The two-electron molecular wave function can be written in the form

$$\Psi = c_1 \psi_1 + c_2 \psi_2, \quad (6)$$

where

$$\psi_1 = \varphi_a(1) \varphi_b(2) \chi_1, \quad \psi_2 = \varphi_a(2) \varphi_b(1) \chi_2. \quad (7)$$

Here $\varphi_{a,b}(1)$ and $\varphi_{a,b}(2)$ are the asymptotic coordinate wave functions of, respectively, the first and the second electrons located mostly near the atomic cores a and b , and χ_i are the functions accounting for electron interaction with each other and with foreign nuclei.¹³

The contribution of the exchange interaction to the dipole moment function as an average of the dipole moment operator with the function (6) in atomic units can be represented in the form

$$\tilde{\mu}(R) = B(R) R^\delta \exp[-R(\beta + \gamma)], \quad (8)$$

where $B(R)$ is a function weakly depending on R ; $(-\beta^2/2)$ and $(-\gamma^2/2)$ are the ionization potentials of the corresponding atoms;

$$\delta = \frac{2}{\beta} + \frac{2}{\gamma} - \frac{2}{\beta + \gamma} + 1.$$

It should be noted here that in this range the multipole interactions also contribute to the dipole moment function, and the total dipole moment function, strictly speaking, is not a simple sum of contributions from multipole and exchange interactions, but a more complex their combination.

Model of the dipole moment function

In this paper, the dipole moment function of a diatomic molecule is modeled as a piecewise continuous function consisting of three parts: the dipole moment function in the subrange of small R , the same in the subrange of large R , as well as at intermediate values of the internuclear separation.

The first case is specified by Eq. (3), in which the coefficients a_i can be found from the known values of the dipole moment function and its derivatives at the point of equilibrium internuclear separation R_e . In this case, the coefficients a_i are the solutions of the system of linear equations found from the conditions of equality of derivatives of the function (3) at the point R_e and the dipole moment function in the vicinity of the equilibrium nuclei configuration in the molecule

$$\mu(R) = \sum_{i=0} M_i x^i, \quad (9)$$

where $x = (R - R_e)/R_e$, and M_i are the known coefficients. Thus, Eq. (3) with the determined coefficients a_i describes the molecular dipole moment function in the subrange of small R , including the vicinity of the equilibrium internuclear separation.

The dipole moment function in the subrange of large R can be represented as a sum of the multipole and exchange parts specified by Eqs. (5) and (8), where $B(R)$ is considered as an effective parameter B , whose value can be determined from fitting to data of *ab initio* calculations. Such a representation of the dipole moment function is a reasonable approximation, if the electron shells of the interacting atoms overlap only slightly.

The dipole moment function in the intermediate subrange is specified as a five-order polynomial of R

$$\mu(R) = \sum_{i=0}^5 b_i R^i, \quad (10)$$

whose coefficients b_i can be found from the conditions of sewing together the dipole moment functions at small and large R accurate to the second derivatives inclusive. It is proposed to select the sewing points as follows: $R_1 \approx 1.1R_e$ is the point of sewing the dipole moment function (3) with the polynomial; $R_2 \approx 2R_1$ is the point of sewing the polynomial with the dipole moment function at large R . The sewing points can be selected somewhat arbitrarily, but this does not significantly change the form of the dipole moment function.

Calculation of the dipole moment function for hydrogen halides

The proposed model was used to construct the dipole moment functions of the hydrogen halides. The coefficients a_i were calculated using the M_i values given in Table 1. The parameters B were determined from the least-square fit to the *ab initio* calculations of the dipole moment functions^{5,6} with $R \geq 2.4, 2.7, 3.2$, and 3.17 \AA , respectively, for the molecules HF, HCl, HBr, and HI. The obtained values of a_i , B , sewing points R_1 and R_2 , as well as b_i of the polynomial (10) are given in Table 2 along with the parameters $\langle r^2 \rangle$ and γ of halogen atoms.¹⁴

Table 1. Expansion coefficients of the dipole moment function of hydrogen halides in the equilibrium configuration, D

M_i	HF (Ref. 6)	HCl (Ref. 2)	HBr (Ref. 1)	HI (Ref. 6)
M_0	1.80306	1.095056	0.82003	0.44722
M_1	1.39366	1.076259	0.5152	-0.07404
M_2	-0.0583	-0.001429	0.192	0.5057
M_3	-0.8861	-1.252768	-1.8263	-1.9794
M_4	-0.599	-0.383620	-0.8447	-0.053
M_5	-0.931	0.104152	1.922	-0.0015
M_6	-	-0.223482	3.114	-
M_7	-	2.024332	17.14	-
M_8	-	-	-76.20	-

Table 2. Parameters for calculation of the dipole moment function of hydrogen halides

Parameter	HF	HCl	HBr	HI
1	2	3	4	5
$a_3, D \cdot \text{\AA}^{-3}$	75.8162	35.3189	3.6293	13.7586
$a_4, D \cdot \text{\AA}^{-3}$	-299.6886	-144.1073	43.0632	-35.0958
$a_5, D \cdot \text{\AA}^{-3}$	517.0631	270.6243	-202.2064	37.0355
$a_6, D \cdot \text{\AA}^{-3}$	-468.0363	-293.5394	375.1328	-19.9642
$a_7, D \cdot \text{\AA}^{-3}$	218.5020	196.0889	-385.8570	5.4668
$a_8, D \cdot \text{\AA}^{-3}$	-41.7282	-80.1325	240.0176	-0.6066
$a_9, D \cdot \text{\AA}^{-3}$	-	18.4678	-90.3969	-
$a_{10}, D \cdot \text{\AA}^{-3}$	-	-1.8461	19.0736	-
$a_{11}, D \cdot \text{\AA}^{-3}$	-	-	-1.7374	-

Table 2 (continued)

1	2	3	4	5
b_0, D	35.2708	24.8061	19.0618	3.1819
$b_1, D \cdot \text{\AA}^{-1}$	-131.6135	-66.9389	-45.5838	-6.3825
$b_2, D \cdot \text{\AA}^{-2}$	195.7454	71.3075	43.3794	5.6702
$b_3, D \cdot \text{\AA}^{-3}$	-137.3458	-35.7508	-19.5636	-2.3712
$b_4, D \cdot \text{\AA}^{-4}$	45.7162	8.4856	4.1876	0.4619
$b_5, D \cdot \text{\AA}^{-5}$	-5.8447	-0.7721	-0.3436	-0.0340
$B, D \cdot \text{\AA}^{-8}$	129.2889	133.1910	74.5566	42.5468
$R_1, \text{\AA}$	1.0	1.4	1.6	1.8
$R_2, \text{\AA}$	2.0	2.8	3.2	3.6
Parameter	F	Cl	Br	I
$\langle r^2 \rangle, \text{a.u.}$	1.544	4.059	5.224	7.221
$\gamma, \text{a.u.}$	1.1316	0.9763	0.9318	0.8764

The parameters $\alpha = 0.6668 \text{ \AA}$ and $\beta = 0.9997 \text{ a.u.}$ of the hydrogen atom were taken from Ref. 14. The calculated dipole moment functions of hydrogen halides are shown in Figs. 1–4.

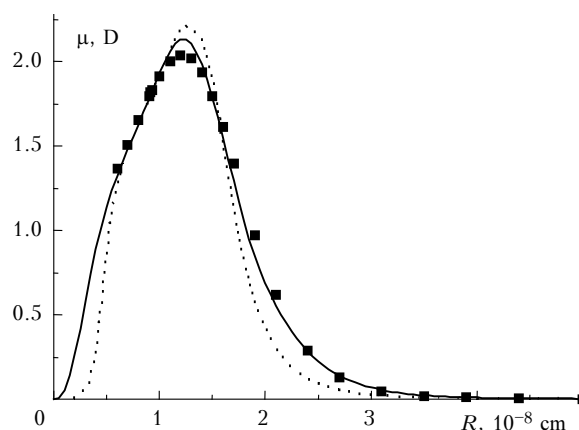


Fig. 1. Dipole moment function of HF molecule: this work (solid curve), Pade approximation⁶ (dashed curve), *ab initio* calculation⁶ (squares).

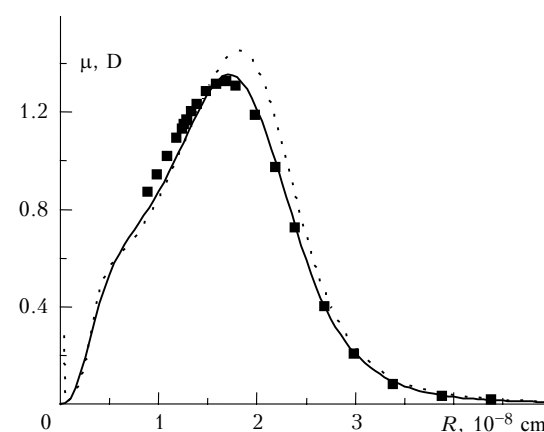


Fig. 2. Dipole moment function of HCl molecule: this work (solid curve), Pade approximation⁸ (dashed curve), *ab initio* calculation⁶ (squares).

These figures depict also the dipole moment functions obtained using the Pade approximation in the following form

$$\mu(R) = M_0(1+x)^3 / \left(1 + \sum_{i=1}^7 e_i x^i \right), \quad (11)$$

in which values of e_i are taken from Ref. 6 for the HF, HBr, and HI molecules and from Ref. 8 for HCl. The comparison of the dipole moment functions calculated by the method proposed and by Eq. (11) demonstrates a satisfactory agreement almost in the whole range of internuclear separations, except for the subrange of small R for the HF, HBr, and HI molecules. This difference is likely caused by the smaller number of dipole moment derivatives in the equilibrium configuration of these molecules (as compared to the HCl molecule), which were used in Ref. 6 to determine e_i .

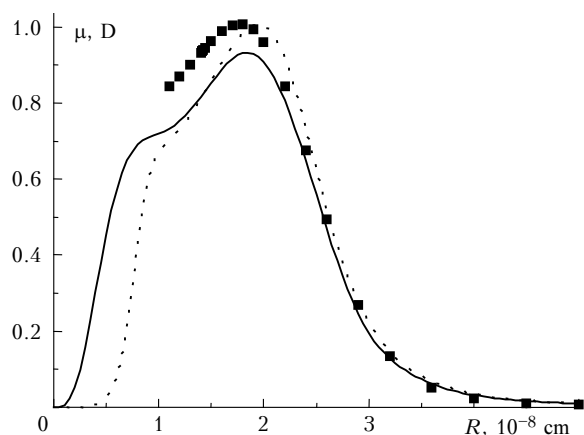


Fig. 3. Dipole moment function of HBr molecule: this work (solid curve), Pade approximation⁶ (dashed curve), *ab initio* calculation⁶ (squares).

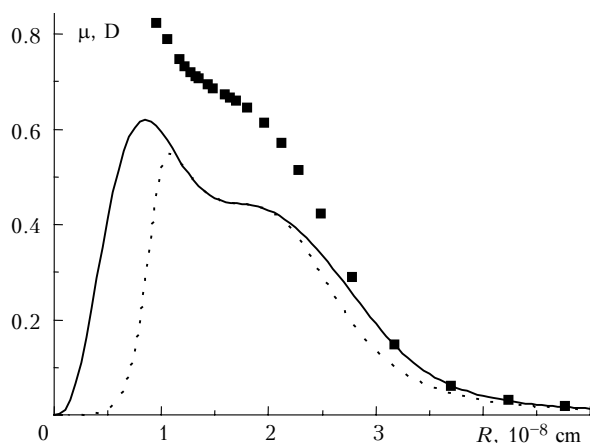


Fig. 4. Dipole moment function of HI molecule: this work (solid curve), Pade approximation⁶ (dashed curve), *ab initio* calculation⁵ (squares).

Besides, to be noted is the presence of breaks in the Pade approximations of the dipole moment functions at $R \approx 0.042 \text{ \AA}$ for the HCl molecule and at $R \approx 22.09 \text{ \AA}$ for the HI molecule. The analysis of the dipole moment functions depicted in Figs. 1–4 shows also that the *ab initio* calculations give the overestimated values near the equilibrium configuration of nuclei of the HBr and HI molecules.

Conclusion

In this paper, we propose the semiempirical method for construction of the dipole moment function of a diatomic molecule in the form of a piecewise continuous function, which has the physically correct asymptotic behavior at small and large internuclear separations and coincides with the dipole moment function in the vicinity of the equilibrium configuration of nuclei of a molecule. The allowance for the multipole and exchange interactions within the framework of this method allows more correct description of the behavior of the dipole moment function at large internuclear separations, including the range of small overlap of the electron shells of the interacting atoms.

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