

# Force Constants

## II. Heteronuclear Molecules

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A general semitheoretical method for the evaluation of quadratic, cubic and quartic force constants described previously is extended, and applied to the ground and excited states of heteronuclear diatomic molecules. The agreement of the results with the experimental values is good considering the very wide range of bond types, (neutral, ionic, covalent, excited) for which calculations have been performed.

Eine allgemeine halbempirische Methode für die Berechnung der Kraftkonstanten  $k_2$ ,  $k_3$ ,  $k_4$  wird auf Grund- und angeregte Zustände von Molekülen aus zwei verschiedenen Atomen angewendet. Die Übereinstimmung mit den experimentellen Werten ist bei Berücksichtigung der recht verschiedenen Bindungsarten gut.

Une méthode semithéorique générale pour l'évaluation des constantes de force d'ordre deux, trois et quatre, décrite précédemment est généralisée et appliquée aux états fondamentaux et excités de molécules diatomiques hétéronucléaires. L'accord des résultats avec les valeurs expérimentales est bon si l'on tient compte du large éventail de types de liaisons étudiés (neutre, ionique, covalente, excitée).

### Introduction

In a recent paper [1] a method was proposed for the evaluation of molecular force constants. The quadratic and higher order force constants are related to the kinetic energy derivatives through a series of equations obtained [2, 3] by differentiating the Virial theorem at  $R = R_e$ :

$$E + T + R(dE/dR)_{R_e} = 0 \quad (1)$$

$$k_2 = (d^2 E/dR^2)_{R_e} = - (R_e)^{-1} (dT/dR)_{R_e} \quad (2)$$

$$k_3 = \frac{1}{3} (d^3 E/dR^3)_{R_e} = (R_e)^{-2} (dT/dR)_{R_e} - (3R_e)^{-1} (d^2 T/dR^2)_{R_e} \quad (3)$$

$$k_4 = \frac{1}{12} (d^4 E/dR^4)_{R_e} = - (R_e)^{-3} (dT/dR)_{R_e} + (3R_e^2)^{-1} (d^2 T/dR^2)_{R_e} - (12R_e)^{-1} (d^3 T/dR^3)_{R_e} \quad (4)$$

Here  $E$  is the total energy,  $T$  the electronic kinetic energy and  $R$  the internuclear distance ( $=R_e$  at equilibrium).

Simple molecular orbitals  $\chi_{\text{mol}}$  are generated by a non-uniform scaling operation from the orbitals [4]  $\chi_{\text{at}}(x, y, z)$  for the united and separated atoms to which the molecule reduces in the limits  $R \rightarrow 0$  and  $R \rightarrow \infty$ . The distortions along the  $x$ -,  $y$ - and  $z$ -axes can be represented:

$$\chi_{\text{mol}} = \chi_{\text{at}}(\eta_x x, \eta_y y, \eta_z z) \quad (5)$$

The  $x$ -,  $y$ - and  $z$ -scale factors ( $\eta$ ) pass smoothly between the united and separated atom limits, and are directly related to the charge density outside a radius equal to the internuclear distance.

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For such a scaled molecular orbital the  $x$ -,  $y$ - and  $z$ -components of the kinetic energy  $T_i(\eta_i)$  can be calculated from the components for the atomic orbital  $T_i(1)$ :

$$T_x(\eta_x) = \eta_x^2 T_x(1) \quad (6)$$

where

$$T_x(1) = \langle \chi(x, y, z) | d^2/dx^2 | \chi(x, y, z) \rangle .$$

The molecular orbital kinetic energy  $T(\eta_x, \eta_y, \eta_z)$  is given in terms of the atomic orbital kinetic energy  $T(1, 1, 1)$  by:

$$\begin{aligned} T(1, 1, 1) &= T_x(1) + T_y(1) + T_z(1), \\ T(\eta_x, \eta_y, \eta_z) &= \eta_x^2 T_x(1) + \eta_y^2 T_y(1) + \eta_z^2 T_z(1). \end{aligned}$$

The kinetic energy derivatives of Eqs. (2), (3) and (4) can be found analytically, given expressions for  $\eta_x(R)$ ,  $\eta_y(R)$  and  $\eta_z(R)$ .

$$dT/dR = \sum_{\text{orbitals}} \sum_{i=x,y,z} dT_i/dR = \sum_{\text{orbitals}} \sum_{i=x,y,z} 2\eta_i T_i(1) d\eta_i/dR. \quad (7)$$

The higher order terms are obtained similarly.

### Heteronuclear Diatomics

Two new problems arise in the application of the method to heteronuclear diatomic molecules. In the first place a standard correlation table cannot be set up which is appropriate to all species. A convenient way of deriving the table for any molecule from a list [4] of united and separated atom orbital exponents is to arrange the orthogonalised orbitals in order of decreasing kinetic energy. Groups of orbitals on the united and separated atoms of the same molecular symmetry can then be correlated in the usual way. The procedure is easily programmed and equally applicable to homonuclear species.

There is generally a difference in the electronegativities of the atoms forming the molecule [5]. The close relationship between the electronegativity of an atom and its valence shell orbital scale factors is to be the subject of a later paper [6]. It should be noted that a good approximation (with average deviation of less than 0.1) to the electronegativity of an atom of the first two periods is given by the expression:

$$G = 3.1\eta/n \quad (8)$$

where  $\eta$  is the average orbital exponent and  $n$  the principle quantum number of the valence shell.

The second difficulty concerns the relative weights of the two atomic orbital components  $\phi_1$  and  $\phi_2$  of the molecular orbital  $\chi$ .

$$\chi = c_1 \phi_1 + c_2 \phi_2. \quad (9)$$

The method described here has been couched in terms such that the only explicit details of the wavefunction appear as its orbital scale factors. The asymmetry of the molecular orbital is implicit in the general expression for the axial and perpendicular scale factors:

$$\eta_x = \eta_y = \eta_s(1 - \varrho + \varrho G_2/G_1)(1 - \varrho) + \varrho \eta_u, \quad (10)$$

$$\eta_z = \eta_s(1 - \varrho) + \varrho(2n/(2n/\eta_u + R G_2/G_1)) \quad (11)$$

where  $\eta_u$  and  $\eta_s$  are the united and separated atom orbital exponents,  $\varrho$  is the integral [1] of the charge density of the separated atom orbital outside a radius  $R = R_e$  and  $G_1$  and  $G_2$  are the electronegativities of the two atoms. For  $\eta_x$  and  $\eta_y$

this amounts to assuming an average value  $\eta_s^{\text{av}}$  for the two separated atom orbital exponents weighted according to  $\varrho$ . Thus

$$\eta_s^{\text{av}} = c_1 \eta_s^{(1)} + c_2 \eta_s^{(2)}$$

where

$$c_1 = 1 - \varrho \quad \text{and} \quad c_2 = \varrho,$$

if

$$\eta_s^{(2)} = \eta_s^{(1)} G_2 / G_1$$

Eq. (10) follows assuming  $\eta_x = \eta_y = \eta_s^{\text{av}}(1 - \varrho) + \eta_u \varrho = \eta_s^{\text{av}} + \Delta \eta \varrho$ .

For  $\eta_z$  the effective internuclear distance [1]  $R$  is scaled in the ratio  $G_2/G_1$ . The expressions (10) and (11) reduce for homonuclear molecules to the simpler Eqs. (15) and (21) of paper [1]. They are semi-empirical expressions whose limits and detailed form are nevertheless reasonable and comprehensible. They are justified by the accuracy of the results they predict, not only for the absolute value of the kinetic energy, but also for its first second and third derivatives.

For the non-bonding orbitals of a heteronuclear diatomic it seemed unreasonable to distort the separated atom orbitals along the molecular axis, and so the  $x$ -,  $y$ - and  $z$ -scale factors were set equal and fixed by Eq. (10). (In this case it would be impossible to describe a pair of non-bonding orbitals in terms of the equivalent orbital transformation of a bonding and antibonding pair.)

One small amendment has been made to paper [1]. This is to achieve a definition of  $\eta_u$  (the united atom orbital exponent), which allows a smooth variation of the kinetic energy between the united and separated atom limits, regardless of changes in orbital form.  $\eta_u$  in (10) and (11) is defined as the number by which the unit-scale separated atom orbital would have to be scaled to give the kinetic energy of the united atom orbital.

$$\eta_u = \eta_s \sqrt{\frac{T_u}{T_s}}. \quad (12)$$

No further allowance need now be made for a change in principle quantum number.

## Results

The results for the ground states of all the diatomic molecules formed from elements of the first and second rows of the periodic table quoted in Herschbach and Laurie's tables [7] are included in Table 1<sup>1</sup>. The excited states of these molecules are too numerous to display. All excited states for which calculations could be made of some representative molecules formed from B, C, N and O are included in Table 2.

It should be mentioned that the factor  $G_2/G_1$  whose effect in Eqs. (10) and (11) is to bias the separated atom limit of  $\eta$  to an average value for the two atoms, has an effect on the kinetic energy of the wavefunction loosely similar to that embodied in "ionic-covalent resonance." As  $R$  decreases from  $\infty$  the wavefunction is bunched up to an increasing extent on the atom of higher electronegativity. The inclusion of the factor raises  $-(d\eta/dR)$  and thus leads to a greater value of  $-(dT/dR)$  and

<sup>1</sup> Revised values for the homonuclear molecules are also included for comparison. Slight variations from these quoted in Paper [1] arise from the new definition of  $\eta_u$  and also from small errors found in Table 1 of that paper for the  $x$ -,  $y$ - and  $z$ -components of the atomic orbitals' kinetic energies. There are fortunately no significant differences.

Table 1. Force constants of Diatomic molecules formed from elements of the first and second rows (ground states)

Molecule	Quadratic force constant		Cubic force constant		Quadratic force constant		
	Calc	Expt	Calc	Expt	Calc	Expt	
Li <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.2	0.3	- 0.2	- 0.2	0.1	0.1
B <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	2.3	3.6	- 4.9	- 6.0	6.4	5.3
C <sub>2</sub>	<sup>3</sup> Π <sub>u</sub>	7.2	9.5	-17.8	-19.8	27.9	25.1
N <sub>2</sub> <sup>+</sup>	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	16.9	20.1	-50.9	-53.5	96.6	89.1
N <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	21.9	23.0	-61.9	-59.2	112.9	99.6
BN	<sup>3</sup> Π	6.4	8.4	-13.4	-21.3	20.4	41.7
CN <sup>+</sup>	<sup>1</sup> Σ	18.4	15.7	-45.4	-13.2	72.9	46.5
CN	<sup>2</sup> Σ <sup>+</sup>	18.1	16.3	-45.0	-37.0	71.9	50.1
O <sub>2</sub> <sup>+</sup>	<sup>2</sup> Π <sub>g</sub>	19.1	16.6	-55.4	-47.6	104.5	83.7
O <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	11.6	11.8	-32.7	-29.1	60.3	45.3
BeO	<sup>1</sup> Σ <sup>+</sup>	5.1	7.5	- 7.7	-15.4	7.8	19.4
BO	<sup>2</sup> Σ <sup>+</sup>	9.8	13.6	-20.9	-29.9	31.7	40.1
CO <sup>+</sup>	<sup>2</sup> Σ <sup>+</sup>	20.6	19.8	-53.5	-48.0	92.8	-
CO	<sup>1</sup> Σ <sup>+</sup>	20.5	19.0	-51.4	-45.5	86.0	66.3
NO	<sup>2</sup> Π	16.6	15.9	-46.6	-41.3	84.5	64.4
F <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.6	2.5	- 5.0	- 4.1	10.1	4.6
BeF	<sup>2</sup> Σ <sup>+</sup>	2.8	5.8	- 4.5	-11.0	4.1	13.7
LiF	<sup>1</sup> Σ <sup>+</sup>	0.3	2.5	- 0.9	- 4.1	1.8	4.6
CF	<sup>2</sup> Π	8.2	7.4	-18.6	-17.9	27.8	30.2
Na <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.1	0.2	- 0.1	- 0.1	0.1	0.1
MgO	<sup>1</sup> Σ <sup>+</sup>	0.5	3.5	- 0.8	- 5.9	0.9	7.5
MgF	<sup>2</sup> Σ <sup>+</sup>	0.7	3.2	- 1.3	- 5.1	1.2	5.0
AlO	<sup>2</sup> Σ <sup>+</sup>	3.8	5.7	- 6.3	-11.6	6.4	13.8
AlF	<sup>1</sup> Σ <sup>+</sup>	4.4	4.2	- 7.3	- 8.0	6.9	10.0
Si <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	0.9	2.1	- 1.5	- 2.9	1.6	2.5
SiN	<sup>2</sup> Σ <sup>+</sup>	5.9	7.3	-10.6	-14.1	11.6	16.4
SiO <sup>+</sup>	<sup>2</sup> Σ	5.7	4.3	-10.3	-13.0	11.2	-
SiO	<sup>1</sup> Σ	7.3	9.2	-12.1	-18.3	11.5	23.2
SiF	( <sup>2</sup> Π) <sup>a</sup>	7.6	6.7	-13.5	- 8.1	14.1	- 3.6
P <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.0	5.6	- 7.7	- 9.1	9.7	8.9
CP	<sup>2</sup> Σ <sup>+</sup>	8.4	7.8	-15.8	-14.6	18.6	16.2
PN	<sup>1</sup> Σ <sup>+</sup>	10.5	10.5	-20.1	-20.5	23.7	24.6
PO	<sup>2</sup> Π	10.9	9.4	-20.5	-19.2	23.2	23.1
S <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	2.2	5.0	- 4.7	- 8.4	6.6	9.0
BS	<sup>2</sup> Σ	5.9	6.7	-11.4	-12.0	13.9	13.2
NS	<sup>2</sup> Π	7.9	8.3	-16.7	-11.4	22.0	-
SO	<sup>3</sup> Σ <sup>-</sup>	12.9	7.9	-26.8	-16.4	34.4	22.1
SiS	<sup>1</sup> Σ <sup>+</sup>	0.4	4.9	- 1.4	7.7	2.2	7.6
CS	<sup>1</sup> Σ <sup>+</sup>	9.2	8.5	-18.8	-16.5	23.9	21.1
Cl <sub>2</sub> <sup>‡</sup>	<sup>2</sup> Π	1.8	4.3	- 4.1	- 8.3	6.2	11.5
Cl <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.4	3.3	- 3.0	- 6.1	4.4	5.1
BCl	<sup>1</sup> Σ	3.3	3.5	- 6.4	- 5.9	8.0	6.8
ClO	<sup>2</sup> Π	12.8	4.9	-28.0	-10.9	38.7	14.3
ClF	<sup>1</sup> Σ	9.9	4.9	-21.4	- 8.7	29.4	7.3
NaCl	<sup>1</sup> Σ <sup>+</sup>	0.2	1.1	- 0.2	- 1.4	0.1	1.1
AlCl	<sup>1</sup> Σ <sup>+</sup>	0.1	2.1	- 0.2	- 3.6	0.2	5.5

<sup>a</sup> Assuming <sup>2</sup>Π-ground state, R<sub>e</sub> = 1.549 Å.

Table 2. Force constants for some excited molecules<sup>a</sup>

Molecule <sup>b</sup>	Quadratic force constant		Cubic force constant		Quartic force constant	
	Calc	Expt	Calc	Expt	Calc <sup>c</sup>	
B <sub>2</sub>	A <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	2.1	2.9	- 4.4	- 4.0	5.6
BN	A <sup>3</sup> Π	5.5	6.3	-11.7	- 9.1	17.6 (13.1)
BO	A <sup>2</sup> Π	5.3	6.1	- 9.6	-13.8	11.8
C <sub>2</sub>	A <sup>3</sup> Π <sub>g</sub>	8.2	11.3	-21.0	-22.9	33.8
	B <sup>3</sup> Π <sub>g</sub>	3.8	4.3	- 8.1	-11.7	11.2
	a <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	13.4	12.2	-32.2	-26.6	49.5
	b <sup>1</sup> Π <sub>u</sub>	6.6	9.1	-16.5	-19.2	26.3
	c <sup>1</sup> Π <sub>g</sub>	7.4	11.6	-19.4	-25.5	31.8
CN <sup>+</sup>	d <sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	12.8	11.8	-31.5	-27.2	49.3
	c <sup>1</sup> Σ	6.0	6.1	-13.9	- 5.4	20.7
CN	f <sup>1</sup> Σ	21.9	27.2	-53.7	-114.0	85.8 (277.0)
	A <sup>2</sup> Π <sub>i</sub>	13.4	12.5	-32.2	-28.4	50.4
CO <sup>+</sup>	B <sup>2</sup> Σ <sup>+</sup>	21.2	17.8	-54.3	-47.4	90.2
	J <sup>2</sup> Δ <sub>i</sub>	4.1	4.8	- 9.6	-11.1	14.6 (14.7)
	A <sup>2</sup> Π <sub>i</sub>	10.0	9.9	-23.4	-23.8	36.3
CO	B <sup>2</sup> Σ <sup>+</sup>	16.5	12.1	-41.7	-38.5	70.1
	A <sup>1</sup> Π	10.1	9.3	-23.4	-23.3	36.0
	B <sup>1</sup> Σ <sup>+</sup>	17.7	17.5	-45.8	-53.7	79.5
	a <sup>3</sup> Π <sub>r</sub>	14.6	12.2	-33.5	-30.1	50.9
	a <sup>1</sup> Σ <sup>+</sup>	6.1	6.0	-14.0	-12.5	21.2
N <sub>2</sub>	b <sup>3</sup> Σ <sup>+</sup>	24.1	19.5	-61.7	-68.3	106.3
	d <sup>3</sup> Π <sub>i</sub>	5.0	5.2	-11.2	-11.3	16.6
	a <sup>1</sup> Π <sub>g</sub>	11.3	11.8	-31.0	-32.3	54.7
	A <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	10.5	8.8	-26.2	-17.2	42.6
	B <sup>3</sup> Π <sub>g</sub>	11.3	12.4	-31.1	-30.5	54.9
N <sub>2</sub> <sup>+</sup>	C <sup>3</sup> Π <sub>u</sub>	21.4	17.1	-57.5	-44.7	99.7
	B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	25.4	24.2	-71.3	-63.2	129.0
NO	A <sup>2</sup> Σ <sup>+</sup>	28.9	24.7	-84.3	-61.1	159.1
	B <sup>2</sup> Π <sub>r</sub>	4.6	4.7	-11.6	- 8.9	19.2
	B <sup>2</sup> Π <sub>r</sub> <sup>*</sup>	6.6	4.7	-17.0	-11.5	28.2
O <sub>2</sub> <sup>+</sup>	E <sup>2</sup> Σ <sup>+</sup>	28.6	24.8	-83.3	-65.6	157.1
	a <sup>4</sup> Π <sub>u</sub>	4.4	5.0	-11.8	-11.8	20.9
	A <sup>2</sup> Π <sub>u</sub>	2.2	3.8	- 6.1	- 6.9	11.1
	b <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>	6.6	6.7	-18.7	-19.3	34.5
O <sub>2</sub>	a <sup>1</sup> Δ <sub>g</sub>	11.1	10.7	-31.3	-27.5	57.5
	b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	10.5	9.7	-29.4	-25.3	53.8
	B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	0.9	2.3	- 2.5	- 4.2	4.4

<sup>a</sup> With the omission of one or two cases which cannot be handled properly with the existing programme all excited states given in Herschbach and Laurie's tables for species formed from B, C, N and O are included.

<sup>b</sup> Simple MO theory was used to determine the atomic states to which the excited molecules dissociate. In a few cases orbital occupancy is ambiguous however.

<sup>c</sup> Very few experimental values are available. These are given in brackets.

hence of  $k_2$  from Eq. (2). In terms of the energy the calculated potential well for the molecule is deeper when ionic-covalent resonance is included, which implies a greater curvature ( $d^2E/dR^2$ ) at the bottom of the well.

To check this interpretation a few specimen calculations were performed on heteronuclear molecules in which  $G_2/G_1$  was set arbitrarily equal to 1. As expected

these restricted wavefunctions yield quadratic force constants which fall below the calculated ones; and do so to an extent which increases markedly as the electronegativity difference between the atoms increases. A few characteristic figures are given in Table 3.

It is gratifying to find that this method gives results close to experiment for homonuclear, heteronuclear, ionised, neutral and excited species. The magnitudes of the force constants of diatomic molecules can evidently be explained in terms

Table 3. *The effect of restricting the electronegativity dependent term on the calculated force constant*

Molecule	N <sub>2</sub>	CO <sup>+</sup>	CO	BF	C <sub>2</sub>	CN	CN <sup>+</sup>	CF
G <sub>2</sub> /G <sub>1</sub> = 1	21.9	17.7	15.5	3.2	6.7	16.5	17.6	3.1
calcd. <i>k</i> <sub>2</sub>	21.9	20.6	20.5	8.0	6.7	18.1	18.4	8.2
using (10) and (11)								
Expt.	23.0	19.8	19.0	8.1	9.5	16.3	15.7	7.4

almost as crude as those describing the overall shape and size of the orbitals. No attempt indeed has been made at this stage to specify a detailed form for the wavefunction. Many features which would certainly be important from the point of view of a calculation of the total energy can be omitted from the calculation of properties which vary with the variation in internuclear distance.

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