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A Poisson Equation for Vibrational Potentials of Diatomic Molecules* **

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A Poisson equation for nuclear motions in diatomic molecules is derived. The working formula is

$$\nabla_\alpha^2 W = 4\pi \mathscr{Z}_\alpha \varrho_\beta(\alpha),$$

where ∇_α^2 is the Laplacian operator for the position of nucleus α, W is the Born-Oppenheimer molecular energy, $\mathscr{Z}_\alpha$ is the atomic number of α, and $\varrho_\beta(\alpha)$ is the electronic charge density evaluated at α due to orbitals centered on β. Harmonic, anharmonic and quartic equilibrium force constants are calculated using Hartree-Fock molecular and atomic electronic charge densities, for a number of first and second row diatomic molecules. A charge-model field gradient formula for harmonic force constants

$$k_e = 3/R_e^3,$$

where k_e is the force constant and R_e the equilibrium internuclear distance, which offers general improvement over a similar formula due to Bratož, is presented.

Eine Poisson-Gleichung für die Kernbewegung in zweiatomigen Molekülen wird abgeleitet. Es wird die Formel

$$\nabla_\alpha^2 W = 4\pi \mathscr{Z}_\alpha \varrho_\beta(\alpha)$$

diskutiert, wobei ∇_α^2 der Laplaceoperator für die Ortskoordinaten des Kerns α, W die molekulare Born-Oppenheimer-Energie, $\mathscr{Z}_\alpha$ die Kernladungszahl von α und $\varrho_\beta(\alpha)$ die elektronische Ladungsdichte bei α ist, die durch Orbitale erzeugt wird, die bei β zentriert sind.

Harmonische, inharmonische und biquadratische Gleichgewichtskonstanten werden mit Hilfe von molekularen und atomaren Hartree-Fock-Elektronendichten für eine Anzahl von zweiatomigen Molekülen mit Elementen der beiden ersten Reihen des Periodensystems berechnet. Eine Feldgradientenformel für ein Ladungsmodell bei harmonischen Kraftkonstanten

$$k_e = 3/R_e^3$$

wird angegeben, wobei k_e die Kraftkonstante und R_e der Atomabstand im Gleichgewicht ist. Diese Formel stellt eine Verbesserung gegenüber einer ähnlichen Formel von Bratož dar.

1. Introduction

In this paper, electrostatic methods will be presented for obtaining equilibrium force constants for diatomic molecules. Accuracy of the formulas appears to be competative with *ab initio* methods [1–4], curve fitting methods [5] and modeling methods [1–4, 6–8]. First we present some analytical formulas, followed by a

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discussion of approximations leading to a field gradient model for harmonic force constants [9] which offers improvement over a formula due to Bratoẑ [7]. Then we obtain a Poisson equation for vibrational potentials [10] which is a theoretical generalization of a formula due to Platt [6] that yields harmonic and higher order force constants in terms of electron densities at the nucleus.

2. Relationships between Vibrational Force Constants and Quadrupole Coupling Constants [9]

The Born-Oppenheimer energy W of a polyatomic molecule or solid in general is a function of the Cartesian coordinates of the nuclei referred to as arbitrary origin. If one of the coordinates X_α, Y_α, Z_α of the particular nucleus α of charge $\mathscr{Z}_\alpha$ is changed, the change in W is given by a Hellmann-Feynman formula of the type

$$\frac{\partial W}{\partial X_\alpha} = \mathscr{Z}_\alpha\left[\sum_{\beta\neq\alpha}\mathscr{Z}_\beta\left(\frac{X_\beta - X_\alpha}{R_{\alpha\beta}^3}\right) - \int \varrho(x - X_\alpha)\frac{\mathrm{d}\tau}{r_\alpha^3}\right], \tag{1}$$

where ϱ is the electronic charge density function, r_α is the distance from $\mathrm{d}\tau$ to nucleus α and x, y, z are Cartesian coordinates of $\mathrm{d}\tau$ relative to a given origin. Differentiation of Eq. (1) with respect to X_α gives a formula for the second derivative $k_{X_\alpha X_\alpha} = \partial^2 W/\partial X_\alpha^2$, and similarly we can obtain formulas for $k_{Y_\alpha Y_\alpha}$, $k_{Z_\alpha Z_\alpha}$, $k_{X_\alpha Y_\alpha} = \partial^2 W/\partial X_\alpha \partial Y_\alpha$, $k_{X_\alpha Z_\alpha}$ and $k_{Y_\alpha Z_\alpha}$. If we identify the corresponding six components of the electric field gradient tensor for the molecular charge distribution with nucleus α as origin,

$$q_{X_\alpha X_\alpha} = \sum_{\beta\neq\alpha}\mathscr{Z}_\beta\left(\frac{3(X_\beta - X_\alpha)^2}{R_{\alpha\beta}^2} - 1\right)(R_{\alpha\beta}^3)^{-1} - \int \varrho\left(\frac{3(x - X_\alpha)^2}{r_\alpha^2} - 1\right)\frac{\mathrm{d}\tau}{r_\alpha^3}, \text{ etc.}, \tag{2}$$

$$q_{X_\alpha Y_\alpha} = 3\sum_{\beta\neq\alpha}\mathscr{Z}_\beta\left(\frac{(X_\beta - X_\alpha)(Y_\beta - Y_\alpha)}{R_{\alpha\beta}^5}\right) - 3\int \varrho\left(\frac{(x - X_\alpha)(y - Y_\alpha)}{r_\alpha^5}\right)\mathrm{d}\tau \text{ etc.}, \tag{3}$$

then these formulas are

$$k_{X_\alpha X_\alpha} = \mathscr{Z}_\alpha\left[q_{X_\alpha X_\alpha} + \frac{4}{3}\pi\varrho(\alpha) - \int (x - X_\alpha)\frac{\partial\varrho}{\partial X_\alpha}\frac{\mathrm{d}\tau}{r_\alpha^3}\right], \text{ etc.}, \tag{4}$$

$$k_{X_\alpha Y_\alpha} = \mathscr{Z}_\alpha\left[q_{X_\alpha Y_\alpha} - \int (x - X_\alpha)\frac{\partial\varrho}{\partial Y_\alpha}\frac{\mathrm{d}\tau}{r_\alpha^3}\right], \text{ etc.} \tag{5}$$

Here the quantity $\varrho(\alpha)$ is the electronic charge density at nucleus α; it enters $k_{X_\alpha X_\alpha}$, $k_{Y_\alpha Y_\alpha}$, and $k_{Z_\alpha Z_\alpha}$ because $\nabla^2(1/r_\alpha) = -4\pi\delta(r_\alpha)$.

The first of Eqs. (4) is the equation discovered and applied by Salem for diatomic molecules [1]. If we add the three Eqs. (4), we obtain a formula for the Laplacian of the energy [9],

$$\nabla_\alpha^2 W = \mathscr{Z}_\alpha[4\pi\varrho(\alpha) - \int \nabla_\alpha\varrho\cdot\nabla_\alpha(\boldsymbol{r} - \boldsymbol{R}_\alpha)^{-1}\mathrm{d}\tau]. \tag{6}$$

According to Salem, in Eq. (4) $\mathscr{Z}_\alpha \frac{4}{3}\pi\varrho(\alpha)$ is generally much larger than $k_{X_\alpha X_\alpha}$ and $\mathscr{Z}_\alpha q_{X_\alpha X_\alpha}$, and similarly $\mathscr{Z}_\alpha 4\pi\varrho(\alpha)$ is greater than $V_\alpha^2 W$ in Eq. (6). However, $\varrho(\alpha)$ can be eliminated from Eqs. (4) by subtraction, giving [9]

$$k_{Z_\alpha Z_\alpha} - \frac{1}{2}(k_{X_\alpha X_\alpha} + k_{Y_\alpha Y_\alpha}) = \mathscr{Z}_\alpha \left[\frac{3}{2} q_{Z_\alpha Z_\alpha} - \frac{1}{2}\int \left(2(z - Z_\alpha)\frac{\partial \varrho}{\partial Z_\alpha} - (x - X_\alpha)\frac{\partial \varrho}{\partial X_\alpha} - (y - Y_\alpha)\frac{\partial \varrho}{\partial Y_\alpha}\right)\frac{d\tau}{r_\alpha^3}\right], \tag{7}$$

$$k_{X_\alpha X_\alpha} - k_{Y_\alpha Y_\alpha} = \mathscr{Z}_\alpha \left[(q_{X_\alpha X_\alpha} - q_{Y_\alpha Y_\alpha}) - \int \left((x - X_\alpha)\frac{\partial \varrho}{\partial X_\alpha} - (y - Y_\alpha)\frac{\partial \varrho}{\partial Y_\alpha}\right)\frac{d\tau}{r_\alpha^3}\right]. \tag{8}$$

Table 1. Predictions of equilibrium harmonic force constants, k_e, for some M^-H^+ and M^+H^- diatomic molecules; 10^5 cgs units

Molecule	$2/Re^3$ [a]	$3/Re^3$ [b]	k_e(exptl.) [c]
HF	5.98	8.97	(9.66)
HCl	2.23	3.34	(5.16)
HBr	1.63	2.45	(4.16)
HI	1.12	1.68	(3.14)
LiH	1.14	1.71	(1.03)
NaH	0.69	1.03	(0.78)
KH	0.41	0.61	(0.56)
RbH	0.35	0.52	(0.51)
CsH	0.30	0.45	(0.47)
BeH	1.14	1.70	(1.03)
BH	2.46	3.70	(3.04)
CH	3.28	4.92	(4.51)
OH	5.05	7.57	(7.79)
MgH	0.89	1.34	(1.28)
AlH	1.03	1.54	(1.62)
SiH	1.31	1.97	(2.96)
CaH	0.57	0.86	(0.98)
MnH	0.89	1.33	(1.30)
ZnH	1.14	1.71	(1.57)
GeH	1.15	1.72	(2.38)
NiH	1.44	2.16	(2.17)
CuH	1.47	2.21	(2.20)
SrH	0.47	0.70	(0.85)
InH	0.74	1.12	(1.28)
CdH	0.84	1.27	(1.20)
AgH	1.09	1.64	(1.82)
BaH	0.42	0.62	(0.81)
TlH	0.71	1.06	(1.14)
BiH	0.78	1.17	(1.71)
HgH	0.88	1.31	(1.14)
AuH	1.30	1.96	(3.14)

[a] This relation is discussed in Refs. [1] and [7] of text.

[b] Eq. (10) of text.

[c] Experimental values from D. R. Herschbach and V. W. Laurie, University of California, Radiation Laboratory Report UCRL 9694 (Berkeley, Calif., 1961).

These formulas and Eqs. (3) are completely general relations among force constants and quadrupole coupling constants eqQ_0.

For a diatomic molecule at equilibrium, there is one non-zero force constant $k_e = [k_{Z_\alpha Z_\alpha}]_e = [k_{Z_\beta Z_\beta}]_e$ and one independent component of the field gradient tensor at α, $q_\alpha = [q_{Z_\alpha Z_\alpha}]_e$, and at β, $q_\beta = [q_{Z_\beta Z_\beta}]_e$. Eq. (8) is trivial. Eq. (7) becomes [9]

$$k_e = \mathscr{Z}_\alpha \left[\frac{3}{2} q_\alpha - \frac{1}{2} \int \left(2(z - Z_\alpha) \frac{\partial \varrho}{\partial Z_\alpha} - (x - X_\alpha) \frac{\partial \varrho}{\partial X_\alpha} - (y - Y_\alpha) \frac{\partial \varrho}{\partial Y_\alpha} \right) \frac{d\tau}{r_\alpha^3} \right]_e , \tag{9}$$

and similarly for β. This is an exact relation between k_e and q_α. When the second term is negligible, which it often appears to be for the hydrogen atom, we have $k_e \approx \mathscr{Z}_\alpha(\frac{3}{2} q_\alpha)$; $k_e \approx \frac{3}{2} q_H$. This relation was derived by Salem for ionic compounds $M^- H^+$, but for ionic compounds $M^+ H^-$ his relation was $k_e \approx q_H$ [1]. The former appears preferable in both cases. For the $M^+ H^-$ cases Salem used the Bratoẑ relation $k_e = 2/R_e^3$ (a.u.) derived for a point charge ionic model [7]. Similar reasoning applied to Eq. (9) leads to the formula

$$k_e = 3/R_e^3 . \tag{10}$$

As may be seen in Table 1, predictions of k_e using Eq. (10) are quite accurate, definitely better than those from Bratoẑ' formula.

3. Harmonic Force Constants from Electron Densities

Eq. (6) is not a particularly useful form for the divergence of the Hellmann-Feynman force on nucleus, because the two terms on the right are difficult to determine accurately and they approximately cancel. However, it greatly simplifies when ϱ is appropriately elucidated, giving a formula which allows approximate determination of vibrational force constants from electron densities alone, with no integrations.

The electronic charge density may be resolved into parts ϱ_α, ϱ_β perfectly following nuclei α and β (we let β represent all nuclei other than α), and the rest, a nonperfectly following part ϱ_{NPF}:

$$\varrho(\boldsymbol{r}, \boldsymbol{R}_\alpha, \boldsymbol{R}_\beta) = \varrho_\alpha(\boldsymbol{r} - \boldsymbol{R}_\alpha) + \varrho_\beta(\boldsymbol{r} - \boldsymbol{R}_\beta) + \varrho_{NPF}(\boldsymbol{r}, \boldsymbol{R}_\alpha, \boldsymbol{R}_\beta) . \tag{11}$$

Putting this into Eq. (6) and using the easily derived relation

$$\mathscr{Z}_\alpha \int \nabla_\alpha \varrho(\boldsymbol{r} - \boldsymbol{R}_\alpha) \cdot \nabla_\alpha |\boldsymbol{r} - \boldsymbol{R}_\alpha|^{-1} d\tau = \mathscr{Z}_\alpha 4\pi \varrho(\alpha) \tag{12}$$

leads to the formula

$$\nabla_\alpha^2 W = 4\pi \mathscr{Z}_\alpha [\varrho(\alpha) - \varrho_\alpha(\alpha)] - \mathscr{Z}_\alpha \int \nabla_\alpha \varrho_{NPF}(\boldsymbol{r}, \boldsymbol{R}_\alpha, \boldsymbol{R}_\beta) \cdot \nabla_\alpha |\boldsymbol{r} - \boldsymbol{R}_\alpha|^{-1} d\tau . \tag{13}$$

The consequence is that in Eq. (6) the density following nucleus α may be ignored and the density following nucleus β contributes nothing to the integral. Eq. (13) is exact.

The contribution of $\varrho_{NPF}(\alpha)$ to the first term in Eq. (13) may be expected to be small, and the integral should be small as well. Making these assumptions, we obtain our final working formula, now approximate,

$$\nabla_\alpha^2 W = 4\pi \mathscr{Z}_\alpha \varrho_\beta(\alpha) . \tag{14}$$

This is of the form of a classical electrostatic Poisson equation.

We may deduce Eq. (14) from Eq. (13) more formally as in these two examples:

Case 1. Suppose ϱ_{NPF} itself perfectly followed some point $K\boldsymbol{R}_\alpha + (1-K)\boldsymbol{R}_\beta$ (for example the midpoint $\frac{1}{2}\boldsymbol{R}_\alpha + \frac{1}{2}\boldsymbol{R}_\beta$): $\varrho_{\mathrm{NPF}} = \varrho_{\mathrm{NPF}}(\boldsymbol{r} - K\boldsymbol{R}_\alpha - (1-K)\boldsymbol{R}_\beta)$. Then one would have $\int \nabla_\alpha \varrho_{\mathrm{NPF}} \cdot \nabla_\alpha |\boldsymbol{r} - \boldsymbol{R}_\alpha|^{-1} \mathrm{d}\tau = 4\pi K \varrho_{\mathrm{NPF}}(\alpha)$, and Eq. (14) follows if we make the reasonable assumption $\varrho_{\mathrm{NPF}}(\alpha) = 0$.

Case 2. Suppose the molecular density may be represented as the sum of atomic densities. Then Eq. (14) follows exactly, making it an "atoms in molecules" result, within the Hellmann-Feynman approximation.

Table 2. Force constants from electron densities: first row hydrides[a]

Molecule		$k_e \times 10^5$			$l_e \times 10^{13}$			$m_e \times 10^{21}$		
		Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.
HeH^+	$\chi^1\Sigma^+$	2.34	0.46		22.4	43.3		189	354	
LiH	$\chi^1\Sigma^+$	0.002	0.88	(1.026)	0.009	3.81	(3.63)	0.06	14.7	(11.5)
		0.468	0.450		1.14	2.26		2.32	9.79	
BeH	$\chi^2\Sigma^+$	2.96	1.52	(2.26)	10.6	7.92	(10.0)	32.1	36.6	(38.4)
		1.72	1.56		6.43	8.19		20.2	37.8	
BeH	$A^2\Pi_r$	0.05	1.31	(2.33)	0.2	6.92	(10.7)	0.6	32.5	
BeH^+	$\chi^1\Sigma^+$	0.05	0.96	(2.64)	0.2	5.53	(11.6)	0.7	27.8	(40.7)
BH	$\chi^1\Sigma^+$	5.10	2.30	(3.04)	23.7	12.7	(15.8)	96.5	62.6	(70.3)
		2.89	2.95		13.8	16.0		56.7	75.8	
BH^+	$\chi^2\Sigma^+$	3.38	1.03		18.2	6.56		82.6	36.9	
BH^+	$A^2\Pi_r$	0.233	0.593		1.31	3.79		6.08	21.4	
CH	$\chi^2\Pi_r$	6.20	2.97	(4.51)	34.8	18.1	(26.7)	171	98.2	(136)
		4.36	5.42		24.9	30.1		124	148	
CH^+	$\chi^1\Sigma^+$	5.45	1.47	(4.11)	34.0	9.84	(23.0)	183	58.5	
CH^-	$\chi^3\Sigma^-$	7.03	4.48		36.4	26.1		169	136	
NH	$\chi^3\Sigma^-$	7.03	3.65	(6.03)	45.3	24.1	(39.6)	259	141	
		5.72	8.62		37.6	49.2		217	250	
NH	$a^1\Delta$	6.79	3.43	(5.62)	43.9	22.6	(21.6)	251	132	
NH^+	$\chi^2\Pi_r$	4.94	1.37		34.5	9.70		211	61.0	
NH^-	$\chi^2\Pi_i$	8.16	5.59		49.9	35.3		273	198	
OH	$\chi^2\Pi_r$	7.57	3.88	(7.79)	55.1	27.6	(54.3)	355	174	(337)
		7.15	12.7		52.0	74.2		335	388	
OH	$A^2\Sigma^+$	3.52	1.72	(5.65)	26.2	12.4	(40.5)	172	79.3	
OH^+	$\chi^3\Sigma^-$	4.85	1.34	(4.88)	37.3	10.0	(32.4)	252	66.9	(202)
OH^+	$a^1\Delta$	4.81	1.28		37.1	9.66		252	64.7	
OH^-	$\chi^1\Sigma^+$	9.09	7.50		63.5	48.3		399	248	
HF	$\chi^1\Sigma^+$	7.88	3.96	(9.66)	63.4	30.0	(69.9)	453	202	(446)
		8.43	17.5		67.0	104		475	561	
HF^+	$\chi^2\Pi_i$	6.93	1.78		59.9	14.8		454	109	
HF^+	$A^2\Sigma^+$	4.07	0.83	(5.00)	36.1	7.23	(34.2)	280	55.9	(133)
NeH^+	$\chi^1\Sigma^+$	3.60	0.75		32.4	6.42		257	48.2	

[a] When possible, two sets of calculations are given. Bader's molecular densities are used first according to the method of Eqs. (15)–(17). Following unlabeled rows employ Clementi atomic densities according to Eqs. (15)–(17). Exceptional cases, labeled a, employ Clementi atomic densities only. Experimental values are in parentheses. See footnote c, Table 1; cgs units.

Columns labeled Z_L employ the charge of the light nucleus; those labeled Z_H employ the heavy nucleus.

Where blanks exist in the molecular density results, insufficient numerical density data was available for a five-point polynomial fit. In these cases the density was exceedingly small and could be expected to yield poor results.

Eq. (14) says that the Laplacian of the molecular potential energy, $V_\alpha^2 W$, is the sum of the orbital densities from the other atoms β. At equilibrium for a diatomic molecule, Eq. (14) yields the harmonic force constant:

$$k_e = [V_\alpha^2 W]_e = 4\pi \mathscr{Z}_\alpha \varrho_\beta(\alpha) . \tag{15}$$

From similar arguments Platt derived the formula for hydrides: $k_e = 4\pi \varrho_{UA}(H)$, where ϱ_{UA} is the united atom density [6]. Predictions of the k_e using Eq. (15) for first row diatomic molecules are in Tables 2–5. Clementi atomic densities [11] and Hartree-Fock quality molecular densities are used according to the method of *Case 2*. In order to use molecular densities, we suppose ϱ_α and ϱ_β to be symmetric about α and β and take $\varrho_\beta(\alpha)$ to be the total density at a distance R_e from β in the opposite directions from α, and similarly for $\varrho_\alpha(\beta)$, as calculated from Hartree-Fock wave functions [12, 13]. The force term $[2/R\,\partial W/\partial R]_e$ is set equal to zero. Heavy atom densities yields accurate predictions of k_e; light atom densities give correct trends, but less accurate predictions, possibly because heavy atom

Table 3. Force constants from electron densities: second row hydrides[a]

Molecule		$k_e \times 10^5$			$-l_e \times 10^{13}$			$m_e \times 10^{21}$		
		Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.
NaH	$\chi^1\Sigma^+$	0.321	0.547	(0.782)	0.744	2.65	(2.61)	1.44	11.1	(7.45)
MgH	$\chi^2\Sigma^+$	1.39		(1.28)	3.88		(4.92)	8.71		(13.3)
		0.862	1.079		2.67	5.32		6.73	22.9	
MgH	$A^2\Pi_r$	0.07		(1.48)	0.31		(6.15)	1.14		
MgH^+	$\chi^1\Sigma^+$	0.09		(1.64)	0.37		(7.20)	1.44		(30.0)
AlH	$\chi^1\Sigma$	2.15		(1.62)	7.55		(6.72)	22.0		(24.6)
		1.35	0.082		4.82	0.51		14.7	2.85	
AlH^+	$\chi^2\Sigma^+$	1.49		(1.48)	6.09		(9.27)	20.4		
AlH^+	$A^2\Pi_r$	0.16		(1.76)	0.73		(9.90)	2.86		
SiH	$\chi^2\Pi_r$	2.56	2.49	(2.96)	10.8	12.6	(13.4)	38.3	56.0	(52.6)
		2.18	2.79		8.99	14.2		31.5	63.2	
SiH^+	$\chi^1\Sigma^+$	2.37	1.58		10.9	8.37		42.1	39.3	
SiH^-	$\chi^3\Sigma^-$	2.75			10.9			36.4		
PH	$\chi^3\Sigma^-$	2.78	2.56	(3.26)[b]	13.5	14.0		58.6	67.3	
		2.96	4.15		13.9	21.5		55.6	97.2	
PH	$a^1\Delta$	2.77	2.52		13.5	13.8		56.2	66.5	
PH^+	$\chi^2\Pi_r$	2.63	1.61	(3.04)	13.7	9.23	(14.6)	61.4	46.6	
PH^-	$\chi^2\Pi_i$	3.15	3.60		14.6	19.4		57.8	90.6	
SH	$\chi^2\Pi_i$	3.10	2.45	(4.19)[b]	16.8	14.5		78.7	75.5	
		3.83	6.06		19.9	31.9		89.2	147	
SH	$A^2\Sigma^+$	1.67	1.30		9.58	8.13		47.1	44.6	
SH^+	$\chi^3\Sigma^-$	2.86	1.46		16.4	9.01		81.1	49.1	
SH^+	$a^1\Delta$	2.85	1.42		16.4	8.82		81.2	48.2	
SH^-	$\chi^1\Sigma^+$	3.20	3.77		16.4	21.1		73.5	103	
HCl	$\chi^1\Sigma^+$	3.44	2.41	(5.16)	20.6	15.4	(28.4)	107	86.1	(167)
		4.83	8.56		27.4	45.8		136	215	
HCl^+	$\chi^2\Pi_i$	2.63	1.16	(4.13)	16.4	7.54	(23.0)	90.0	43.1	(92.2)
HCl^+	$A^2\Sigma^+$	0.534	0.271	(1.49)	3.32	1.73	(7.74)	18.4	9.65	

[a] Footnote a, Table 2.

[b] Experimental values from Varshni, Y. P.: J. chem. Physics **28**, 108 (1958).

densities are less perturbed in molecules. Five-point polynomial fits of density values spaced 0.1 a.u. apart for the atomic densities and 0.1 Å apart for the molecular densities were employed. (This allows us to evaluate derivatives of the densities later on.)

Table 4. Force constants from electron densities: first row homonuclear molecules[a]

Molecule		$k_e \times 10^5$		$-l_e \times 10^{13}$		$m_e \times 10^{21}$	
H_2	$^1\Sigma_g^+$	2.64	(5.69)[b]	19.0	(36.7)	125	(233)
		3.79		23.2		148	
Li_2[a]	$\chi^1\Sigma_g^+$	0.397	(0.255)	1.01	(0.546)	2.05	(0.857)
B_2	$^3\Sigma_g^-$	4.31	(3.58)	19.3	(18.1)	72.2	(63.7)
		4.61		20.8		81.6	
B_2	$^1\Delta_g$	4.27		19.1		75.7	
B_2	$^1\Sigma_g^+$	4.22		18.9		79.9	
B_2^+	$^2\Pi_u$	3.26		16.0		70.6	
B_2^-	$^2\Pi_u$	5.17		21.5		76.3	
C_2	$^1\Sigma_g^+$	12.0	(12.2)	67.2	(79.8)	327	
C_2[a]	$\chi^3\Pi_u$	12.3	(9.523)	67.4	(59.4)	322	(301)
C_2	$^3\Sigma_g^-$	14.7		78.9		378	
C_2	$^1\Delta_g$	14.6		78.5		367	
C_2	$^1\Sigma_g^-$	14.6		78.3		371	
C_2	$^1\Sigma_g^+$	16.3		88.3		411	
C_2^+	$^2\Pi_u$	11.4		64.7		324	
C_2^+	$^2\Pi_u$	9.57		57.2		305	
C_2^-	$^2\Pi_u$	18.2		92.5		408	
C_2^-	$^2\Pi_u$	29.4		153		694	
C_2^-	$^2\Sigma_g^+$	22.7		120		549	
C_2^-	$^2\Sigma_u^+$	24.3		128		573	
N_2	$^1\Sigma_g^+$	37.4	(23.0)	245	(178)	1416	(1195)
		30.9		200		1136	
N_2^+	$^2\Sigma_g^+$	20.3	(20.1)	145	(160)	900	
N_2^+	$^2\Pi_u$	19.9		139		838	
N_2^+	$^2\Pi_u$	27.4		193		1182	
N_2^+	$^2\Sigma_u^+$	29.3	(24.2)	206	(190)	1264	
N_2^{++}	$^3\Sigma_g^-$	29.3		216		1405	
O_2	$^3\Sigma_g^-$	14.5	(11.8)	101	(87.3)	626	(544)
		16.9		114		680	
O_2	$^1\Delta_g$	13.7	(10.7)	96.4	(82.5)	586	
O_2	$^1\Sigma_g^+$	12.8	(9.67)	89.8	(75.9)	562	
O_2^+	$^2\Pi_g$	18.6	(16.6)	144	(143)	983	(1004)
O_2^-	$^2\Pi_g$	13.1		83.2		461	
O_2^{++}	$^1\Sigma_g^+$	9.33		70.7		481	
F_2	$^1\Sigma_g^+$	2.36	(4.73)	18.0	(38.4)	124	(230)
		4.86		32.9		199	
F_2	$^1\Sigma_g^+$	2.82		20.2		120	
F_2	$^1\Sigma_g^+$	4.45		32.7		207	
F_2^+	$^2\Pi_g$	3.48		26.0		170	
F_2^+	$^2\Pi_u$	3.44		25.9		177	
F_2^+	$^2\Sigma_g^+$	2.15		16.5		122	
F_2^+	$^2\Sigma_u^-$	3.31		24.5		169	
F_2^{++}	$^3\Sigma_g^-$	2.61		20.2		140	

[a] Footnote a, Table 2.

[b] Experimental values for H_2 from data in Hertzberg, G.: Spectra of diatomic molecules. Princeton: D. Van Nostrand Company, Inc. 1950.

Table 5. Force constants from electron densities: first row heteronuclear molecules[a]

Molecule		$k_e \times 10^5$			$-l_e \times 10^{13}$			$m_e \times 10^{21}$		
		Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.
LiF	$\chi^1\Sigma^+$	0.93		(2.48)	6.04		(12.4)	34.8		(55.1)
		0.800	4.47		5.24	10.8		30.8	21.9	
LiF	$^3\Sigma^-$	0.72			4.51			25.6		
LiF	$a^1\Delta$	0.70			4.43			25.2		
LiF^+	$\chi^2\Pi_i$	0.14			2.47			19.2		
LiF^+	$A^2\Sigma^+$	0.35			2.34			14.1		
BeF	$\chi^2\Sigma^+$	3.00	20.6	(5.77)	20.5	75.1	(33.0)	121	239	(164)
		2.84	14.8		19.5	55.5		119	175	
BeF	$A^2\Pi_i$	2.32	23.2	(4.95)	15.4	82.5	(27.3)	92.7	255	
BeF	$H^2\Pi_r$	2.54	0.003		17.3	0.02		104	0.4	
BeF^+	$\chi^1\Sigma^+$	2.62	0.01		18.2	0.1		113	1	
BeF^+	$A^3\Sigma^-$	2.06	15.1		13.7	63.8		86.5	228	
BeF^+	$a^1\Delta$	2.03	15.0		13.5	63.5		85.4	227	
BeF^-	$^1\Sigma^+$	3.38	32.5		22.6	100		135	270	
BF	$\chi^1\Sigma^+$	5.69	38.0	(8.07)	41.0	150	(51.6)	262	2029	(231.6)
		5.98	23.5		42.1	111		265	456	
BF^+	$\chi^2\Sigma^+$	4.75	20.3		35.1	107		231	498	
BF^+	$A^2\Pi_i$	2.31	16.8		16.2	82.6		102	358	
BF^+	$H^2\Pi_r$	4.72	0.110		34.8	0.572		229	2.21	
CF	$\chi^2\Pi_r$	5.79	26.2	(7.42)	42.1	146	(53.7)	273	712	(362)
		6.96	21.7		48.9	120		307	578	
CF^+	$\chi^1\Sigma^+$	5.76	26.2		44.0	160		299	862	
NF	$\chi^3\Sigma^-$	4.64	12.3		33.7	77.7		219	432	
NF	$a^1\Delta$	4.86	12.7		35.5	80.5		231	448	
NF	$b^1\Sigma^+$	5.08	13.0		37.2	82.9		242	464	
NF^+	$\chi^2\Pi_r$	3.44	10.3		25.9	67.4		174	394	
NF^-	$\chi^2\Pi_i$	5.90	13.5		41.9	83.6		264	449	
LiO	$\chi^2\Pi_i$	1.25			6.79			33.8		
LiO	$A^2\Sigma^+$	0.613			3.37			16.6		
LiO^+	$\chi^3\Sigma^-$	0.948			5.15			25.0		
LiO^+	$A^1\Sigma^+$	0.0514			0.398			2.72		
BeO	$\chi^1\Sigma^+$	6.40	0.15	(7.51)	39.0	0.40	(46.2)	213	0.48	(233)
		4.54	14.1		29.6	52.9		171	166	
BeO	$A^3\Sigma^-$	5.42	24.6		33.6	87.8		191	273	
BeO	$a^1\Delta$	3.51	24.5		33.1	87.3		188	272	
BeO^+	$\chi^2\Pi_i$	5.32	0.004		33.4	0.071		189	1.2	
BeO^+	$A^2\Sigma^+$	2.77	0.007		18.1	0.067		107	0.66	
BeO^-	$^2\Pi_i$	50.9	14.4		329	49.2		1905	150	
BO	$\chi^2\Sigma^+$	13.1	27.7	(13.6)	87.2	135	(89.7)	514	571	(481)
		10.7	25.2		72.1	121		431	499	
BO	$A^2\Pi_i$	5.87	26.7	(6.11)	24.7	122	(41.4)	115	486	
BO	$H^2\Pi_r$	12.6	1.57		83.4	6.99		489	25.1	
BO^+	$\chi^1\Sigma^+$	10.6	0.748		72.9	3.87		446	15.9	
BO^+	$^3\Sigma^-$	4.89	19.7		32.1	96.0		189	414	
BO^+	$a^1\Delta$	4.80	19.5		31.7	95.5		187	411	
BO^-	$^1\Sigma^+$	15.2	50.0		98.4	217		563	812	
CO	$\chi^1\Sigma^+$	20.1	47.8	(19.0)	140	277	(136)	867	1402	(796)
		19.0	33.8		131	193		801	956	
CO	$a^3\Pi$	12.4	18.0		84.2	110		510	576	
CO^+	$\chi^2\Sigma^+$	17.7	24.1		129	156		839	890	
CO^+	$A^2\Pi_i$	8.95	23.3		61.9	140		384	795	
CO^+	$H^2\Pi_r$	15.8	3.08		115	19.2		744	106	

Table 5 (continued)

Molecule		$k_e \times 10^5$			$-l_e \times 10^{13}$			$m_e \times 10^{21}$		
		Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.
CO^{++}	$^1\Sigma^+$	12.1	1.66		92.5	11.5		627	7.12	
NO	$\chi^2\Pi_r$	18.6	28.8	(15.9)	131	190	(124)	816	1098	(775)
		19.7	27.1		135	173		821	967	
NO^+	$\chi^1\Sigma^+$	25.0	38.6		191	275		1301	1723	
NO^-	$^3\Sigma^-$	22.4	33.7		151	213		898	1166	
LiN	$^3\Sigma^-$	1.05			5.74			27.3		
BeN	$^2\Pi_i$	1.16			6.58			32.7		
BeN	$^2\Sigma^+$	0.257			1.60			8.79		
BN[a]	$\chi^3\Pi$	9.27	17.4	(8.41)	57.3	82.2	(63.9)	311	336	(500)
BN	$^3\Sigma^-$	13.3	30.8		81.8	141		443	562	
BN	$a^1\Delta$	13.2	30.5		79.7	140		425	550	
BN^+	$\chi^2\Pi_i$	10.0	1.85		62.9	9.76		347	43.7	
BN^+	$^2\Sigma^+$	5.94	0.167		38.7	0.986		222	4.65	
BN^-	$^2\Pi_i$	16.1	36.2		93.8	156		476	576	
CN[a]	$\chi^2\Sigma^+$	18.4	24.9	(16.3)	117	141	(111)	652	692	(601)
CN	$H^2\Pi_r$	15.4	11.2		97.8	62.9		542	310	
CN^+	$A^3\Sigma^-$	7.89	13.0		48.8	75.1		267	384	
CN^+	$a^1\Sigma^+$	14.0	8.20		93.4	43.9		547	190	

[a] Footnote a, Table 2.

Table 6. Representative force constants calculated for periods 1 – 2 and 2 – 2 diatomic molecules using Clementi atomic densities[a, b]

Molecule	$k_e \times 10^5$			$-l_e \times 10^{13}$			$m_e \times 10^{21}$		
	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.	Z_L	Z_H	Exptl.
PO	22.6	7.98	(9.44)	106	49.0	(57.6)	425	267	(277)
PN	17.1	10.6	(10.5)	79.7	62.7	(61.5)	320	327	(295)
SO	6.83	18.0	(7.93)	41.5	91.1	(49.2)	223	402	(265)
SiO	18.0	5.55	(9.24)	74.2	33.6	(54.9)	261	181	(278)
ClO	13.0	5.82	(4.89)	69.9	35.0	(32.7)	331	187	(172)
P_2	9.50	9.50	(5.56)	42.1	42.1	(27.2)	163	163	(106)
SiS	6.29	10.8	(4.94)	2.97	4.25	(23.2)	123	146	(91.3)
Cl_2	4.32	4.32	(3.29)	21.8	21.8	(18.3)	96.6	96.6	(61.2)
AlCl	1.87	6.94	(2.08)	9.36	23.6	(10.8)	41.0	69.7	(66)
Si_2	3.70	3.70	(2.12)	14.0	14.0	(8.55)	45.8	45.8	(29.5)
NaCl	0.637	2.83	(1.10)	3.15	6.66	(4.29)	13.8	13.1	(13.0)
Na_2	0.547	0.547	(0.172)	1.30	1.30	(0.315)	2.66	2.66	(0.276)

[a] Eqs. (15) to (17) of text.

[b] Columns labeled Z_L employ the charge of the light nucleus, those labeled Z_H the heavy nucleus. Experimental values from footnote c, Table 1; cgs units.

4. Anharmonic Force Constants from Electron Densities

Formulas for the anharmonic equilibrium force constant l_e and for the quartic equilibrium force constant m_e for diatomic molecules are got by taking derivatives of Eq. (14):

$$l_e = 4\pi\mathscr{Z}_\alpha(\mathrm{d}\varrho_\beta/\mathrm{d}R_\alpha)_e - 2k_e/R_e\,; \tag{16}$$

$$m_e = 4\pi\mathscr{Z}_\alpha(\mathrm{d}^2\varrho_\beta/\mathrm{d}R_\alpha^2)_e - 2l_e/R_e + 4k_e/R_e^2\,. \tag{17}$$

Table 7. Examples of the effects of modifying the number of valence electrons in second row Clementi atomic charge densities on equilibrium force constants determined using Eqs. (15) to (17) of text; cgs units

Molecule	$k_e \times 10^5$		$-l_e \times 10^{13}$		$m_e \times 10^{21}$	
	Calc.	Exptl.[a]	Calc.	Exptl.[a]	Calc.	Exptl.[a]
Si_2	3.70	(2.12)	14.0	(8.55)	45.8	(29.5)
Si_2^{+2}	2.31	(2.12)	9.12	(8.55)	31.5	(29.5)
P_2	9.50	(5.56)	42.1	(27.2)	163	(106)
P_2^{+2}	7.07	(5.56)	31.9	(27.2)	126	(106)
P_2^{+4}	4.64	(5.56)	21.7	(27.2)	89.2	(106)

[a] Table 1, footnote c.

Predictions of l_e and of m_e using Eqs. (16), (17) are given in Tables 2–6, and they follow the same trends as for k_e. Predictions using second row Clementi atomic densities tend to be too large, as seen in Table 6. However, removing the contributions of one or two valence electrons can largely correct for this, as seen in Table 7. This suggests modifying the atomic valence population to fit the experimental k_e exactly in Eq. (14), and then calculating accurate higher order force constants with the modified density [14].

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