S.Ü. Fen-Edebiyat Fakültesi Fen Dergisi Sayı 20 (2002) 141-148, KONYA

Calculation of Electric Quadrupole Moments for HF, HCl and BH Molecules

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Abstract: An expression for electric quadrupole moments of diatomic molecules have been derived and applied to HF, HCl and BH for calculations. The calculations have been performed by using both Guseinov's translation formula over Slater-type orbitals (STOs) and GAMESS programme working with Gaussian-type basis sets (GTOs). The expressions which involve factorials are given in terms of binomial coefficients in order to make calculations faster. The results have been obtained in agreement with the literature.

Key words: **Multipole moments, quadrupole moments, Slater-type orbitals**

HF, HCl ve BH Moleküllerinin Elektrik Kuadrupol Momentlerinin Hesaplanması

Özet: İki atomlu moleküllerin elektrik kuadrupol momentlerinin ifadeleri türetilmiş ve HF, HCl ve BH' a uygulanmıştır. Hesaplamalar hem Guseinov' un taşıma formülü kullanılarak Slater-tipi orbitaller (STO) üzerinden hem de Gauss-tipi baz setleri (GTO) kullanan GAMESS programı kullanılarak gerçekleştirilmiştir. Hesaplamaların hızlandırılması için faktöriyel içeren ifadeler binom katsayıları cinsinden ifade edilmiştir. Elde edilen sonuçlar literatürle uyum içerisindedir.

Anahtar Kelimeler: **Çok kutup momentleri, kuadrupol momenti, Slater-tipi orbitaller**

1. Introduction

Determination of the molecular electronic structure is very important to understand interaction between molecule and other molecules. The molecules can be considered as a special charge distribution and the molecular interaction potentials can be determined in this way. The molecular electrostatic potential [1] is

$$V(\vec{r}_1)=\sum_a \frac{Z_a}{r_{1a}}-\int \frac{\rho(\vec{r}_2)}{r_{12}}d\vec{r}_2 \tag{1}$$

where Z is nuclear charge, $\rho(\vec{r}_2)$ is charge density at point $\vec{r}_2$, r_{12} is the distance between points 1 and 2. This potential can be written as an expansion in terms of multipole moments [2],

$$V(\vec{r})=\frac{q}{r}+\frac{\vec{\mu}\vec{r}}{r^3}+\frac{1}{2}\sum_{ij}\theta_{ij}\frac{r_i r_j}{r^5}+\Lambda \tag{2}$$

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where q, μ, θ_{ij} are monopole, dipole and quadrupole terms respectively. Molecular electric quadrupole moment (MEQM) comes out from the charge asymmetry of the molecular system. MEQM determines the Coulomb interaction between the molecule and other molecules or with non-uniform external electric fields [3]. Determination of the exact molecular potential of any molecule depends on the MEQM calculation sensitivity of the molecule. In theoretical determination of the MEQM, choosing of the calculation method and the basis set are very important.

The values of multipole moments of molecules can be obtained experimentally by using different methods. It can be seen in literature that dipole moments determined by Stark effect [4, 5] or other methods [6, 7, 8, 9] and Quadrupole moments determined by Electric-Field-Gradient Induced Birefringence (EFGB) method [10, 11, 12].

2. Theory

In atomic units, the traceless quadrupole moment tensor is given by

$$Q_{\alpha\beta}=\frac{1}{2}\sum_{a} Q_a\left(3R_{a\alpha}R_{a\beta}-R_a^2\delta_{\alpha\beta}\right)-\frac{1}{2}\sum_{i}\left(3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta}\right)\quad \alpha,\beta=x,y,z \tag{3}$$

where the first summation runs over nuclei and the second one runs over electrons [13]. The MEQM for a molecule with N-electron is defined by [14]

$$M_{ks}=\sum_{a} Z_a\hat{M}_{ks}(\vec{R}_a)-\sum_{i=1}^{N}\hat{M}_{ks}(\vec{r}_i) \tag{4}$$

where $\hat{M}_{ks}$ is the multipole moment operator and can be written in terms of solid spherical harmonics [15],

$$\hat{M}_{ks}(\vec{r})=\left(\frac{4\pi}{2k+1}\right)^{1/2} r^k\, Y_{ks}(\theta,\varphi). \tag{5}$$

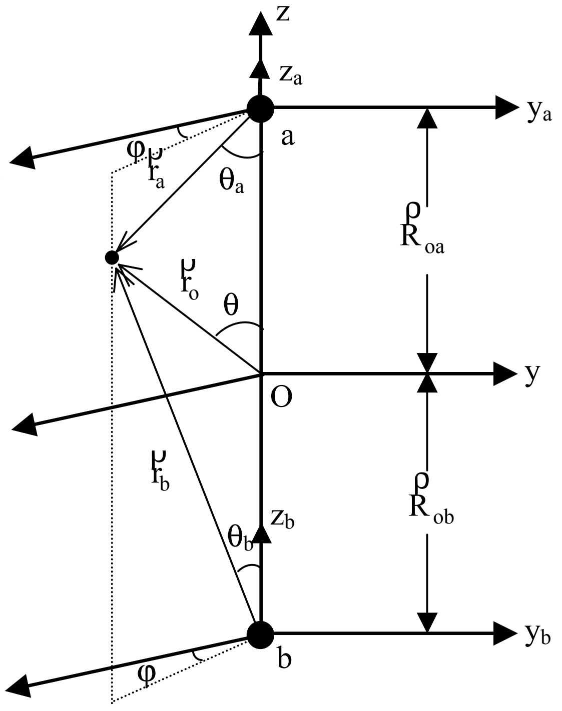

Figure 1. The axis frame for diatomic molecular systems using for MEQM calculations MEQM is defined through the center of mass of the molecule. a, b are show the nuclei of the molecule and O is the center of mass of the molecule.

and k is the degree of the multipole moment and s parameter represents the component of the multipole moment. For k=2 and s=0, z-component of the MEQM can be written as

$$\hat{M}_{20}=\left(\frac{4\pi}{5}\right)^{1/2} r^2\, Y_{20}(\theta,\varphi)\ . \tag{6}$$

Expectation values of any multipole moment are

$$\overline{M}_{ks}=\int u^*\, \hat{M}_{ks}\ u\, d\tau\, . \tag{7}$$

Where u is the determinant wave function of the molecule and integration runs over all space. If Eq. (4) substitutes in Eq. (7) then

$$\overline{M}_{ks}=\sum_a Z_a M_{ks}(\vec{R}_a)-\sum_{i=1}^{n} N_i \int u_i^*(\vec{r}) M_{ks} u_i(\vec{r}) dV \tag{8}$$

u_i is one-electron wavefunction and can be written for Slater-type orbitals, $u_i=\sum_p c_{ip}\chi_p$. Then, from Eq.(8)

$$\overline{M}_{ks}=\sum_a Z_a M_{ks}(\vec{R}_a)-\sum_i N_i \sum_{pq} c_{ip}^* c_{iq} \left\langle M_{p,ks,q}\right\rangle . \tag{10}$$

$\left\langle M_{p,ks,q}\right\rangle$ is written as

$$\left\langle M_{p,ks,q}\right\rangle=\int \chi_p^*\, \hat{M}_{ks}\, \chi_q dv\, . \tag{11}$$

While calculating MEQM, four different types of integral can be obtained as follows

$$\left\langle M_{p,ks,q}\right\rangle_{aoa}=\int \chi_p^*(\zeta_a,\vec{r}_a)\hat{M}_{ks}(\vec{r}_o)\chi_q(\zeta_a',\vec{r}_a)dV \tag{12-a}$$

$$\left\langle M_{p,ks,q}\right\rangle_{bob}=\int \chi_p^*(\zeta_b,\vec{r}_b)\hat{M}_{ks}(\vec{r}_o)\chi_q(\zeta_b,\vec{r}_b)dV \tag{12-b}$$

$$\left\langle M_{p,ks,q}\right\rangle_{boa}=\int \chi_p^*(\zeta_b,\vec{r}_b)\hat{M}_{ks}(\vec{r}_o)\chi_q(\zeta_a,\vec{r}_a)dV \tag{12-c}$$

$$\left\langle M_{p,ks,q}\right\rangle_{aob}=\int \chi_p^*(\zeta_a,\vec{r}_a)\hat{M}_{ks}(\vec{r}_o)\chi_q(\zeta_b,\vec{r}_b)dV \tag{12-d}$$

χ_p ($p \equiv n\lambda m$) is the Slater orbital defined by

$$\chi_{n\lambda m}(\zeta,r\theta\varphi)=\frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1}e^{-\zeta r}\, Y_{\lambda m}(\theta,\varphi)\, . \tag{13}$$

$\left\langle M_{p,ks,q}\right\rangle_{aoa}$ and $\left\langle M_{p,ks,q}\right\rangle_{bob}$ are two-center integrals, $\left\langle M_{p,ks,q}\right\rangle_{aob}$ and $\left\langle M_{p,ks,q}\right\rangle_{boa}$ are three-center integrals in Eqs. (12). $\left\langle M_{p,ks,q}\right\rangle_{aoa}$ and $\left\langle M_{p,ks,q}\right\rangle_{bob}$ integrals are equivalent to each other and so they are the integrals $\left\langle M_{p,ks,q}\right\rangle_{aob}$ and $\left\langle M_{p,ks,q}\right\rangle_{boa}$. These integrals can be reduced to one-center and two-center integrals by using translation process, and quadrupole moments of diatomic molecules can be easily calculated by these integrals. We have calculated MEQMs through the center of the molecule. At first, quadrupole moment operator was located at the center of mass and then translated to any center (atom) by using *Guseinov's translation formula* [16].

$$\hat{M}_{ks}(\vec{r}_o)=\sum_{k'=0}^{k}\sum_{s'=-k'}^{k'}\Omega_{ks,k's'}^*(\vec{R}_{oa})\hat{M}_{k's'}(\vec{r}_a) \tag{14}$$

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

$$\Omega^{*}_{ks,k's'}(\vec{R})=\hat{M}_{k-k',s-s'}(\vec{R})\,\Lambda_{ks,k's'} \qquad (15)$$

for complex spherical harmonics. The axis frame which used is shown in Figure 1.
The $\Lambda_{ks,k's'}$ in Eq. (15) is

$$\Lambda_{ks,k's'}=(-1)^{s+(1/2)(|s|+|s'|+|s-s'|)}\left[F_{k'+s'}(k+s)\,F_{k'-s'}(k-s)\right]^{1/2} \qquad (16)$$

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

$$F_m(n)=\frac{n!}{m!(n-m))!} \qquad (17)$$

The one-center integral given in Eq.(12-a) has been derived using by translation formula as

$$\begin{aligned}\left\langle M_{p,ks,q}\right\rangle_{aoa}=&\sqrt{4\pi}\,\frac{(2\zeta_a)^{n_a+1/2}(2\zeta'_a)^{n'_a+1/2}}{\sqrt{(2n_a)!(2n'_a)!}}\sum_{L=\max(0,|\lambda_a-\lambda'_a|,|m_a-m'_a|)}^{\min(k,\lambda_a+\lambda'_a)}{}^{(2)}\sqrt{2L+1}\,C^{L}(\lambda_a m_a,\lambda'_a m'_a)\\&\times\frac{R_{oa}^{k-L}Y_{k-L,s-m_a+m'_a}(0,0)}{\sqrt{(2L+1)(2k-2L+1)}}\,\frac{(n_a+n'_a+L)!}{(\zeta_a+\zeta'_a)^{n_a+n'_a+L+1}}(-1)^{s+(1/2)[|m_a-m'_a|+|s|+|s-m_a+m'_a|]}\\&\times\left[F_{L+m_a-m'_a}(k+s)\,F_{L-m_b+m'_b}(k-s)\right]^{1/2}\end{aligned} \qquad (18)$$

and the other two-center integral given in Eq(12-c) as follows

$$\begin{aligned}\left\langle M_{p,ks,q}\right\rangle_{boa}=&\sqrt{4\pi}\sum_{k'=0}^{k}R_{ob}^{k-k'}\,Y_{k-k',s}(\pi,0)\frac{(-1)^{s+(|s|+|s'|+|s-s'|)/2}}{(2\zeta_b)^{k'}\sqrt{(2k'+1)(2k-2k'+1)}}\\&\times\left[F_{k'+s'}(k+s)\,F_{k'-s'}(k-s)\right]^{1/2}\sqrt{(2k')!F_{2n_b}(2n_b+2k')}\\&\times\sum_{L=\max(|\lambda_b-k'|,|m_b-s'|)}^{\lambda_b+k'}{}^{(2)}\sqrt{2L+1}\,C^{L}(\lambda_b m_b,k's')\,S_{(n_b+k')L\lambda,\,n_a\lambda_a\lambda}\,.\end{aligned} \qquad (19)$$

Where $C^{L}(\lambda m, \lambda' m')$ is the Gaunt coefficients [17], $Y_{\lambda m}(\theta\varphi)$ is the complex spherical harmonics and $S_{n\lambda m,n'\lambda' m'}$ is the overlap integral [18] defined by

$$S_{n\lambda m,n'\lambda' m'}=\int\chi_{n\lambda m}\chi_{n'\lambda' m'}d\tau \qquad (20)$$

Taking k=2 and s=0, z-component of MEQMs for HCl, HF and BH molecules have been calculated over Slater-type obrbitals by using Eq.(19) and Eq.(20). In calculations, Cade and Huo's Slater-type Hartree-Fock-Roothaan wave functions have been used as basis sets [19]. MEQM's of these molecules have been also computed with GAMESS programme [20].

3. Results and discussion

The expression of MEQM for diatomic molecules has been derived over STOs by using Guseinov's translation formula. The expressions which involve factorials have been written in terms of binomial coefficients in order to make calculations faster. MEQMs of HF, HCl and BH molecules have been calculated by using FORTRAN 77 programming language on a personal computer. Futhermore, MEQMs of these molecules have also been computed with GAMESS programme over GTOs on 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 behaviour 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 successfuly than GTOs. Because of the computational difficulties, STOs are rarely used in practical applications.

The MEQM values obtained by using Guseinov's translation formula are agreement with both of the values obtained from the GAMESS programme and these found in the literature. The results obtained with respect to the center of mass of the molecule are given in atomic units (a.u.) in Table 1. Where, first two cloumns are show the results obtained in this study by using translation formula and GAMESS programme respectively. The methods and basis sets used in the literature are indicated as upper index of the given values in Table 1. The results obtained by using translation formula over STOs for HCl, HF and BH are 2.360 a.u., 1.558 a.u. and–3.005 a.u. respecticely. It is very important that the basis sets and the calculation method should be chosen carefully in order to obtain accurate values. Especially, if the basis set is not fit for the molecular system, the results can not be obtained as accurate as expected. In order to show the effect of the basis set, two different basis sets have been used for each molecule in computing by GAMESS programme. MEQM values for HCl molecule have been obtained as 1.856 a.u. with STO-3G basis sets but it has been obtained as 2.560 a.u. with MINI basis sets by using GAMESS. By using Guseinov's translation formula over STOs this value has been obtained as 2.360 a.u. The last two values are in agreement with the literature but the first one is not, so basis sets must be chosen carefully otherwise the values may not be correct. The multipole moments depend on the orientation, so MEQM values can be taken positive (+) or negative (-) sign. Sometimes choosing of the basis set can influence the sign of the MEQM.

ROHF wavefunctions have been used in calculations by using Guseinov's translation formula. These types of wavefunctions do not include any perturbative or correctional term. Furthermore, the basis set and the calculation method don't include any correctional term. However, In this present study, the MEQM values obtained by using both methods mentioned above are in sufficent with the literature. Of course, there exist small differences between the values calculated in this study and the values obtained experimentally. The differences are mostly due to the fact that our wave functions do not include any correctional or perturbative terms as mentioned above. However, here our main goal is to demonstrate that, Slater-type orbitals may be used in practical calculations by employing Guseinov's translation formula. We belive that even better agreement with experiment can be obtained if correctional and perturbative terms included, in conjuction with STO's.

Table 1. Calculated and reference MEQM values for HF, HCl and BH molecules in atomic units (a.u.).

Molecule	This study with STO	This study with GAMESS	(a)	(b)	(c)	(d)	(f)
HCl	2.360	1.856 (1)	2.858 (5)	-	2.800 (9)	2.857 (11)	2.780 (13)
		2.560 (2)	2.738 (6)	-	2.740 (10)	2.783 (12)	
HF	1.558	1.514 (3)	1.744 (5)	1.683 (7)	-	1.742 (11)	1.754 (14)
		1.474 (2)	1.716 (6)	1.649 (8)	-	1.739 (12)	1.758 (15)
BH	-3.005	-2.782 (2)	-	-2.428 (7)	-	-	-
		-2.996 (4)	-	-2.497(8)	-	-	-

(1) STO-3G basis sets
(Pople' s STO-NG minimal basis set)
(2) MINI basis sets
(Pople's N-21G split valance basis set)
(3) MIDI basis sets
(Huzinaga's 3 gaussian minimal basis set)
(4) N-21G basis
(Huzinaga's 21 split valance basis set)

(a) Ref. [21]
(5) SCF
(6) SD-CI
(b) Ref. [22]
(7) LDA
(8) BP86
(c) Ref. [23]
(9) SCF
(10) Møller-Plesset (MP2)

(d) Ref. [24]
(11) SCF
(12) Møller-Plesset (MP2)
(f) Experimental values
(13) Ref. [21]
(14) Ref. [25]
(15) Ref. [26]

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