

# Electric multipole moments of some diatomic molecules

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## Abstract

Molecular Electric Multipole Moment (MEMM) integrals have been derived for diatomic molecular systems, and then some lower multipole moments as dipole moments and quadrupole moments have been calculated for some diatomic molecules. The calculations have been performed by using our analytical formula over Slater-Type orbitals (STOs) with Cade and Huo's basis sets and the GAMESS program package working with Gaussian-Type basis sets (GTOs). The expressions which involve factorials are given in terms of binomial coefficients in order to speed up calculations. The results have been obtained in agreement with data found in the literature.

**Key Words:** Multipole moments, quadrupole moments, dipole moments, Slater-type orbitals.

## 1. Introduction

Determining the electronic structures of atomic and molecular systems is very important for understanding the interactions between atoms and molecules. Many studies have been performed on the magnetic properties and electronic structures of molecules as Zeeman effects, magnetizabilities, electric-field-gradients, electric polarizabilities, etc. [1–13].

MEMMs are important to explain interactions between molecular systems. Molecules can be considered as a special charge distribution, and the molecular interaction potentials can be determined by using MEMMs which come out from the charge asymmetry of any molecular system. Molecular electric quadrupole moment (MEQM) determines the Coulomb interaction between the molecule and other molecules [14]. Determination of the exact molecular potential of any molecule depends on the MEMM calculation sensitivity of the molecule. MEQM is used for molecular long-range interactions and it can be used for verifying test wave functions used in other molecular calculations as well [15].

Molecular Electric Dipole Moments (MEDM) and MEQMs can be determined by different experimental or theoretical methods. They can be measured by collision-induced spectroscopy [16–18]. MEDMs are measured

by Stark effect experiments [19–22]. MEQMs are measured by electric-field-gradient induced birefringence experiment [23, 24] and X-ray diffraction measurements [25]. There are also many different experimental methods, but no one experimental method can be easily applied to all molecular systems. MEMMs can be determined by using some theoretical calculation methods [26–30]. In numerical calculation of the MEMMs, choosing of the calculation method and the basis set are very important in order to obtain good results.

In this study, EMM expressions for diatomic molecules are altered; from which, MEDMs and MEQMs have been calculated for HCl, HF, BH, CO, NO<sup>+</sup> and CN<sup>-</sup> diatomic molecular systems, over Slater-type wave functions, using Cade and Huo’s basis sets and the GAMESS [31] computational package over different Gaussian-type basis sets.

## Theory

The molecular electrostatic potential at point  $r$  is [32]

$$\varphi(r) = \frac{1}{4\pi\epsilon_o} \int \frac{\rho(r')}{|r - r'|} dV', \quad (1)$$

where  $\rho(r')$  is the charge density at  $r'$ . If the quantity  $|r - r'|$  is expanded in a power series, then, equation (1) can be written as

$$\varphi(r) = \frac{1}{4\pi\epsilon_o} \left\{ \frac{1}{r} \int \rho(r') dV' + \frac{r}{r^3} \int r' \rho(r') dV' + \sum_{i=1}^3 \sum_{j=1}^3 \frac{1}{2} \frac{x_i x_j}{r^5} \int (3x'_i x'_j - \delta_{ij} r'^2) \rho(r') dV' \right\}, \quad (2)$$

where,  $(x_i, x_j)$  and  $(x'_i, x'_j)$  are the Cartesian components of  $r$  and  $r'$ , respectively. The integrals in equation (2) are, respectively, the monopole, dipole and quadrupole terms. This equation expresses the potential in terms of electric multipole moments (EMM). The molecular multipole moment operator for any molecule with  $N$  electrons is defined by [33]

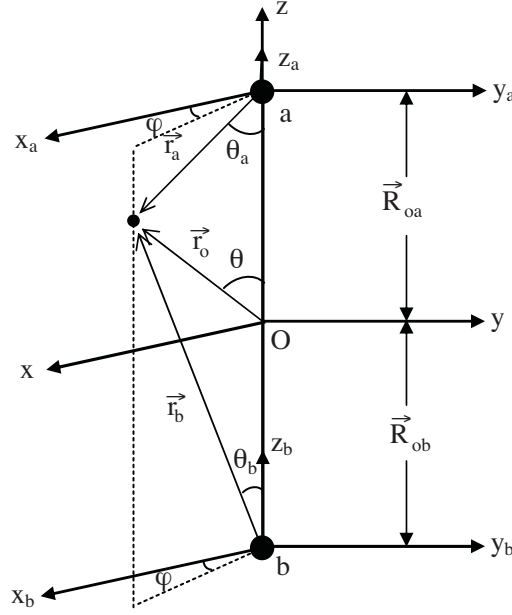
$$\hat{M}_{ks} = \sum_a Z_\alpha \hat{M}_{ks}(R_\alpha) - \sum_{i=1}^N \hat{M}_{ks}(r_i), \quad (3)$$

where  $\mathbf{R}_\alpha$  denotes coordinates for the nucleus relative the molecule’s center or mass, and  $r_i$  denotes coordinates for the electrons relative the nuclei, as seen in Figure.  $\hat{M}_{ks}$  is the multipole moment operator and can be written in terms of solid spherical harmonics [34]:

$$\hat{M}_{ks}(r) = \left( \frac{4\pi}{2k+1} \right)^{1/2} r^k Y_{ks}(\theta, \varphi). \quad (4)$$

Here,  $k$  is the degree of the multipole moment and parameter  $s$  denotes the component of the multipole moment. Expectation values of any multipole moment is

$$\langle M_{ks} \rangle = \int u^* \hat{M}_{ks} u d\tau, \quad (5)$$



**Figure.** The axis frame for diatomic molecular systems using for MEMM calculations. MEMM is defined through the center of mass of the molecule; a, b show the nuclei of the molecule's components and O is the center of mass of the molecule.

where  $u$  is the determinant wave function of the molecule and integration runs over all space. Since the expected value of the operator  $\hat{M}_{ks}(R_\alpha)$  is not related to the electron coordinates, the first sum in equation (3) can be written as a sum in terms of spherical harmonics. If equation (3) is substituted in equation (5), then

$$\langle M_{ks} \rangle = \sum_{\alpha} Z_{\alpha} M_{ks}(R_{\alpha}) - \sum_{i=1}^n N_i \int u_i^*(r) \hat{M}_{ks} u_i(r) dV. \quad (6)$$

$u_i$  is a one-electron wavefunction and can be written for Slater-type orbitals as  $u_i = \sum_p c_{ip} \chi_p$ . Since  $\hat{M}_{ks}$  is a one-electron operator, equation (6) can be written as

$$\langle M_{ks} \rangle = \sum_{\alpha} Z_{\alpha} \langle M_{ks}(R_{\alpha}) \rangle - \sum_i N_i \sum_{pq} c_{ip}^* c_{iq} \langle M_{p,ks,q} \rangle, \quad (7)$$

where  $p, q = n\lambda m$  quantum numbers and  $\langle M_{p,ks,q} \rangle$  denotes

$$\langle M_{p,ks,q} \rangle = \int \chi_p^* \hat{M}_{ks} \chi_q dV. \quad (8)$$

While calculating MEMM, two different types of integral can be obtained:

$$\langle M_{p,ks,q} \rangle_{\alpha\alpha\alpha} = \int \chi_p^*(\zeta_{\alpha}, \vec{r}_{\alpha}) \hat{M}_{ks}(\vec{r}_o) \chi_q(\zeta'_{\alpha}, \vec{r}_{\alpha}) dV \quad (9a)$$

$$\langle M_{p,ks,q} \rangle_{\alpha\alpha\alpha'} = \int \chi_p^*(\zeta_{\alpha}, \vec{r}_{\alpha}) \hat{M}_{ks}(\vec{r}_o) \chi_q(\zeta_{\alpha'}, \vec{r}_{\alpha'}) dV \quad (9b)$$

In equations (9),  $\chi_p$  ( $p \equiv n\lambda m$ ) is the Slater orbital defined by

$$\chi_{n\ell m}(\zeta, r\theta\varphi) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} e^{-\zeta r} Y_{\ell m}(\theta, \varphi). \quad (10)$$

$\langle M_{p,ks,q} \rangle_{\alpha o\alpha}$  is a two-center integral, and  $\langle M_{p,ks,q} \rangle_{\alpha o\alpha'}$  is a three-center integral in equations (9). These integrals can be reduced to one-center and two-center integrals by using translation process, and MEMMs can be easily calculated by using these integrals. We have calculated MEMMs through the center of the molecule. At first, multipole moment operator was located at the center of mass and then translated to any center (atom) by using translation formula [35]

$$\hat{M}_{ks}(r_o) = \sum_{k'=0}^k \sum_{s'=-k'}^{k'} \Omega_{ks,k's'}^*(R_{o\alpha}) \hat{M}_{k's'}(r_a), \quad (11)$$

where  $\Omega_{ks,k's'}$  are called translation coefficients and given by

$$\Omega_{ks,k's'}^*(R) = \hat{M}_{k-k',s-s'}(R) \Lambda_{ks,k's'} \quad (12)$$

for complex spherical harmonics. The axis frame used is shown in Figure. The  $\Lambda_{ks,k's'}$  in equation (13) is

$$\Lambda_{ks,k's'} = (-1)^{s+(1/2)(|s|+|s'|+|s-s'|)} [F_{k'+s'}(k+s) F_{k'-s'}(k-s)]^{1/2}, \quad (13)$$

where  $F_m(n)$  is the binomial coefficient defined by

$$F_m(n) = \frac{n!}{m!(n-m)!}. \quad (14)$$

The one-center integral given in equation (9a) has been derived by translation formula to

$$\begin{aligned} \langle M_{p,ks,q} \rangle_{\alpha o\alpha} &= \sqrt{4\pi} \frac{(2\zeta_\alpha)^{n_\alpha+1/2} (2\zeta'_\alpha)^{n'_\alpha+1/2}}{\sqrt{(2n_\alpha)!} (2n'_\alpha)!} \sum_{L=\max(0, |\ell_\alpha-\ell'_\alpha|, |m_\alpha-m'_\alpha|)}^{\min(k, \ell_\alpha+\ell'_\alpha)} {}^{(2)}\sqrt{2L+1} C^L(\ell_\alpha m_\alpha, \ell'_\alpha m'_\alpha) \\ &\times \frac{R_{o\alpha}^{k-L} Y_{k-L, s-m_\alpha+m'_\alpha}(0, 0)}{\sqrt{(2L+1)(2k-2L+1)}} \frac{(n_\alpha + n'_\alpha + L)!}{(\zeta_\alpha + \zeta'_\alpha)^{n_\alpha+n'_\alpha+L+1}} (-1)^{s+(1/2)[|m_\alpha-m'_\alpha|+|s|+|s-m_\alpha+m'_\alpha|]} \\ &\times [F_{L+m_\alpha-m'_\alpha}(k+s) F_{L-m_\alpha+m'_\alpha}(k-s)]^{1/2}, \end{aligned} \quad (15)$$

and, similarly, the two-center integral given in equation (9b) can be expressed as

$$\begin{aligned} \langle M_{p,ks,q} \rangle_{\alpha' o\alpha} &= \sqrt{4\pi} \sum_{k'=0}^k R_{o\alpha'}^{k-k'} Y_{k-k', s}(\pi, 0) \frac{(-1)^{s+(|s|+|s'|+|s-s'|)/2}}{(2\zeta_{\alpha'})^{k'} \sqrt{(2k'+1)(2k-2k'+1)}} \\ &\times [F_{k'+s'}(k+s) F_{k'-s'}(k-s)]^{1/2} \sqrt{(2k')! F_{2n_{\alpha'}}(2n_{\alpha'}+2k')} \\ &\times \sum_{L=\max(|\ell_{\alpha'}-k'|, |m_{\alpha'}-s'|)}^{\ell_{\alpha'}+k'} {}^{(2)}\sqrt{2L+1} C^L(\ell_{\alpha'} m_{\alpha'}, k' s') S_{(n_{\alpha'}+k')L, n_{\alpha'} \ell_{\alpha'} \lambda}. \end{aligned} \quad (16)$$

Here,  $C^L(\lambda m, \lambda' m')$  is the Gaunt coefficients [36],  $Y_{\ell m}(\theta\varphi)$  expresses complex spherical harmonics and  $S_{n\ell m, n'\ell' m'}$  is the overlap integral defined by

$$S_{n\ell m, n'\ell' m'} = \int \chi_{n\ell m} \chi_{n'\ell' m'} d\tau. \quad (17)$$

## 2. Results and Discussion

Using equations (15) and (16), z-component of dipole and quadrupole moments of CO, HCl, HF, BH, NO<sup>+</sup> and CN<sup>-</sup> have been calculated by using Fortran compiler on a personal computer with Cade and Huo's Slater-type Hartree-Fock-Roothaan wave functions [37, 38]. Furthermore, MEMMs of these molecules have also been computed with GAMESS program over GTOs on a computer running a Linux operating system. In doing so, we intend to compare computations over STOs and GTOs. GTOs are employed widely in molecular calculations since two GTOs at different centers can be expressed easily in terms of one GTO at a new center. However, GTOs do not represent the correct behavior of the wavefunction in the regions which are very close to and far away from the nucleus so a lot of basis functions must be used for representing the wavefunction. STOs represent the system more successfully than GTOs. However, because of the computational difficulties, STOs are rarely used in practical applications.

The MEMM values obtained by using translation formula are in agreement with those obtained from the GAMESS program package and these found in the literature. Dipole moment and quadrupole moment results obtained with respect to the center of mass of the molecule are given in atomic units (a.u.) in Table 1 and Table 2. All of the molecules are in the ground state in this study. The second and the third columns show the results obtained in this study over STOs from the GAMESS package, respectively. Columns (a) to (e) in Tables 1 and 2 show the theoretical reference values. The last column in both tables show experimental reference values. The methods and basis sets used in the literature are indicated as upper index of the given values in Tables 1 and 2.

It is very important that the basis sets and the calculation method be chosen carefully in order to obtain accurate values. Critically, if the basis set does not fit the molecular system, the obtained results may not be as accurate as expected. In order to show the effect of the basis set in GAMESS, different basis sets have been used for each molecule. The multipole moments depend on the orientation, so MEMM values can be taken positive (+) or negative (-). Sometimes, choice of basis set can influence sign of the MEMM.

RHF wavefunctions have been used in calculations over STO's. Such wavefunctions do not include perturbative or correctional terms, and the basis sets and method of calculation do not include correctional terms. However, in this present study, the MEMM values obtained using both methods mentioned above are in agreement with those found in the literature. Generally, only small differences were found between the values calculated in this study and those obtained experimentally. The differences are mostly due to the fact that our wave functions do not include any correctional or perturbative terms. Our main goal is to demonstrate that Slater-type orbitals may successfully be used in practical calculations by employing translation formula. We believe that even better agreement with experiment can be obtained if correctional and perturbative terms are included, in conjunction with STO's.

**Table 1.** Calculated and reference dipole moment values for some diatomic molecules in atomic units (a.u.).

Molecule	This work with STO values	This work with GAMESS (GTO) values	(a)	(b)	(c)	(d)	(e)	(f)
HCl	-0.664	-0.601 <sup>(1)</sup>	0.474 <sup>(6)</sup>	0.443 <sup>(8)</sup>	0.468 <sup>(10)</sup>	0.474 <sup>(12)</sup>		0.430 <sup>(15)</sup>
		-0.752 <sup>(2)</sup>	0.438 <sup>(7)</sup>	0.425 <sup>(9)</sup>	0.432 <sup>(11)</sup>	0.449 <sup>(13)</sup>		0.436 <sup>(17)</sup>
HF	-0.853	-0.845 <sup>(3)</sup>	0.757 <sup>(6)</sup>	0.716 <sup>(8)</sup>		0.756 <sup>(12)</sup>		0.706 <sup>(15)</sup>
		0.762 <sup>(2)</sup>	0.700 <sup>(7)</sup>	0.694 <sup>(9)</sup>		0.708 <sup>(13)</sup>		0.718 <sup>(16)</sup>
BH	0.781	0.577 <sup>(2)</sup>	-	0.599 <sup>(8)</sup>				
		0.455 <sup>(4)</sup>	-	0.582 <sup>(9)</sup>				
CO	0.051	-0.015 <sup>(4)</sup>	-0.099 <sup>(6)</sup>	0.092 <sup>(8)</sup>		-0.098 <sup>(12)</sup>		0.048 <sup>(15)</sup>
		-0.022 <sup>(5)</sup>	0.070 <sup>(7)</sup>	0.075 <sup>(9)</sup>		0.121 <sup>(13)</sup>		
NO <sup>+</sup>	-0.185	-0.151 <sup>(1)</sup>					-0.253 <sup>(14)</sup>	
		-0.342 <sup>(3)</sup>						
CN <sup>-</sup>	0.152	0.164 <sup>(1)</sup>					0.160 <sup>(14)</sup>	
		0.161 <sup>(4)</sup>						
(1) STO-3G basis sets		(a) Ref. [39]	(c) Ref. [41]	(e) Ref. [43]				
(2) MINI basis sets		(6) SCF	(10) SCF	(14) HF				
(3) MIDI basis sets		(7) SD-CI	(11) MP2	(f) Experimental values				
(4) N-21G basis		(b) Ref. [40]	(d) Ref. [42]	(15) Ref. [39]				
(5) STO-6G basis sets		(8) LDA	(12) SCF	(16) Ref. [44]				
		(9) BP86	(13) MP2	(17) Ref. [45]				

**Table 2.** Calculated and reference quadrupole moment values for some diatomic molecules in atomic units (a.u.).

Molecule	This work with STO values	This work with GAMESS (GTO) values	(a)	(b)	(c)	(d)	(e)	Experimental
HCl	2.360	1.856 <sup>(1)</sup>	2.858 <sup>(6)</sup>		2.800 <sup>(10)</sup>	2.857 <sup>(12)</sup>		2.780 <sup>(15)</sup>
		2.560 <sup>(2)</sup>	2.738 <sup>(7)</sup>		2.740 <sup>(11)</sup>	2.783 <sup>(13)</sup>		
HF	1.558	1.474 <sup>(2)</sup>	1.744 <sup>(6)</sup>	1.683 <sup>(8)</sup>		1.742 <sup>(12)</sup>		1.754 <sup>(16)</sup>
		1.514 <sup>(3)</sup>	1.716 <sup>(7)</sup>	1.649 <sup>(9)</sup>		1.739 <sup>(13)</sup>		1.758 <sup>(17)</sup>
BH	-3.005	-2.782 <sup>(2)</sup>		-2.428 <sup>(8)</sup>				
		-2.996 <sup>(4)</sup>		-2.497 <sup>(9)</sup>				
CO	-2.130	-2.132 <sup>(4)</sup>	1.537 <sup>(6)</sup>	-1.528 <sup>(8)</sup>		-1.536 <sup>(12)</sup>		-1.440 <sup>(15)</sup>
		-2.236 <sup>(5)</sup>	-1.519 <sup>(7)</sup>	-1.549 <sup>(9)</sup>		-1.526 <sup>(13)</sup>		-2.110 <sup>(18)</sup>
NO <sup>+</sup>	0.529	-0.591 <sup>(1)</sup>					0.519 <sup>(14)</sup>	
		-0.332 <sup>(3)</sup>						
CN <sup>-</sup>	-4.542	-3.655 <sup>(1)</sup>					-3.156 <sup>(14)</sup>	
		-3.908 <sup>(4)</sup>						
(1) STO-3G basis sets		(a) Ref. [39]	(c) Ref. [41]	(e) Ref. [43]				
(2) MINI basis sets		(6) SCF	(10) SCF	(14) HF				
(3) MIDI basis sets		(7) SD-CI	(11) MP2	(f) Experimental values				
(4) N-21G basis sets		(b) Ref. [40]	(d) Ref. [42]	(15) Ref. [39]				
(5) STO-6G basis sets		(8) LDA	(12) SCF	(16) Ref. [46]				
		(9) BP86	(13) MP2	(17) Ref. [44]				
				(18) Ref. [23]				

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