Theor Chem Acc (2006) 115: 276–280
DOI 10.1007/s00214-005-0006-z

REGULAR ARTICLE

Ken Sakata

An attempt to decompose the force constants for some diatomic molecules by the derivatives of the electronic kinetic energy

Received: 11 April 2005 / Accepted: 28 July 2005 / Published online: 19 October 2005

Abstract The force constants for several diatomic molecules were calculated by the derivatives of the electronic kinetic energy within the restricted Hartree–Fock formalism. The uniform scaling procedure was utilized in order to satisfy the virial theorem. The decomposition of the force constant was performed by partitioning the derivatives of the kinetic energy in several ways.

Keywords Electronic kinetic energy · Uniform scaling procedure · Virial theorem · Force constant · Diatomic molecules

1 Introduction

In the Born–Oppenheimer approximation, the molecular electronic virial theorem for a diatomic molecule is expressed as [1,2]

$$2T + V + R\frac{\mathrm{d}E}{\mathrm{d}R} = 0. \tag{1}$$

Here, T is the electronic kinetic energy, V is the potential energy, which includes the internuclear repulsion energy, E is the molecular electronic energy,

$$E = T + V, \tag{2}$$

and R is the internuclear distance. Using Eq. 2, the virial theorem can be rewritten in either of two forms:

$$T + E + R\frac{\mathrm{d}E}{\mathrm{d}R} = 0, \tag{3}$$

$$-V + 2E + R\frac{\mathrm{d}E}{\mathrm{d}R} = 0. \tag{4}$$

At the equilibrium internuclear distance $R = R_\mathrm{e}$ (where $\mathrm{d}E/\mathrm{d}R = 0$), the following relation is obtained by differentiating Eqs. 3 and 4 with respect to R:

$$\left(\frac{\mathrm{d}^2E}{\mathrm{d}R^2}\right)_{R_\mathrm{e}} = -\left(\frac{1}{R}\frac{\mathrm{d}T}{\mathrm{d}R}\right)_{R_\mathrm{e}} = \left(\frac{1}{R}\frac{\mathrm{d}V}{\mathrm{d}R}\right)_{R_\mathrm{e}}. \tag{5}$$

Equation 5 shows that the force constant $(\mathrm{d}^2E/\mathrm{d}R^2)_{R_\mathrm{e}}$ is given by the derivative of T or V with respect to R. Several theoretical calculations of quadratic or higher force constants have been carried out using the variation in the electronic kinetic energy [3–8].

In the present letter, we took notice of the relation between the force constant and the electronic kinetic energy in Eq. 5 and investigated the force constants for some diatomic molecules by differentiating the kinetic energies. Moreover, the decomposition of the force constant was performed by partitioning the derivatives of the electronic kinetic energy in several ways. We used the Hartree–Fock wave functions in which the virial theorem is satisfied by the uniform scaling technique [9,10]. The force constants for diatomic molecules have mainly been discussed in terms of the Hellmann–Feynman theorem [11,12] and the perturbation theory [13]. On the other hand, the significance of the electronic kinetic energies in the chemical bond has been emphasized from many points of view [14–24], so the discussion of the relation between the force constant and the electronic kinetic energy is also considered an interesting problem.

2 Method of calculations

The restricted Hartree–Fock (RHF) method was used with the Pople's 6–31G(d, p) basis set. The uniform scaling procedure proposed by Lehd and Jensen [25] was utilized in order to satisfy the virial theorem. The derivative of the electronic kinetic energy with respect to R was estimated by the numerical differentiation of the five-point formula ($\Delta R = \pm 0.0005$Å, ± 0.001Å). All the ab initio calculations were performed using the *GAMESS* program package [26].

3 Results and discussion

3.1 Effect of the uniform scaling

The results of exponent optimization in the uniform scaling are shown in Table 1. For comparison, the results without the

---

K. Sakata
Faculty of Pharmaceutical Sciences, Hoshi University,
Shinagawa-ku, Tokyo 142-8501, Japan
E-mail: sakata@hoshi.ac.jp

Table 1 Results with the uniform scaling

	R_e(Å)	s_{opt}	$E(=-T)$ (au)	$T_\perp$ (au)	$T_{\|}$(au)	$\partial T/\partial R$ (au)	$\partial T/\partial s$	$\mathrm{d}s/\mathrm{d}R$	$\mathrm{d}T/\mathrm{d}R$(au/Å)	$-(1/R)\mathrm{d}T_\perp/\mathrm{d}R$ (mDyn/Å)	$-(1/R)\mathrm{d}T_{\|}/\mathrm{d}R$ (mDyn/Å)	$-(1/R)\mathrm{d}T/\mathrm{d}R$ (mDyn/Å)
H_2 ($^1\Sigma_g^+$)	0.7338	0.970254	−1.131402	0.846775	0.284628	−1.0056	0.1108	−0.4147	−1.0515	4.0870	2.1602	6.2472
HeH^+ ($^1\Sigma^+$)	0.7704	0.989587	−2.924751	2.090081	0.834671	−0.7795	0.4953	−0.2334	−0.8951	4.1644	0.9010	5.0654
LiH ($^1\Sigma^+$)	1.6300	0.998708	−7.981351	5.297781	2.683570	−0.3817	13.1195	−0.0008	−0.3916	0.5131	0.5343	1.0474
N_2 ($^1\Sigma_g^+$)	1.0781	1.002857	−108.944476	72.590248	36.354228	−7.0999	128.4154	−0.0051	−7.7584	17.8062	13.5676	31.3739
CO ($^1\Sigma^+$)	1.1136	1.002118	−112.738164	75.169108	37.569056	−5.6714	127.4506	−0.0037	−6.1393	12.7620	11.2733	24.0354

Table 2 Results without the uniform scaling

	R (Å)	E (au)	$\mathrm{d}^2E/\mathrm{d}R^2$ (mDyn/Å)	$-V/2T$
H_2	0.7326	−1.131334	6.3786	0.998005
HeH^+	0.7693	−2.924721	5.2053	0.999007
LiH	1.6300	−7.981340	1.0476	0.998938
N_2	1.0784	−108.943949	31.3789	1.001700
CO	1.1138	−112.737877	24.0320	1.001205

uniform scaling are also shown in Table 2. The equilibrium distance R_e, the total electronic energy E, and the optimized scaling factor s_{opt} are in agreement with the previous study by Koga and Kobayashi [10]. The improvement of the equilibrium distance and the total energy by the uniform scaling is small. On the other hand, the differences between the force constant estimated by the derivative of the kinetic energy, $-(1/R)\mathrm{d}T/\mathrm{d}R$, and the analytical second derivative of the total energy calculated without the uniform scaling are large for the H_2 and HeH^+ molecules, while the differences are small in LiH, N_2, and CO molecules.

In the uniform scaling method, the electronic kinetic energy T is regarded as a function of the two parameters R and s, and the parameter s also depends on R. The following relation

$$\frac{\mathrm{d}T}{\mathrm{d}R} = \frac{\partial T}{\partial R} + \frac{\partial T}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}R} \tag{6}$$

is then satisfied. Each component estimated by the numerical differentiation is shown in Table 1. It is found that the derivative of T with respect to R is significantly related to s.

3.2 The orbital partitioning

The decomposition of the force constant was examined in terms of the orbital kinetic energy. Concerning the ab initio energy decomposition, the orbital kinetic energy partitioning under the virial theorem has been applied to the Walsh-type diagrams [21,22]. Since the electronic kinetic energy is the expectation value for the one-electron operator, the kinetic energy T for the RHF wave function is expressed as the sum of the orbital kinetic energy $\tau_i (i = 1 \ldots occ.)$. Therefore, Eq. 5 becomes

$$\left(\frac{\mathrm{d}^2E}{\mathrm{d}R^2}\right)_{R_e} = \sum_i^{\mathrm{occ.}} \left(-\frac{2}{R}\frac{\mathrm{d}\tau_i}{\mathrm{d}R}\right)_{R_e}. \tag{7}$$

In Eq. 7, it is shown that the force constant is composed of the derivatives of the orbital kinetic energy with respect to R [4]. By using this relation, the decomposition of the force constant into the derivatives of each orbital kinetic energy was performed. The results are represented in Table 3. In the case of LiH, the derivative term of the 1σ orbital, $-(2/R)\mathrm{d}\tau_1/\mathrm{d}R$, is nearly zero and the 2σ orbital mostly contributes to the force constant. In the N_2 molecule, the derivative terms of the $1\sigma_u$, $2\sigma_g$ and $1\pi_u$ orbitals positively contribute to the force

Table 3 The orbital energy ε_i, the orbital kinetic energy τ_i, and the derivative of the orbital kinetic energy

ith MO	ε_i (au)	τ_i (au)	$-(2/R)\mathrm{d}\tau_{i\perp}/\mathrm{d}R$ (mDyn/Å)	$-(2/R)\mathrm{d}\tau_{i\parallel}/\mathrm{d}R$ (mDyn/Å)	$-(2/R)\mathrm{d}\tau_i/\mathrm{d}R$ (mDyn/Å)
H_2					
1	−0.5969	0.565701	4.0870	2.1602	6.2472
HeH^+					
1	−1.6354	1.462376	4.1644	0.9010	5.0654
LiH					
1 (1σ)	−2.4529	3.603193	−0.0299	−0.0258	−0.0557
2 (2σ)	−0.2982	0.387483	0.5429	0.5602	1.1031
N_2					
1 (1σ_g)	−15.6856	22.149450	−0.3141	−0.5126	−0.8267
2 (1σ_u)	−15.6818	22.186874	0.6389	0.5831	1.2220
3 (2σ_g)	−1.4881	2.576364	11.2139	12.0331	23.2470
4 (2σ_u)	−0.7696	2.284422	−3.4304	0.3362	−3.0942
5 (3σ_g)	−0.6313	2.013870	−0.7479	0.2978	−0.4501
6, 7 (1π_u)	−0.6199	1.630629	5.2229	0.4150	5.6379
CO					
1 (1σ)	−20.6706	29.227638	0.2707	0.1130	0.3837
2 (2σ)	−11.3526	16.054637	−0.3108	−0.2374	−0.5482
3 (3σ)	−1.5292	2.889485	6.8992	8.1159	15.0151
4 (4σ)	−0.7976	2.643774	0.5538	8.9203	9.4741
5, 6 (1π)	−0.6391	1.987008	3.1392	−0.1194	3.0198
7 (5σ)	−0.5456	1.579531	−0.9292	−5.3998	−6.3290

Table 4 Decomposition of the electronic kinetic energy based on the atom-bond partitioning

A–B	T_A (au)	T_AB (au)	T_B (au)	$-(1/R)\mathrm{d}T_A/\mathrm{d}R$ (mDyn/Å)			$-(1/R)\mathrm{d}T_{AB}/\mathrm{d}R$ (mDyn/Å)			$-(1/R)\mathrm{d}T_B/\mathrm{d}R$ (mDyn/Å)		
				⊥	∥	(total)	⊥	∥	(total)	⊥	∥	(total)
H–H	0.410949	0.309505	0.410949	0.7553	0.3776	1.1329	2.5764	1.4050	3.9814	0.7553	0.3776	1.1329
(He–H)$^+$	2.562091	0.222948	0.139712	−1.8903	−0.9617	−2.8520	4.7306	1.1683	5.8989	1.3242	0.6944	2.0186
Li–H	7.405974	0.145222	0.430155	0.3433	0.2281	0.5714	0.1050	0.2721	0.3772	0.0647	0.0341	0.0988
N–N	53.670241	1.603993	53.670241	3.6968	3.1212	6.8180	10.4126	7.3253	17.7379	3.6968	3.1212	6.8180
C–O	37.175257	1.401994	74.160913	3.8279	2.3504	6.1783	9.3200	5.7955	15.1155	−0.3859	3.1273	2.7415

constant and the 2σ_g-orbital term is the largest. At the equilibrium distance, these orbital kinetic energies decrease as R increases. On the other hand, the terms of the other orbitals (1σ_g, 2σ_u, and 3σ_g) negatively contribute to the force constant. For the isoelectronic molecule CO, the derivative terms of the 1σ, 3σ, 4σ, and 1π orbitals have positive contributions while the terms of the 2σ and 5σ orbitals have negative contributions. Thus, the terms of the 2$s\sigma$ (2σ_g in N_2 and 3σ in CO) and 1π orbitals have positive contributions to the force constants in both the N_2 and CO molecules, although the characteristics of the kinetic energies of the other σ orbitals in CO are different from those in N_2. The force constants calculated by differentiating the electronic kinetic energies are 31.3739 mDyn/Å for N_2 and 24.0354 mDyn/Å for CO as shown in Table 1, and therefore, the force constant of N_2 is larger than that of CO. The values of the 1π-orbital term are 5.6379 mDyn/Å for N_2 and 3.0198 mDyn/Å for CO, so the difference in the 1π-orbital term is 2.6181 mDyn/Å. The sums of the σ-orbital terms are 20.0980 mDyn/Å for N_2 and 17.9957 mDyn/Å for CO and the difference in the σ-orbital part is 2.1023 mDyn/Å. Concerning the difference in the force constants between the two molecules, the π-orbital part is found to be larger than the σ-orbital one.

Bader et al. [27, 28] examined the contribution of the electrons in each molecular orbital to the total electronic force acting on the nuclei and discussed the chemical binding and properties of the diatomic molecules. In LiH, the 2σ orbital, which is localized on the proton, has been reported to have the binding character. In N_2, the 2σ_g orbital has the highest binding of the orbital charge distribution while the 2σ_u orbital has the highest anti-binding. The electronic density in the 3σ_g orbital is weakly anti-binding. They also clarified that the chemical binding of the isoelectronic system CO differs from that in N_2. These tendencies are in agreement with the present results based on the derivatives of the orbital kinetic energies.

3.3 The atom-bond partitioning

The atom-bond partitioning [29], which is one of the methods used for the energy decomposition, was applied to the decomposition of the force constant. In a linear combination of atomic orbitals for the molecular orbital (LCAO-MO), the electronic kinetic energy is also represented as

$$T = \sum_{rs} P_{rs} t_{rs}. \tag{8}$$

Here, t_{rs} is the AO kinetic energy integral and P_{rs} is the bond-order matrix. The electronic kinetic energy is divided into the following three terms according to the centers of the constituent AOs [29,30]:

$$T = T_{\mathrm{A}} + T_{\mathrm{AB}} + T_{\mathrm{B}}, \tag{9}$$

with

$$\begin{aligned} T_{\mathrm{A}} &= \sum_{r\in\mathrm{A}}\sum_{s\in\mathrm{A}} P_{rs}t_{rs}, \\ T_{\mathrm{AB}} &= 2\sum_{r\in\mathrm{A}}\sum_{s\in\mathrm{B}} P_{rs}t_{rs}, \\ T_{\mathrm{B}} &= \sum_{r\in\mathrm{B}}\sum_{s\in\mathrm{B}} P_{rs}t_{rs}. \end{aligned} \tag{10}$$

The one-center terms T_{A} and T_{B} are regarded as the electronic kinetic energy for atoms A and B, respectively. The two-center term T_{AB} is the kinetic energy between atoms A and B, which is expected to contribute to the chemical bond through the overlap. By estimating the derivatives of these kinetic energy terms, the decomposition of the force constant based on the atom-bond partitioning method was performed. As shown in Table 4, the derivatives of T_{AB} have positive contributions to the force constants $(-(1/R)\mathrm{d}T_{\mathrm{AB}}/\mathrm{d}R > 0)$ in all the molecules, so the kinetic energies in the overlap decrease for the increasing R at $R = R_{\mathrm{e}}$. The derivatives of the atomic kinetic energies T_{A} and T_{B} also have positive contributions in all the molecules except for HeH^+. In the case of HeH^+, the electron distribution lies very close to the He atom. It is well-known that the partitioning method based on AOs involves arbitrariness, so it is necessary to examine carefully the validity of this method not only for the force constant partitioning but also for the energy partitioning in the future study.

3.4 The Cartesian components partitioning

Based on the kinetic energy operator in the Cartesian coordinate, the electronic kinetic energy can also be decomposed into the Cartesian components. If the z axis is chosen to coincide with the internuclear axis, the kinetic energy is divided into the bond-parallel component $T_{||}$ and the bond-perpendicular component $T_{\perp}$ as follows:

$$T = T_{\perp} + T_{||}, \tag{11}$$

with

$$\begin{aligned} T_{\perp} &= T_x + T_y, \\ T_{||} &= T_z. \end{aligned} \tag{12}$$

Ruedenberg et al. [14,15] examined the formation of the chemical bond in the H_2^+ system and found that the bond-parallel component of the kinetic energy plays an important role in the bond formation. Bader and Preston [17] also discussed the relation between the kinetic energy and the electron density by examining the parallel and the perpendicular kinetic energies.

This partitioning method was applied to both the force constants and the derivatives of each orbital kinetic energy, which constitute the force constant. The results of the decomposition of the force constant $(-(1/R)\mathrm{d}T_{\perp}/\mathrm{d}R$, $-(1/R)\mathrm{d}T_{||}/\mathrm{d}R)$ are shown in Table 1. The results of the application to the constituent orbital terms $(-(2/R)\mathrm{d}\tau_{i\perp}/\mathrm{d}R$, $-(2/R)\mathrm{d}\tau_{i||}/\mathrm{d}R)$ are shown in Table 3. Moreover, this type of decomposition is able to be applied to the atom-bond partitioning as shown in Table 4.

In H_2 and HeH^+ molecules, the derivative terms of the perpendicular component, $-(1/R)\mathrm{d}T_{\perp}/\mathrm{d}R$, are larger than those of the parallel component, $-(1/R)\mathrm{d}T_{||}/\mathrm{d}R$. In LiH molecule, the term of the perpendicular component is smaller than that of the parallel component. Thus, the ratio of the two components in each molecule is totally different.

For the isoelectronic molecules N_2 and CO, it has been reported that the kinetic energies of these molecules are isotropic [23, 24]. In the present study, the $T_{||} - T_{\perp}/2$ values are 0.059 a.u. and −0.015 a.u. for N_2 and CO, respectively, as shown in Table 1, so the kinetic energies are certainly isotropic in the present calculation. However, it was found that the derivatives of these energies are not isotropic as shown in Table 1. Then the two components of each orbital term are discussed. In the $2s\sigma$ orbitals in N_2 and CO molecules, which contribute mostly to the force constants, the terms of the parallel component are slightly larger than those of the perpendicular one. The other σ-orbital terms show various tendencies. In the case of the $2\sigma_u$ and $3\sigma_g$ orbitals in N_2, the perpendicular components negatively contribute to the force constant while the parallel components positively contribute. As a result, the total derivatives in these orbitals are negative. On the other hand, both components of the 4σ orbital in CO are positive values, while in the 5σ orbital they are negative. In the case of the 1π orbitals, the perpendicular components contribute mostly to the orbital term in both the N_2 and CO molecules.

4 Concluding remarks

For some diatomic molecules, the restricted Hartree–Fock calculations with the uniform scaling method were performed. By using the result that the obtained wave function satisfies the virial theorem, the force constants were calculated by the derivatives of the electronic kinetic energy. The electronic kinetic energy is the expectation of the one-electron operator, so it is easy to decompose the force constant. The derivatives of the electronic kinetic energy were decomposed by some methods and the contributions of each term to the force constant were estimated. As a result, it was shown that the force constant is able to be analyzed on the basis of the electronic kinetic energy.

References

1. Levine IN (1991) Quantum chemistry, 4th edn. Prentice Hall, Englewood Cliffs
2. Weislinger E, Olivier G (1974) Int J Quantum Chem Symp 8:389

3. Goodisman J (1981) In: Deb BM (ed) The force concept in chemistry. Van Nostrand Reinhold, New York, pp 246–293
4. Goodisman J (1973) Diatomic interaction potential theory vol 1: Fundamentals. Academic, New York
5. Clinton WL (1960) J Chem Phys 33:1603
6. Empedocles P (1967) J Chem Phys 46:4474
7. Thorhallsson J, Chong DP (1969) Chem Phys Lett 4:405
8. Rossikhin VV, Morozov VP, Bezzub LI (1968) Theor Exp Chem (USSR) 4:22
9. Löwdin P-O (1959) J Mol Spectrosc 3:46
10. Koga T, Kobayashi H (1985) J Chem Phys 82:1437
11. Nakatsuji H, Kanda K, Yonezawa T (1982) J Chem Phys 77:1961
12. Bader RFW, Bandrauk AD (1968) J Chem Phys 49:1666
13. Bader RFW (1960) Mol Phys 3:137
14. Feinberg MJ, Ruedenberg K, Mehler EL (1970) Adv Quantum Chem 5:27
15. Ruedenberg K (1975) In: Chalvet O, Daudel R, Diner S, Malrieu JP (eds) Localization and delocalization in quantum chemistry vol 1. Reidel, Dordrecht, pp 223–245
16. Wilson CW Jr, Goddard WA III (1972) Theoret Chim Acta 26:195
17. Bader RFW, Preston HJT (1969) Int J Quantum Chem 3:327
18. Koga T (1981) Theoret Chim Acta 58:173
19. Thakkar AJ, Sharma BS, Koga T (1986) J Chem Phys 85:2845
20. Tachibana A (2001) J Chem Phys 115:3497
21. Takahata Y, Parr RG (1969) Chem Phys Lett 4:109
22. Allen TL, Scheiner AC, Schaefer HF III (1990) Inorg Chem 29:1930
23. Sharma BS, Thakkar AJ (1986) Int J Quantum Chem 29:323
24. Simas AM, Smith VH Jr, Thakkar AJ (1984) Int J Quantum Chem Symp 18:385
25. Lehd M, Jensen F (1991) J Comput Chem 12:1089
26. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JJ, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
27. Bader RFW, Keaveny I, Cade PE (1967) J Chem Phys 47:3381
28. Bader RFW, Bandrauk AD (1968) J Chem Phys 49:1653
29. Kollmar H (1978) Theoret Chim Acta 50:235
30. Ichikawa H, Yoshida A (1999) Int J Quantum Chem 71:35