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Molecular electronic virial theorem

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The partitioning of the molecular electronic energy into true one-electron quantities defined by a molecular electronic virial theorem (MEVT) is studied for a number of molecules. Since the theorem is derived for exact wavefunctions, its applicability to various *ab initio* wavefunctions at different levels of accuracy is examined. The average percentage deviations of the theorem for near Hartree-Fock, double zeta, STO-6G and STO-3G type wave functions are 0.4, 1.7, 2.3 and 3.3, respectively.

Key words: Electronic energy partitioning - molecular electronic virial theorem

1. Introduction

A partitioning of molecular energy into various components helps to understand various chemical phenomena-like mechanism of chemical bonding [1], molecular shape variations upon excitation and ionisation [2] and non-bonded interactions [3]. Unfortunately, as the molecular Hamiltonian is composed of both one electron and two electron terms and mono- and bicentric terms, a direct partitioning, either in terms of electrons or in terms of atomic centres is not evident. Even in the conventional independent particle Hartree-Fock (HF) approximation, the canonical orbital energies are not true "one-electron energies", as their sum does not equal the total molecular electronic energy. This has made a large number of attempts to break up the total molecular energy into various components necessary so as to serve various purposes. Foremost among these attempts is the Ruedenberg method [1] which was applied to elucidate the mechanism of chemical bonding in H_2^+. This approach involves a number of theoretical steps in forming a chemical bond from separated atoms. Since it is a rather involved approach, its extension and interpretation to polyatomic molecules is difficult. A similar approach, modified for left-right correlation was used by Driessler and Kutzelnigg [4, 5] to describe bonding. Kollmar [6] developed an *ab initio* energy partitioning scheme in terms of atomic centers, similar to the one employed in Zero Differential Overlap (ZDO) methods [7], and applied it to the study of non-bonded interactions. Goddard [8], using the generalised valence bond wave-functions, separated the total kinetic and potential energies into classical and exchange parts. He concluded that exchange part of the kinetic energy plays the dominant role in chemical bonding. Takahata and Parr [9], Coulson and Neilson [10], Davidson [11], Politzer [12], and Coulson and Deb [13] derived various one-electron quantities for use in the construction of the Walsh-Mulliken Diagrams [14]. Clementi [15] used "electron-energies" in the study of Li-$(H_2O)_n$ systems.

It is desirable that a general partitioning scheme should satisfy the following criteria:

a. Summability, i.e. the sum of the derived one-electron terms should add to give the total molecular energy or at least total molecular electronic energy.
b. These quantities should have a simple and clear physical meaning.

Each of the schemes discussed above has been devised to suit a particular purpose on hand and does not serve as a general partitioning scheme; nor can the partitioned quantities be easily assigned a simple physical meaning. We have recently proposed a method of partitioning the electronic energy of a molecule [16], based on a *molecular electronic virial theorem* (MEVT) which divides the total molecular electronic energy into truly one-electron components. Though derived for exact wavefunctions, the theorem was shown [16] to be numerically valid for molecular wavefunctions of near Hartree-Fock quality for simple systems. In this paper, we present the results for various diatomic and polyatomic molecules, using *ab initio* wavefunctions of different quality and discuss the applicability and numerical validity of the molecular electronic virial theorem at equilibrium and non-equilibrium geometries.

2. The method

The molecular electronic virial theorem (MEVT), derived earlier [16], can be stated as follows:

$$E^e = \sum_i \langle f_i \rangle \tag{1}$$

$$\langle f_i \rangle = -\langle t_i \rangle + W_i \tag{2}$$

with

$$W_i = \sum_\alpha Z_\alpha \left\langle \boldsymbol{R}_\alpha \cdot \frac{\boldsymbol{r}_i - \boldsymbol{R}_\alpha}{R_{\alpha i}^3} \right\rangle. \tag{3}$$

Here E^e is the total molecular electronic energy, excluding nuclear repulsion, at the given nuclear configuration; t_i is the kinetic energy operator for the ith electron; W_i is the Hellmann-Feynman work due to ith electron, $\boldsymbol{R}_\alpha$ is the position vector of αth nucleus and $\boldsymbol{r}_i$ is the position vector of ith electron. The expectation values are over the *exact* wavefunction of the system at any given nuclear configuration.

We have called Eq. (1) as *molecular electronic virial theorem* (MEVT). This must be distinguished from the well-known molecular virial theorem (MVT) of Slater [17], which is concerned with the total energy including nuclear repulsions.

It is easily seen that the terms $\langle f_i \rangle$ satisfy the desirable criteria for a truly one-electron quantity. Summability is evident since molecular electronic energy is exactly equal to the sum of $\langle f_i \rangle$, where f_i is a *one-electron* operator. Also its physical meaning is simple. $\langle f_i \rangle$ is equal to the work done by the charge density due to the ith electron in bringing the isolated nuclei to the given nuclear configuration, less the kinetic energy acquired by the electron in the process. This directly corresponds to the gain in the energy of this electron, during molecule formation. The relationship of MEVT to the familiar virial theorem can be established as follows. MEVT is valid at any nuclear configuration. When we consider it at equilibrium geometry we get the following equation:

$$E^e(R_{eq}) = -\sum_i \langle t_i \rangle_{R_{eq}} + \sum_i \sum_\alpha Z_\alpha \left\langle \boldsymbol{R}_\alpha \frac{\boldsymbol{r}_i - \boldsymbol{R}_\alpha}{R_{\alpha i}^3} \right\rangle_{R_{eq}} . \tag{4}$$

By adding the internuclear repulsion energy V^{nn}, which is constant at a given geometry, to both sides of Eq. (4), we get

$$E^e(R_{eq}) + V^{nn}(R_{eq}) = -\sum_i \langle t_i \rangle_{R_{eq}} + \sum_i \sum_\alpha Z_\alpha \left\langle \boldsymbol{R}_\alpha \frac{\boldsymbol{r}_i - \boldsymbol{R}_\alpha}{R_{\alpha i}^3} \right\rangle_{R_{eq}} + V^{nn}(R_{eq}). \tag{5}$$

At the equilibrium geometry nuclear repulsions are exactly balanced by the attractive forces. Thus, the second and third terms on rhs of Eq. (5) cancel each other and leave us with

$$E^e(R_{eq}) + V^{nn}(R_{eq}) = -\sum_i \langle t_i \rangle_{R_{eq}} \tag{6}$$

or

$$E^{\text{total}} = -T$$

which is the molecular virial theorem at equilibrium geometry. Similarly the molecular virial theorem at nonequilibrium geometry can be shown to be related to MEVT, at a given nuclear configuration by assuming nuclear wavefunctions to be δ-functions.

3. Numerical method

In this section, we briefly discuss the numerical procedure employed to evaluate the one-electron quantity $\langle f_i \rangle$ of Eq. (2). The evaluation of expectation values $\langle t_i \rangle$ is straightforward [18]. The values of W_i are evaluated using the following integral transformation similar to the one used in molecular calculations for the nuclear-electron attraction operator V_n^i [18],

$$\frac{1}{R^n} = \frac{1}{\sqrt{(n/2)}} \int_0^\infty ds\, s^{(n/2)-1}\, e^{-sR^2}. \tag{7}$$

The form of the transformed operator suggests that it would be more tractable in a Gaussian-type orbital (GTO) basis rather than in a Slater-type orbital (STO) basis. The advantage is that, since closed form expressions are available for integrals over Gaussian function products, we can combine the e^{-sR^2} part of the operator with basis orbitals and obtain a polynomial in the variable s alone, which can then be numerically integrated using standard techniques.

Thus we may write Eq. (3) in detail as:

$$W_i = \sum_\alpha Z_\alpha \left\langle \Psi(i) \middle| \mathbf{R}_\alpha \frac{\mathbf{r}_i - \mathbf{R}_\alpha}{R^3_{\alpha i}} \middle| \Psi(i) \right\rangle \tag{8}$$

where Ψ is a molecular orbital written in the LCAO form,

$$\Psi = \sum_k c_k \phi_k, \tag{9}$$

ϕ_k being the basis functions. Since we take ϕ's as GTO's, we can write

$$\phi = f(x_A, y_A, z_A)\, e^{-\alpha r_A^2} \tag{10}$$

with $f = 1$ for s-type function and $f = x_A$ for p_x-type function. Here $x_A = x - A_x$; similarly for y_A and z_A; $r_A^2 = x_A^2 + y_A^2 + z_A^2$. A_x, A_y, A_z are the Cartesian coordinates of the atomic centre A, on which ϕ is based.

The product of two Gaussian functions is another Gaussian, with its center between the centers of original Gaussians. Thus, we can write the product of ϕ_k and ϕ_l, on centers A and B respectively as a Gaussian on center C as

$$\phi_m^C = \phi_k^A \phi_l^B = f_k(x_A, y_A, z_A) f_l(x_B, y_B, z_B)\, e^{-\alpha_k r_A^2}\, e^{-\alpha_l r_B^2}. \tag{11}$$

This can be condensed to

$$\phi_m^C = f_m(x_C, y_C, z_C)\, e^{-(\alpha_k + \alpha_l) r_C^2}. \tag{12}$$

Substituting for Ψ in Eq. (8) using Eqs. (9), (10) and (12), we have,

$$\begin{aligned} W_i = {} & \frac{\sum_k \sum_l c_k c_l}{\sqrt{(3/2)}} \int_{s=0}^{s=\infty} s\, ds \\ & \times \int_{x,y,z=-\infty}^{x,y,z=\infty} (x\alpha_x + y\alpha_y + z\alpha_z - \alpha_x^2 - \alpha_y^2 - \alpha_z^2) f(x_C, y_C, z_C) \\ & \times e^{-(\alpha_k + \alpha_l) r_C^2}\, e^{-sR_{i\alpha}^2}\, dx\, dy\, dz. \end{aligned} \tag{13}$$

Putting

$$e^{-(\alpha_k + \alpha_l) r_C^2}\, e^{-sR_{i\alpha}^2} = e^{-\beta R^2}$$

We can write the integral part in Eq. (13) as

$$\int_{s=0}^{s=\infty} s\,ds \int_{x,y,z=-\infty}^{x,y,z=+\infty} (x\alpha_x + y\alpha_y + z\alpha_z - \alpha_x^2 - \alpha_y^2 - \alpha_z^2) \cdot f(x_C, y_C, z_C)\, e^{-\beta R^2}\, dx\, dy\, dz. \tag{14}$$

This can be simplified further to facilitate integration over x, y, z as

$$\int_{s=0}^{s=\infty} s\,ds (X + Y + Z + K) \tag{15}$$

where

$$X = \int_{x,y,z=-\infty}^{x,y,z=+\infty} f(x_C, y_C, z_C) x\alpha_x\, e^{-\beta R^2}\, dx\, dy\, dz \tag{16}$$

and similar expressions for Y and Z. K is given by

$$K = -\int (\alpha_x^2 + \alpha_y^2 + \alpha_z^2)\, e^{-\beta R^2} f(x_C, y_C, z_C)\, dx\, dy\, dz. \tag{17}$$

The integrals X, Y, Z and K are simple integrals over Gaussians and can be analytically evaluated. Thus, we are left with a single numerical integration over s. We have used Gaussian Quadrature for this final numerical integration. The fact that the accuracy of the present method is comparable to those usually employed in molecular calculations is evident from the results of the test calculations performed on the electric field components of some molecules for which reported values are available [19]. These are shown in Table 1.

Table 1. Electric Field Values using the present integration method

Molecule		Present calculation	SB[a]
BH_3	H(x)	0.0304	0.0307
	H(y)	0.0000	0.0000
	H(z)	−0.0537	−0.0531
CH_4	H(x)	0.0367	0.0372
	H(y)	0.0367	0.0372
	H(z)	0.0367	0.0372
H_2O	O(z)	−0.2525	−0.2482
	H(y)	0.0996	0.1010
	H(z)	0.0385	0.0372
BF	B(z)	−0.1302	−0.1306
	F(z)	0.2714	0.2662
CO	C(z)	−0.1889	−0.1871
	O(z)	0.3007	0.2907
N_2	N(z)	−0.2174	−0.2489

[a] Reference values are from Ref. [19].

4. Results and discussion

4.1. Basis set dependence

In the present work Gaussian type wavefunctions have been used, considering the computational advantages discussed earlier. We have used basis sets of varying size and accuracy to check the dependence of MEVT on the quality of the wavefunctions. Since we have already established [16] that MEVT is, in theory, valid for fully variational functions, the present work is restricted to basis sets of double zeta (DZ) quality and minimal (STO-NG type) basis sets. DZ functions used in this work have been obtained from the compendium of Snyder and Basch [19]. These wavefunctions have been used by a large number of workers for a variety of calculations [20] and thus form a set of reference wavefunctions.

In addition to DZ functions, we have used the minimal STO-3G and STO-6G wavefunctions obtained from the GAUSSIAN-70 program [21]. For comparing the effect of the quality of wavefunctions on MEVT, deviations from MEVT, defined as

$$\Delta = E^e - \sum_i \langle f_i \rangle \tag{18}$$

are listed for some molecules calculated with various wavefunctions in Table 2. The percentage deviations, defined as $(\Delta/E^e)\times 100$, are also listed in this Table. It is evident that there is a trend in these deviations. The average percentage deviations are least in the case of Hartree-Fock wavefunctions (0.39), higher for DZ (1.66) and STO-6G (2.38) functions and maximum (3.28) for STO-3G functions. This obviously is in accordance with the order of the quality of the wavefunctions. Another important point is the following: These deviations are small ($<1\%$) for some molecules (e.g. H_2O, HF) while they are significantly large ($\sim 5\%$) for some others, regardless of the quality of the wavefunctions, except in the Hartree-Fock case. We will return to investigate the reasons for this in the next section.

4.2. MEVT at the equilibrium geometry

The sum of the expectation values W_i of the operator W_i is presented in Table 3 along with the corresponding total kinetic energy (T) and the total electronic

Table 2. Δ, deviations from MEVT for various wavefunctions. Percentage error is given in parentheses

Molecule	HF	DZ	STO-6G	STO-3G
H_2O	0.30 (0.35)	0.40 (0.47)	0.04 (0.05)	0.60 (0.71)
CO	0.70 (0.52)	3.63 (2.68)	6.40 (4.74)	7.26 (5.38)
HCHO	0.81 (0.55)	3.12 (2.17)	3.54 (2.45)	3.69 (2.57)
Li CN	−0.20 (0.15)	—	2.95 (2.32)	3.74 (2.97)
HCN	—	2.25 (1.92)	2.63 (2.26)	3.46 (2.99)
BF	—	3.09 (2.16)	6.30 (4.42)	7.19 (5.09)
HF	—	0.44 (0.42)	0.15 (0.14)	—
Average	(0.39)	(1.66)	(2.38)	(3.28)

Table 3. MEVT at equilibrium geometry, with DZ wavefunctions (Ref. [19]). All values in atomic units

						Δ^a		
Molecule	T	$-W$	V^{nn}	$-f$	$-E^e$	abs.	%	F^b
BH_3	26.3384	7.0180	7.4030	33.3564	33.7770	0.42	1.24	0.1607
CH_4	40.1718	12.8591	13.3918	53.0309	53.5741	0.54	1.00	0.1933
NH_3	56.1572	11.2763	11.9356	67.4335	68.1050	0.67	0.98	1.4653
H_2O	76.0787	8.7186	9.1950	84.7973	85.1985	0.40	0.47	2.2008
HF	99.9681	4.7965	5.1933	104.7646	105.2083	0.44	0.42	2.3083
BF	124.1264	15.6744	18.8242	139.8008	142.8962	3.09	2.16	3.0488
CO	112.6576	18.9047	22.5141	131.5623	135.1904	3.63	2.68	3.4482
N_2	108.7360	20.0267	23.6247	128.7627	132.4942	3.73	2.81	3.4846
HCN	92.6966	21.7741	23.8928	114.4707	116.7214	2.25	1.93	1.8000
C_2H_2	76.5847	24.1162	24.7917	100.7009	101.5835	0.88	0.87	0.4036
HCHO	113.8195	28.0760	31.1681	141.8955	144.9890	3.09	2.13	2.5750
C_2H_4	77.9411	32.5871	33.2665	110.5282	111.2719	0.74	0.66	0.2556
B_2H_6	52.7067	29.9152	31.7461	82.6219	84.5736	1.95	2.30	0.8759
C_2H_6	79.1522	40.9748	41.9310	120.1271	121.1291	1.00	0.82	0.3711
N_2H_4	111.1361	38.5154	40.7611	149.6515	151.8872	2.24	1.47	2.8855
H_2O_2	150.9020	33.1560	36.7588	184.0581	187.4960	3.44	1.83	4.0750
F_2	198.3950	26.1715	30.2239	224.5665	228.9170	4.35	1.90	3.1392
CH_3F	138.9942	34.1262	37.2542	173.1204	176.2795	3.16	1.79	2.4944
						Average	1.53	

[a] Deviation from MEVT (see text). [b] Residual force (see text).

energy (E^e) for DZ wavefunctions for a number of molecules at the equilibrium geometry. The value of W (column 3) should be equal to the negative of the internuclear repulsion energy V^{nn} (column 4) at the equilibrium geometry; or, according to Eq. 1, the sum $f = \sum \langle f_i \rangle$ (column 5) should be equal to the electronic energy E^e (column 6). It is seen from Table 3 that the percentage deviation for DZ wavefunctions varies from 0.42 in the case of HF to a maximum of 2.81 for N_2. The average percentage deviation for this set of molecules is 1.53.

Similar results as in Table 3 are given for STO-6G functions at the equilibrium geometry, in Table 4. We note that in this case also the deviations are quite small for some molecules (e.g. for C_2 the percentage deviation is 0.4). The average deviation for this set of molecules is 2.32, which is higher than the corresponding value for the DZ case.

Considering the Hartree-Fock functions as the reference, for which MEVT deviations are the minimum, we can identify the following sources of error for results at the equilibrium geometry:

1. Incomplete geometry optimisation,
2. inaccurate numerical procedure and,
3. poor quality of the wavefunctions.

Among these the first two contribute only a little as the following arguments show. Virial theorem is fairly well satisfied with the deviation of (V/T) from -2.0 being approximately the same ($<10^{-3}$) for all these molecules for all the

Table 4. MEVT for STO-6G wavefunctions at equilibrium geometry. All values are in atomic units

						Δ^a		
Molecule	T	$-W$	V^{nn}	$-f$	$-E^e$	abs.	%	F^b
Li_2	15.1692	2.5080	1.7960	17.6772	16.5905	1.08	6.51	0.2364
BF	26.1902	2.0499	2.2065	28.2401	27.2082	1.03	3.78	0.8255
BH_2	26.3170	4.5302	4.6375	30.8472	30.3010	0.54	1.78	1.9620
CH_2	39.2634	5.9327	6.1517	45.1961	44.9648	0.23	0.51	1.5031
NH_2	55.6079	7.2535	7.5648	62.8614	62.9343	0.07	0.11	2.0101
B_2	51.5098	3.3484	4.4020	54.8582	53.0840	1.77	3.33	0.3812
H_2O	75.9392	8.9394	9.2400	84.8786	84.9160	0.04	0.05	2.5200
HF	99.5119	5.0310	5.1935	104.5429	104.6934	0.15	0.14	1.9370
C_2	76.9108	6.3929	8.1129	83.3037	82.9693	0.33	0.40	0.5944
LiF	106.3294	6.8539	9.1364	113.1833	115.5095	2.32	2.00	1.8783
CO	110.3132	16.1616	22.5140	126.4748	132.8748	6.40	4.81	3.6348
BF	124.0920	11.9600	18.8241	136.0520	142.3510	6.30	4.42	3.3770
						Average	2.32	

[a] Deviation from MEVT (see text).

[b] Residual force (see text).

wavefunctions. Also, since the quadrature procedure used is the same for all the molecules, the numerical errors are nearly the same. In addition to these arguments, the reason for the observed large deviations for some molecules will become apparent if we look at the intra-molecular forces as computed from these wavefunctions. The total residual force in a molecule F, is given by

$$F = \sum_{\alpha}^{\text{atoms}} F_\alpha \tag{19}$$

where F_α is norm of the force on the αth nucleus. F values are given along with E^e and Δ values in Tables 3 and 4. We recall that deviations from MEVT given by Δ are large for some molecules like CO, BF and F_2. The residual forces F are also found to be significantly large for these molecules. This is especially true for molecules containing comparatively heavier atoms like O and F. Even though the electric fields on these atoms are of similar magnitude to those on other atoms, forces are much higher due to their large nuclear charge compared to the smaller atoms like H and B.

Ideally, these forces should be zero at the equilibrium geometry in order to obey the Hellmann-Feynman theorem. However, such a situation is obtained only for exact wavefunctions and floating or stable [22, 23] wavefunctions. Thus for practical wavefunctions, we have a non-zero net force. Since, in applying MEVT, the energy term is computed *via force*, it follows that greater the residual force in a molecule, greater will be the deviation from MEVT. This is evident from Fig. 1, where we observe that the deviation from MEVT, Δ, has a fair correlation with the residual force F, using DZ wavefunctions. Thus, we conclude that the

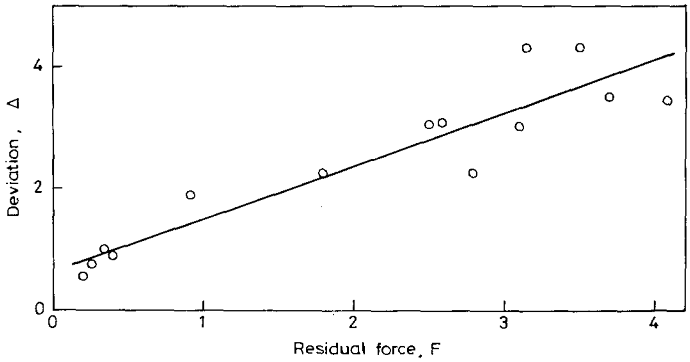

Fig. 1. Correlation between residual forces on nuclei and deviation from molecular electronic virial theorem.

inadequate quality of the wavefunctions is the major contributor to the observed deviations from MEVT.

4.3. MEVT at non-equilibrium geometries

As noted in Sect. 2, MEVT is valid, in principle, at all geometries. Computations were performed to verify MEVT at non-equilibrium geometries for various molecules using STO-6G basis. These results are given in Table 5. For diatomic molecules, two additional bond lengths, one on either side of the equilibrium value, are considered. For triatomic molecules, the bond angle is varied between 90° and 180°. Mostly, the molecules whose wavefunctions are good enough to satisfy MEVT at the equilibrium geometry are chosen for this study. A few calculations were made for the unsatisfactory cases also. For the molecules tested, it is found that MEVT is valid at non-equilibrium geometries to approximately the same degree as in the equilibrium case. For the molecules listed in Table 5, the average percentage deviation from MEVT is 1.95.

Table 5. MEVT at non-equilibrium geometries. All values are in atomic units

Molecule	Bond length/ Bond angle	T	$-W$	$-f$	$-E^e$	Δ^c	
						abs.	%
Li_2	4.00	15.2175	2.5278	17.7453	17.0406	0.70	4.13
	5.01^a	15.1692	2.5080	17.6772	16.5905	1.08	6.55
	6.00	15.0134	2.2857	17.2990	16.3016	0.99	6.11
HF	1.51	99.7489	5.4300	104.8902	105.4133	0.52	0.49
	1.73^a	99.5119	5.0310	104.5429	104.6934	0.15	0.14
	2.27	99.3412	4.0980	103.4392	103.4209	0.02	0.02
BH	1.80	26.2920	2.1105	28.4025	27.7287	0.67	2.43
	2.26^a	26.1902	2.0499	28.2401	27.2082	1.03	3.79
	3.40	26.1832	1.6169	27.8001	26.3760	1.42	5.38

Table 5. (*cont.*)

Molecule	Bond length/ Bond angle	T	$-W$	$-f$	$-E^e$	Δ[c]	
						abs.	%
BH_2	1.51	27.1566	4.8504	32.0069	32.3504	0.34	1.06
	2.27	26.3170	4.5302	30.8472	30.3010	0.55	1.80
	2.83	26.2217	4.0548	30.2765	29.2890	0.99	3.37
CH_2	1.51	39.8591	6.3459	46.1850	46.8851	0.70	1.49
	2.04	39.2634	5.9327	45.1961	44.9648	0.23	0.51
	2.83	39.1265	4.8635	43.9900	43.0689	0.92	2.13
NH_2	1.51	56.1228	7.9124	64.0352	64.8639	0.83	1.28
	1.93[a]	55.6079	7.2535	62.8614	62.9344	0.07	0.11
	2.83	55.5814	5.4253	61.0067	60.3505	0.66	1.09
H_2O	1.32	76.9028	10.1433	87.0461	87.9133	0.86	0.98
	1.81[a]	75.9392	8.9394	84.8786	84.9160	0.04	0.05
	2.26	75.5834	7.5921	83.1755	82.9435	0.23	0.27
CO	1.89	110.835	17.8580	128.6930	136.5436	7.85	5.75
	2.13[a]	110.3132	16.1616	126.4750	133.7380	7.26	5.43
	2.50	110.2763	13.3880	123.6630	130.3619	6.69	5.13
BF	1.89	124.4192	16.0618	140.5536	147.2093	6.65	4.51
	2.39	124.092	11.9600	136.0520	142.3511	6.30	4.42
	2.83	124.2320	9.4400	133.6700	139.3493	5.68	4.07
BH_2[b]	90	26.3737	4.5649	30.9386	30.3405	0.59	1.94
	130[a]	26.371	4.5305	30.8476	30.3010	0.55	1.81
	150	26.3216	4.5413	30.8629	30.2751	0.59	1.95
	180	26.3055	4.5677	30.8732	30.2519	0.62	2.05
CH_2[b]	90	39.2733	5.9624	45.2357	45.0173	0.22	0.49
	120	39.2395	5.9445	45.1840	44.9898	0.22	0.49
	140[a]	39.2634	5.9334	45.1968	44.9648	0.23	0.51
	180	39.2816	5.9606	45.2422	44.9300	0.31	0.69
NH_2[b]	90	55.6210	7.2130	62.8340	62.9644	0.13	0.21
	103[a]	55.6079	7.2535	62.8614	62.9343	0.07	0.11
	150	55.5788	7.3668	62.9456	62.8090	0.13	0.21
	180	55.5597	7.3699	62.9297	62.7693	0.16	0.25
H_2O[b]	90	75.9536	8.8889	84.8425	84.8833	0.04	0.05
	105[a]	75.9316	8.8979	84.8295	84.8429	0.01	0.01
	120	75.9264	8.9212	84.8476	84.8026	0.04	0.05
	180	75.9947	9.088	85.0827	84.6624	0.42	0.49
						Average	1.95

[a] Equilibrium bond length/bond angle.

[b] Equilibrium bond length for bond angle variation.

[c] Deviation from MEVT (see text).

It is interesting to note that for BF and CO, which have large Δ values at equilibrium, the Δ value remains approximately the same at other geometries also. This is another evidence to show that the large deviations from MEVT for these cases is mainly due to the poor quality of the wavefunctions.

The validity of MEVT at non-equilibrium geometries is of great interest as we can use f_i, a one-electron term with a clear physical meaning as the partitioned quantity, for example, to discuss the nature of molecular bonding or as a possible ordinate in Walsh type diagrams. More studies in this direction are in progress.

5. Conclusions

In this work, we have studied a method previously proposed to unambiguously partition the total molecular electronic energy into individual molecular orbital contributions in polyatomic molecules. The validity of the molecular electronic virial theorem (MEVT) which defines these quantities is examined for wavefunctions of different size and quality. The average percentage deviations from the theorem for the sets of molecules studied using Hartree-Fock, double zeta, STO-6G and STO-3G wavefunctions are 0.39, 1.66, 2.32 and 3.28 respectively.

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