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A further test on an effective nuclear charge model for the prediction of valence force constants

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An effective nuclear charge model, capable of predicting valence force constants, has been recently presented. The method includes in its development some *ad hoc* expressions. The expressions are examined here and alternative formulas are derived. Numerical results are compared with previous theoretical ones and with available experimental data.

INTRODUCTION

It is widely accepted that a model capable of predicting molecular force constants is necessary; accordingly, several approaches[1-7] have been carried out up to now, leading to more or less successful results. One of these approaches, presented by Ohwada,[8-10] consists in a simple effective nuclear charge model which requires the preliminary derivation of the effective nuclear charges of atoms, from the force constant expression. The latter is obtained by the application of the second order perturbation theory to homonuclear diatomic molecules. Successively, one may straightly and quite successfully calculate the force constants corresponding to heteronuclear polyatomic molecules.

The concept of effective nuclear charge thus defined [see Eq. (1)], includes a molecular shielding factor f_{ii}, the expression of which, is given by Eq. (2)[11]:

$$Z_i^* = Z_i e(1 - f_{ii})^{1/2} = (k_{ii}\bar{R}_{ii}^3/2)^{1/2} , \qquad (1)$$

where Z_i = atomic number, e = electronic charge, k_{ii} = quadratic force constant of the homonuclear molecule, and $\bar{R}_{ii}$ = equilibrium internuclear distance of the same molecule:

$$f_{ii} = \bar{R}_{ii}^3 \langle \rho_{00}(ii) | \cos^2 \theta_i / r_i^4 \rangle / [\bar{E}(ii) - E_0(ii)] . \qquad (2)$$

Integration is here carried out over the electronic coordinates $\cos \theta_i$ and r_i; $\rho_{00}(ii)$ is the electron density in the ground state $\bar{E}(ii)$ is the average energy of the excited electronic states and $\bar{E}_0(ii)$ is the ground state energy.

TABLE I. α_{ii} values and atomic shielding factors corresponding to different assumptions of Z_i, used to predict the valence force constant of heteronuclear diatomics.

Molecule	α_{ii} (mdyn Å²)[a]	ASF [Eq. (6)]		ASF [Eqs. (12) and (6)]		ASF (Ohwada)[b]
		Z_i = AN	$Z_i = N_i$	$Z_i = 1/2 (N_i + 1)$	$Z_i = N_i$	
H_2	2.307 00	0.707	0.707	0.671	0.671	0.705
Li_2	4.890 84	0.940	0.0	0.316	0.316	0.0
B_2	14.589 24	0.935	0.806	0.474	0.810	0.471
C_2	21.455 10	0.933	0.842	0.633	0.875	0.443
N_2	30.083 28	0.931	0.860	0.516	0.858	0.518
O_2	20.624 58	0.965	0.936	0.767	0.927	0.796
F_2	13.080 69	0.982	0.971	0.907	0.942	0.936
Na_2	5.031 10	0.996	0.0	0.0	0.0	0.0
Si_2	24.376 41	0.986	0.818	0.484	0.837	0.380
P_2	37.923 64	0.982	0.819	0.320	0.823	0.302
S_2	33.688 12	0.986	0.893	0.715	0.913	0.639
Cl_2	25.607 70	0.990	0.942	0.891	0.966	0.810
K_2	5.996 86	0.998	0.0	0.0	0.0	0.0
As_2	36.802 49	0.996	0.825	0.0	0.723	0.0
Se_2	35.649 85	0.997	0.886	0.532	0.885	0.599
Br_2	29.068 20	0.997	0.934	0.838	0.950	0.780
Rb_2	6.062 08	0.999	0.0	$\cdots$	$\cdots$	0.0
Sb_2	45.065 67	0.998	0.780	$\cdots$	$\cdots$	0.0
Te_2	41.339 98	0.998	0.867	$\cdots$	$\cdots$	0.521
I_2	32.298 00	0.999	0.926	$\cdots$	$\cdots$	0.747
Cs_2	6.320 38	0.999	0.0	$\cdots$	$\cdots$	0.0

[a] The α_{ii} values of the first seven tabulated molecules and for Cl_2, Br_2, and I_2 were taken from Ref. 13. The $\bar{R}_{ii}$ values necessary for the computation of the remaining molecules, have been extracted from Ref. 14 or 16.
[b] Reference 12.

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TABLE II. Internuclear distances $\bar{R}_{ij}$ (Å) and valence force constants k_{ij} (mdyn/Å) for alkali hydrides.

Molecule	$\bar{R}_{ij}$[b]	Ohwada's f_i values (Ref. 12) and Eq. (11)	k_{ij} calculated with				Zerner's expression [i.e., Eqs. (12)][a]	k_{ij} according to	
			$f_i = f_i(Z_i)$					Ohwada's report (Ref. 12)	Experimental data (Ref. 12)
			$Z_i = $ AN	$Z_i = N_i$	$Z_i = \dfrac{N_i+1}{2}$[a]	$Z_i = N_i$[a]			
LiH	1.5953	1.167	1.150	1.170	0.895	0.895	1.169	1.137	1.026
NaH	1.8873	0.715	2.373	0.717	0.686	0.686	0.947	0.686	0.776
KH	2.244	0.464	2.168	0.465	0.408	0.408	0.690	0.408	0.557
RbH	2.367	0.398	2.619	0.399	$\cdots$	$\cdots$	$\cdots$	0.348	0.511
CsH	2.494	0.347	2.286	0.348	$\cdots$	$\cdots$	$\cdots$	0.298	0.464

[a]Totally theoretical values.   [b]Extracted from Ref. 14 or 16.

Further on, however, Ohwada has conveniently defined[12] the atomic shielding factor f_i (ASF) of atom i in a molecule, as

$$f_i \equiv (f_{ii})^{1/2} . \qquad (3)$$

With the help of this equation and making use of some straightforward algebra, a simple expression of the molecular shielding factor (MSF) f_{ij} for a heteronuclear diatomic molecule is obtained[12]

$$f_{ij} = (f_{ii}f_{jj})^{1/2} = f_i f_j. \qquad (4)$$

Following Murrell's expression for the force constant k_{ij} of a heteronuclear molecule[11] and applying Eq. (4), the former parameter may be calculated by means of

$$k_{ij} = (2Z_iZ_je^2/\bar{R}_{ij}^3)(1 - f_if_j) . \qquad (5)$$

Thus, in order to predict this value for a heteronuclear molecule, the knowledge of the equilibrium distance $\bar{R}_{ij}$ and of the ASF's f_i, f_j is necessary. These last values

are determined from experimental data referred to homonuclear molecules, for from Eqs. (1) and (3),

$$f_i = [1 - (\alpha_{ii}/2Z_i^2e^2)]^{1/2} , \qquad (6)$$

where

$$\alpha_{ii} \equiv k_{ii}\bar{R}_{ii}^3 . \qquad (7)$$

In Eq. (5), Z_i and Z_j may be selected according to different criteria (e.g., as the atomic number itself or the number of electrons outside a complete shell). Ohwada, however, based on empirical reasons, chose[12]

$$Z_i = 1/2(N_i + 1) , \qquad (8)$$

where N_i is the number of electrons outside a complete shell.

Both the definition of ASF f_i [Eq. (3)] and Z_i [Eq. (8)], called very much our attention; consequently, we have intended to test them and the results of our examination are reported in the following sections.

TABLE III. Internuclear distances $\bar{R}_{ij}$ (Å) and valence force constants k_{ij} (mdyn/Å) for alkali halides.

Molecule	$\bar{R}_{ij}$[b]	Ohwada's f_i values (Ref. 12) and Eq. (11)	k_{ij} calculated with				Zerner's expression [i.e., Eqs. (12)][a]	k_{ij} according to	
			$f_i = f_i(Z_i)$					Ohwada's report (Ref. 12)	Experimental data (Ref. 12)
			$Z_i = $ AN	$Z_i = N_i$	$Z_i = \dfrac{N_i+1}{2}$[a]	$Z_i = N_i$[a]			
LiF	1.59	5.653	2.375	8.323	3.275	5.643	2.152	4.861	2.491
LiCl	1.97	2.496	2.111	4.362	1.734	2.935	1.060	2.239	1.480
LiBr	2.17	1.865	2.776	3.266	1.328	2.212	0.916	1.806	1.199
LiI	2.392	1.381	3.669	2.432	$\cdots$	$\cdots$	$\cdots$	1.352	0.923
NaF	2.0	2.881	1.318	4.241	2.307	4.037	1.510	2.567	1.776
NaCl	2.51	1.224	0.795	2.139	1.167	2.042	0.702	1.404	1.180
NaBr	2.64	1.050	0.664	1.840	1.003	1.755	0.697	1.181	1.041
NaI	2.90	0.786	0.654	1.384	$\cdots$	$\cdots$	$\cdots$	0.927	0.938
KF	2.55	1.517	0.893	2.234	1.113	1.948	0.915	1.806	1.373
KCl	2.79	0.973	0.767	1.700	0.850	1.487	0.625	0.970	0.853
KBr	2.94	0.830	0.530	1.454	0.726	1.271	0.614	0.823	0.823
KI	3.23	0.621	0.438	1.094	$\cdots$	$\cdots$	$\cdots$	0.651	0.611
RbF	2.31	2.052	1.624	3.022	$\cdots$	$\cdots$	$\cdots$	1.578	1.277
RbCl	2.89	0.880	0.899	1.538	$\cdots$	$\cdots$	$\cdots$	0.850	0.779
RbBr	2.945	0.830	0.600	1.455	$\cdots$	$\cdots$	$\cdots$	0.726	0.672
RbI	3.26	0.607	0.404	1.070	$\cdots$	$\cdots$	$\cdots$	0.574	0.502
CsF	2.34	2.016	1.595	2.968	$\cdots$	$\cdots$	$\cdots$	1.422	1.231
CsCl	3.06	0.757	0.774	1.323	$\cdots$	$\cdots$	$\cdots$	0.749	0.762
CsBr	3.14	0.700	0.506	1.225	$\cdots$	$\cdots$	$\cdots$	0.638	0.651
CsI	3.41	0.542	0.360	0.954	$\cdots$	$\cdots$	$\cdots$	0.504	0.552

[a]Totally theoretical values.   [b]Extracted from Ref. 14 or 16.

TABLE IV. Internuclear distances $\bar{R}_{ij}$ (Å) and valence force constants k_{ij} (mdyn/Å) for general diatomics.

Molecule	$\bar{R}_{ij}$ [b]	Ohwada's f_i values (Ref. 12) and Eq. (11)	k_{ij} calculated with $f_i = f_i(Z_i)$				Zerner's expression [i.e., Eqs. (12)]	k_{ij} according to Ohwada's report (Ref. 12)	Experimental data (Ref. 12)
			$Z_i = AN$	$Z_i = N_i$	$Z_i = \frac{N_i+1}{2}$ [a]	$Z_i = N_i$ [a]			
CO	1.1281	17.48	15.472	16.350	14.468	14.569	21.212	18.21	19.02
CS	1.534	7.74	9.937	7.610	6.122	6.170	6.090	8.02	8.49
CN	1.1718	15.87	15.791	15.823	14.482	14.295	11.685	16.57	16.29
CH	1.1198	5.42	6.701	5.315	4.726	5.427	6.192	5.65	4.45
NO	1.1508	18.55	17.344	17.747	19.207	18.586	14.305	18.67	15.94
NH	1.038	7.80	9.862	8.091	8.091	8.752	8.277	7.81	5.87
OH	0.9706	7.71	12.924	10.250	8.572	11.444	10.739	7.74	7.73
SO	1.4933	8.35	8.781	8.202	7.665	7.664	7.953	8.34	7.93
SH	1.34	3.69	9.411	4.244	3.492	4.457	4.622	3.61	4.16
BO	1.2049	11.61	10.420	11.688	11.751	11.828	10.749	12.57	13.65
BN	1.281	9.99	9.971	10.124	9.949	10.043	4.116	7.47	8.32
BH	1.2325	3.31	4.188	3.184	3.361	3.375	4.085	2.47	3.02
BF	1.262	12.38	8.396	10.557	10.470	11.424	7.576	7.70	8.04
BCl	1.715	4.58	5.695	4.644	4.227	4.179	3.079	3.39	3.47
BBr	1.88	3.55	7.655	3.623	3.349	3.361	2.790	2.68	2.66
CCl	1.73	5.52	6.807	5.172	3.885	3.861	3.326	6.59	3.77
CF	1.271	15.13	10.058	11.540	9.570	11.058	7.964	13.16	7.42
SiH	1.52	2.38	5.485	2.213	2.218	2.304	2.970	2.40	2.96
SiF	1.603	8.58	4.370	6.485	6.284	6.635	4.897	7.26	4.86
SiCl	2.00	3.98	3.168	3.712	3.280	3.092	2.466	3.99	2.63
SiBr	2.15	3.25	3.519	3.076	2.760	2.663	1.932	3.27	2.21
SiN	1.571	7.09	9.413	7.055	6.696	6.708	5.776	7.15	7.29
SiO	1.510	8.11	7.225	7.538	7.373	7.208	7.158	8.18	9.25
SiS	1.928	4.26	3.999	4.163	3.684	3.644	3.466	4.26	4.94
CP	1.562	7.59	9.227	7.505	7.241	6.777	5.528	7.87	7.83
OP	1.449	12.10	9.719	10.624	12.016	10.787	8.404	12.10	9.41
PN	1.491	10.54	12.675	10.290	10.460	10.227	7.035	10.57	10.16
ClF	1.628	4.97	4.428	4.509	3.282	4.716	3.442	4.13	4.56
BrF	1.756	4.42	5.164	3.928	3.274	4.392	3.393	3.69	4.06
ICl	2.321	2.33	4.009	2.319	$\cdots$	$\cdots$	$\cdots$	2.33	2.39
FH	0.917	9.70	16.300	13.205	9.365	15.181	8.973	8.14	9.65
AsN	1.59	9.68	18.457	8.338	8.508	8.359	7.188	8.02	7.93
PH	1.432	3.71	7.290	3.304	3.701	3.518	3.670	3.70	3.23
ClH	1.275	3.83	11.164	5.223	3.584	5.487	3.698	3.82	5.16
BrH	1.413	2.94	15.650	3.902	2.863	4.151	3.294	2.94	4.12
IH	1.604	2.10	19.429	2.705	$\cdots$	$\cdots$	$\cdots$	2.12	3.12
SbN	1.79	7.50	19.716	6.618	$\cdots$	$\cdots$	$\cdots$	6.45	6.56

[a] Totally theoretical values.   [b] Extracted from Ref. 14 or 16.

METHOD

With the purpose of verifying the degree of correctness of the assignment of f_i, the force constants k_{ij} of homo- and heteronuclear diatomics have been calculated by means of an expression not dependent of Z_i, Z_j, but merely of the ASF [see Eq. (11)].

Thus, for a homonuclear diatomic molecule, from Eqs. (4), (5), and (7),

$$\alpha_{ii} = 2Z_i^2 e^2 (1 - f_i^2) \qquad (9)$$

and consequently

$$Z_i = [\alpha_{ii}/2e^2(1 - f_i^2)]^{1/2} . \qquad (10)$$

By substitution in Eq. (5) of Z_i, Z_j for the corresponding expressions of Eq. (10), the force constant k_{ij} for a heteronuclear diatomic molecule is

$$k_{ij} = \left[\frac{\alpha_{ii}\alpha_{jj}}{(1 - f_i^2)(1 - f_j^2)}\right]^{1/2} \frac{(1 - f_i f_j)}{R_{ij}^3} . \qquad (11)$$

In order to apply Eq. (11), the values of α_{ii} and α_{jj} are necessary and they are reported in Table I, column 1. These values have been either extracted from disposable data[13] or computed by means of experimental data and the expression[14]

$$k_{ij} \equiv k_e = 5.8883 \times 10^{-2} \ \mu_A w_e^2 (\text{dyn/cm}) ,$$

where μ_A = reduced mass, w_e = classical vibrational frequency for an infinitesimal amplitude of an anharmonic oscillator, and k_e = force constant of this oscillator.

The results obtained with Eq. (11) and using Ohwada's ASF f_i, f_j are shown in the second column of Tables II (alkali hydrides), III (alkali halides), and IV (general diatomic molecules). The experimental values have also been included for comparison purposes (see column 9 in Tables II–IV).

Next, the ASF have been recalculated by means of Eq. (6), first selecting Z_i = atomic number (AN) and second

$Z_i = N_i$ (see above). Both sets of results are presented in Table I, columns 2 and 3. The first set turns out to be far from reasonable and especially not dependent to horizontal progress in the Periodic Table. The derived constant values are reported in Tables II–IV, column 3. The values of k_{ij} obtained with the second set of ASF are presented in the fourth column of Tables II–IV.

Looking forward to putting Eq. (4) to a further test, we have chosen the expressions deduced by Zerner and Parr[13] for α_{ij}. According to them,

$$\alpha_{ij}(\text{a. u.}) = [1 + 0.5(n_i\xi_j + n_j\xi_i)]\eta/2 , \quad \text{if } m_i = m_j = 1 ,$$
(12a)

$$\alpha_{ij}(\text{a. u.}) = [1 + n_i\xi_j + 0.5\xi_i(n_j + \xi_j)]\eta/2 ,$$

$$\text{if } m_i = 1 \text{ and } m_j = 4 ,$$
(12b)

$$\alpha_{ij}(\text{a. u.}) = (1 + n_i\xi_j + n_j\xi_i)\eta/2 , \quad \text{if } m_i = m_j = 4 ,$$
(12c)

where $m_{i,j} =$ number of orbitals supplied by atoms i, j, $n =$ principal quantum number, $\xi =$ orbital exponent of the valence electron (either from Slater's rules or from Ref. 15), and $\eta =$ number of bonds.

According to Zerner, some rules seem to be of suitable application for predicting α_{ij}.[13] Thus, "$\eta = 1$ for hydrides or when both atoms are generally univalent, $\eta = 3/2$ when only one of the atoms is univalent, and $\eta = 2$ otherwise. Exceptions to this rule are CO and N_2 both with $\eta = 3$." In the present work, this last value has been also used for calculations involving P.

In this way, applying Eqs. (12) to homo- and heteronuclear molecules successively, we have first obtained the f_i factors theoretically and then, we have used them to recalculate the k_{ij} for heteronuclear diatomics. Z_i and Z_j have been now selected (a) $1/2(N_i + 1)$ according to Ohwada's choice, and (b) N_i, following Murrell's suggestion.

The results of the ASF are reported in Table I, columns 4 and 5, and the values corresponding to k_{ij} appear in columns 5 and 6 of Tables II–IV.

It should be pointed out that not all k_{ij} have been computed, for Slater's rules [necessary to calculate $\xi_{i,j}$ in Eqs. (12)] are not applicable with much success when $n > 4$.

Finally, as mentioned above, all valence constants

corresponding to heteronuclear molecules, have been obtained by direct application of Zerner's formulas and the expression $\alpha_{ij} = k_{ij}\bar{R}_{ij}^3$. These results are presented in the seventh column of Tables II–IV and they are to be compared with those belonging to the two preceding columns.

RESULTS AND DISCUSSION

From the results tabulated for k_{ij} with $Z_i =$ atomic number (AN), it is easily derived that the latter is not a happy choice for Z_i: some values may appear which are most insensible, while a good approximation to experimental values may be also some times obtained. Obviously, such a hazardous model is not useful.

Thus, the approximation $Z_i = 1/2(N_i + 1)$ seems most accurate, for even though a certain degree of coincidence with the results derived from $Z_i = N_i$ seems to be observable for hydrides and general molecules, $a \sim 0.5$ factor appears to be necessary for alkali halides, when considering this second alternative.

Referring to the relation $f_{ij} = f_i f_j$ it turns out to be acceptable within limits, for it is bound to reflect amply little variations of the ASF.

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