On a Unified Potential Energy Function for Ionic and Non-ionic Bonds and the Question of Chemical Bonding

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For 39 diatomic ionic and non-ionic molecules, the anomalous behaviour of the spectral parameters α_e and $\omega_e x_e$ with respect to the bond type is reviewed. It is shown that on using a "universal" Sutherland parameter defined as $\Delta = \frac{1}{2} k_e r_e^2 / D_{ion}$, the anomalous behaviour disappears. Hard spectroscopic evidence is thus presented, for the first time to the author's knowledge, that just one bond type, in fact an ionic one, can account, in first approximation, for the spectral behaviour of both non-ionic and ionic bonds, H_2 included.

Introduction

For over half a century, the search for a simple two- or three-constant universal potential energy (PE) function is going on [1, 2]. Numerous functions have been suggested in order to reproduce spectroscopic data with ever more precision for an ever increasing number of different bonds. No function, however, has yet been found that can bridge the "spectroscopic gap" that exists between ionic and non-ionic bonds. Very reliable spectroscopic constants, such as the rotational (α_e) and vibrational ($\omega_e x_e$) constants (or their equivalent functions F and G[2], obtained through Dunham's expansion [3]), exhibit this pertinent anomaly very clearly when plotted against the Sutherland parameter Δ [4]. In this work, 39 diatomic molecules are selected, for which the spectroscopic data are shown in Table 1. A method is proposed to eliminate this gap by means of a modification of Sutherland's parameter. The results obtained will be discussed in the context of chemical bonding.

Graphical Review of Spectroscopic Data and Potential Energy Functions

Varshni [2, 5] has argued that graphical comparison of PE-functions is by far the most elegant and instructive way to distinguish between the possibilities of each function. Therefore this method is followed throughout. The "spectroscopic gap" is clearly shown in Figs. 1a and b, where F and G, respectively, are plotted against the Sutherland parameter Δ. All data are taken from Table 1. The Sutherland parameter is defined as $2\Delta = k_e \cdot r_e^2 / D$, where k_e is the force constant, r_e the equilibrium distance and D the dissociation energy of the bond under consideration. However, for covalent bonds

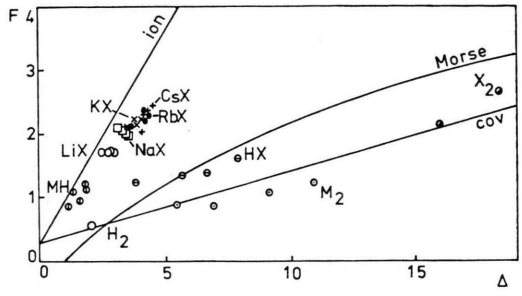

Fig. 1a. Plot of F versus the Sutherland parameter Δ. Solid lines represent theoretical predictions (ion, Morse) and an empirical relation (cov). The following symbols have been used: ○ H_2, ⊙M_2, ◒ X_2, ◍ HX, ⊖ MH, ○ LiX, □ NaX, × KX, ● RbX, + CsX.

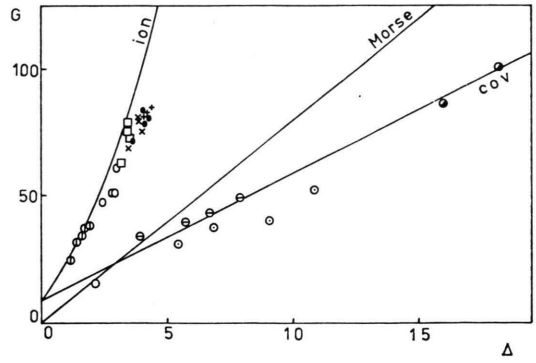

Fig. 1b. Plot of G versus the Sutherland parameter Δ. Same notation as in Fig. 1a.

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Table 1[a]

Bond	$r_e(10^8)$ (Å)	D_{cov} (eV)[a]	D_{ion} (eV)[b]	$k_e(10^5$ dyne/cm)[a]	F[c]	G[d]	t[g]	Δ[e]	Δ_{ion}
1. HH	0.74144	4.47813	17.32	5.7477	0.6066	15.95	3.016	2.202	0.569
2. HF	0.91681	5.869	16.06	9.6511	1.2533	34.30	5.225	4.314	1.576
3. HCl	1.27455	4.4336	14.43	5.1600	1.3645	39.88	6.632	5.901	1.813
4. HBr	1.41444	3.758	13.94	4.1130	1.4373	42.72	7.047	6.834	1.842
5. HI	1.60916	3.0541	13.58	3.1390	1.5735	48.70	7.671	8.306	1.868
6. LiH	1.5957	2.42871	7.08	1.0253	0.8849	24.70	3.806		1.151
7. NaH	1.8874	1.88	6.28	0.7812	1.1004	32.18	4.277		1.383
8. KH	2.2425	(1.86)	5.46	0.5597	1.1503	33.56	4.737		1.609
9. RbH	2.367	1.84	5.26	0.5148	1.2328	37.62	4.960		1.711
10. CsH	2.4938	1.81	4.96	0.4676	1.1708	38.16	5.144		1.830
11. LiLi	2.6729	1.046	6.44	0.2551	0.9114	31.03	4.112	5.438	0.884
12. NaNa	3.0788	0.720	5.86	0.1714	0.9680	37.50	4.169	7.043	0.865
13. KK	3.9051	0.514	4.85	0.0971	0.7860	39.87	4.507	8.991	0.952
14. RbRb		0.49	4.65	0.0821					
15. CsCs	4.47	0.394	4.28	0.0691	1.1446	(51.84)	4.676	10.937	1.006
16. LiF	1.56386	5.91	7.90	2.5003	1.7008	47.14	6.146		2.416
17. LiCl	2.02067	4.84	6.63	1.4240	1.7204	50.95	7.094		2.737
18. LiBr	2.17043	4.33	6.31	1.2032	1.7174	50.83	7.334		2.803
19. LiI	2.39192	3.54	5.86	0.9715	1.7289	61.18	7.765		2.960
20. NaF	1.92595	5.33	7.07	1.7597	2.1335	62.24	7.451		2.882
21. NaCl	2.36080	4.23	5.77	1.0941	2.0844	75.19	8.242		3.299
22. NaBr	2.50104	3.74	5.47	0.9567	2.0709	79.31	8.490		3.416
23. NaI	2.71145	3.00	5.07	0.7629	2.0070	73.32	8.594		3.454
24. KF	2.17146	5.07	6.01	1.3776	2.1255	68.57	8.142		3.374
25. KCl	2.66665	4.34	5.08	0.8569	2.2357	80.83	9.045		3.744
26. KBr	2.82078	3.91	4.84	0.7380	2.1784	78.78	9.182		3.787
27. KI	3.04784	3.31	4.58	0.6107	2.2463	75.41	9.497		3.867
28. RbF	2.27033	5.00	5.76	1.2924	2.1503	72.13	8.558		3.610
29. RbCl	2.78674	4.34	4.90	0.7582	2.2444	83.96	9.115		3.750
30. RbBr	2.94474	3.90	4.65	0.6916	2.3251	77.91	9.657		4.025
31. RbI	3.17688	3.30	4.39	0.5747	2.3440	81.60	9.990		4.124
32. CsF	2.34535	5.15	5.64	1.2166	2.0322	70.06	8.805		3.703
33. CsCl	2.90627	4.58	4.87	0.7477	2.3184	81.10	9.958		4.047
34. CsBr	3.07225	4.17	4.65	0.6331	2.3776	82.93	10.512		4.138
35. CsI	3.31519	3.56	4.38	0.5429	2.4288	84.79	10.577		4.252
36. FF	1.41193	1.602	15.62	4.6997	2.6695	100.95	7.736	18.253	1.872[f]
37. ClCl	1.9879	2.479367	11.89	3.2252	2.3349	87.69	12.986	16.044	3.346[f]
38. BrBr	2.28105	1.9707	10.40	2.4590	2.5632	104.95	14.655	20.263	3.840[f]
39. II	2.6663	1.54238	8.93	1.7191	2.9129	131.55	16.129	24.730	4.273[f]

[a] All values taken or computed from the constants collected in K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of diatomic molecules, Van Nostrand-Reinhold, New York, 1979. Values between brackets are uncertain. k_e is calculated from $k_e = 5.8883 \times 10^{-2}\ \mu\ \omega_e^2$. Zero point energies are neglected throughout.

[b] $-D_{ion} = IE_A + E_{AB} - EA_B$, where $E_{AB} = -D_{cov}$. The following atomic parameters have been used:
— IE: H(13.595), F(17.48), Cl(13.01), Br(11.884), I(10.454), Li(5.39), Na(5.138), K(4.339), Rb(4.16) and Cs(3.89).
— EA: H(0.74), F(3.4), Cl(3.6), Br(3.41) and I(3.07). The EA value for alkalimetals was neglected (see however 14).

[c] $F = \alpha_e\ \omega_e / 6 B_e^2$ [2]. [d] $G = \omega_e x_e \mu r_e^2 / 2.1078 \times 10^{-16}$ [2].

[e] If no value for Δ is shown, the ,,normally,, used value is the one shown in the next column.

[f] tentatively calculated by means of experimental IE values (see footnote b), although valence state quantities should have been used. Therefore halogens are mostly excluded from the computations (see text).

[g] Born-Landé relations for $F(t)$ and $G(t)$, not given in the text, are $F = t/3$ and $G = (1/3)\ (2t^2 + 15t + 9)$. These lines are drawn in Figure 3.

$D = -E_{AB}$, where E_{AB} is the bond energy, and for ionic bonds, $D = -(IE_A + E_{AB} - EA_B)$, if IE_X and EA_X are the ionization energy and electron affinity of element X, respectively.

In the same plot, the predictions of some elementary PE functions are also shown.

Standard ionic PE functions [5, 6], i.e. with an explicit Coulombic attraction term appearing in it, mostly yield equations of the type $F = a\Delta + b$ or $F = \Delta f(x)$, where $f(x)$ is a simple function of parameters introduced in the PE function. The original Born-Landé PE function [7], which may be con-

sidered as an elementary form of the more general Mie-Mecke-Sutherland PE function [4, 8], yields explicitly

$$F = (2/3)\,\Delta + 1/3\,, \tag{1}$$

a relation shown in Fig. 1a, denoted by "ion". Morse's PE function [9], as a prototype of covalent PE functions, yields

$$F = \Delta^{1/2} - 1\,, \tag{2}$$

also shown in Fig. 1 as the curve denoted by "Morse". Functions closely related to Morse's, such as Rydberg's [10], yield comparable relations. Nevertheless, also Morse's function can be considered as an alternative form of the Mie-equation [11].

Finally, an empirical relation, obtained by Varshni [2] for covalent molecules

$$F = 0.11\,\Delta + 0.36 \tag{3}$$

is also drawn in Fig. 1, with the notation "cov". For the $G(\Delta)$ relation, similar curves have been drawn, i e.
ion (Born-Landé)

$$G = (1/3)\,(26 + 38\,\Delta + 8\,\Delta^2)\,, \tag{4}$$

Morse

$$G = 8\,\Delta\,, \tag{5}$$

cov (Varshni)

$$G = 5\,\Delta + 9\,. \tag{6}$$

Neither of these (or related [2]) functions represents the actual situation. The existence of this "spectroscopic gap" is one of the basic problems in finding a universal PE function. The hard spectroscopic evidence for a distinction between non-ionic and ionic bond types found its very first generalization in the development of different bonding theories. Its roots may be traced back into the different theories of Kossel [12] and Lewis [13].

In order to have at least some idea about a possible unification of chemical behaviour, irrespective of bond type, a plot of experimental G values versus experimental F values was made [17].

The result is shown in Figure 2. Surprisingly enough, there is no gap at all, so that all molecules indeed show a very similar behaviour, except perhaps the M_2 molecules, where M is an alkali-metal,

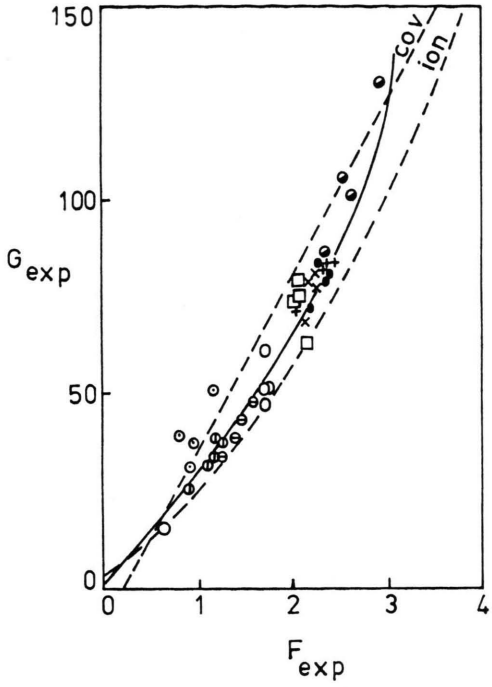

Fig. 2. Plot of experimental G versus experimental F values. Same notation as in Fig. 1a.

for which the spectroscopic data are not always reliable [18].

A second remarkable point however is that all "theoretical" predictions, whether ionic or non-ionic, now seem to be reasonable approximations of the "experimental" $G(F)$ relation. Indeed, when the relations given above are combined to yield $G(F)$, the following expressions are obtained:
ion (Born-Landé)

$$G = 3(1 + 5F + 2F^2)\,, \tag{7}$$

cov (Varshni)

$$G = 45.45\,F - 7.36\,, \tag{8}$$

Morse

$$G = 8(1 + 2F + F^2)\,. \tag{9}$$

The Morse curve has not been drawn in Fig. 2 since it is too close to the solid line, which is obtained by a parabolic curve fit of experimental G and F values, except those for the M_2 and X_2 molecules (M = alkali-metal, X = halogen) (see below).

The result of such fit is

$$G = 0.4 + 22.57\,F + 5.32\,F^2 \tag{10}$$

and is represented by the solid line in Figure 2. It

should be mentioned that Varshni's relation (8) was obtained for non-ionic molecules only, and that it now applies equally well for ionic species. As all bonding approximations now seem plausible and, since the experimental $G(F)$ plot shows no spectroscopic gap at all, it seems that a single bonding approximation, with a corresponding universal PE function, should be valid.

Obviously, something is wrong with the Sutherland parameter Δ, or its evaluation. *Since there are no ionic or non-ionic spectral constants*, the rather ambiguous choice between D_{cov} and D_{ion} seems to be the weak point. This corresponds to the question whether or not the spectroscopic behaviour of bonds is governed by ionic or non-ionic dissociation processes allone.

As an intermediate step in eliminating this ambiguity in D-values, a different parameter t was used, defined as $t = 2 + k_e r_e^3/e^2$ and being independent of D. This parameter t was introduced by Varshni [5], in comparative work on *ionic* bonding functions. $F(t)$ and $G(t)$ plots are shown in Figure 3.

In this figure, again the essential gap no longer appears, but it seems that finer details of chemical

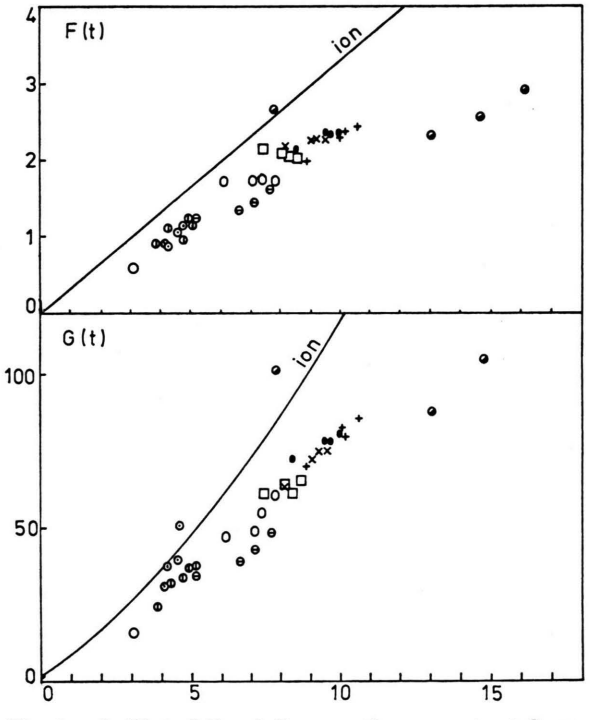

Fig. 3a—b. Plot of F and G versus the parameter t. Same notation as in Fig. 1a.

behaviour are lost in the transformation. The $F(t)$ plot shows this most clearly. Furthermore, the anomaly of the M_2 molecules, revealed in the $G(F)$ plot, is reproduced in the $G(t)$ plot. It is essential, however, that t, being a parameter characteristic in ionic PE functions [5, 6], where it is independent of D, even brings in line non-ionic molecules. Finally, the Born-Landé approximation remains plausible for all molecules in both $F(t)$ and $G(t)$ plots.

A Universal Sutherland Parameter

Sufficient evidence has been collected above for attributing the spectroscopic gap between ionic and non-ionic molecules to the rather inconsistent use of D_{cov} and D_{ion}. In fact, one can not a priori decide what is going to be determining the spectral behaviour of a molecule. Therefore, the Sutherland parameter was now determined for all molecules in Table 1, either as function of D_{cov} or D_{ion} allone.

Since a preliminary check of using D_{cov} proved to be fallacious, the following universal definition of the Sutherland parameter was retained

$$\Delta = \tfrac{1}{2} k_e r_e^2 / D_{\text{ion}} . \tag{11}$$

This is a straigthforward practical procedure for very ionic and homonuclear bonds, where it is clear which ionic structure is the most important. For bonds of intermediate polarity, however, the situation is not so clear. It was therefore assumed for the time being that for such bonds D_{ion} may still be determined by the definition given above, for the ionic structure in which the more electronegative element in the bond will be considered as anion. This point needs further attention, as it touches the basic ideas underlying the newly defined Sutherland parameter.

Results

All data are collected in Table 1. The resulting $F(\Delta)$ and $G(\Delta)$ plots are shown in Figure 4.

Discussion

The transition to standard Δ-values for all molecules produces essentially simple $F(\Delta)$ and $G(\Delta)$ relations, showing no "gap" between so called ionic and non-ionic molecules, despite the fact that some

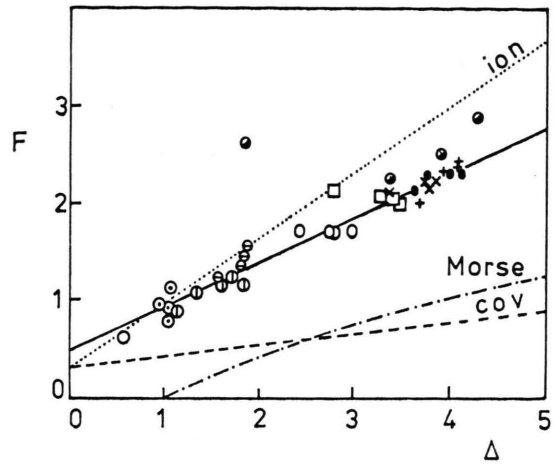

Fig. 4a. Plot of F versus the "universal" Sutherland parameter Δ. Same notation as in Fig. 1a.

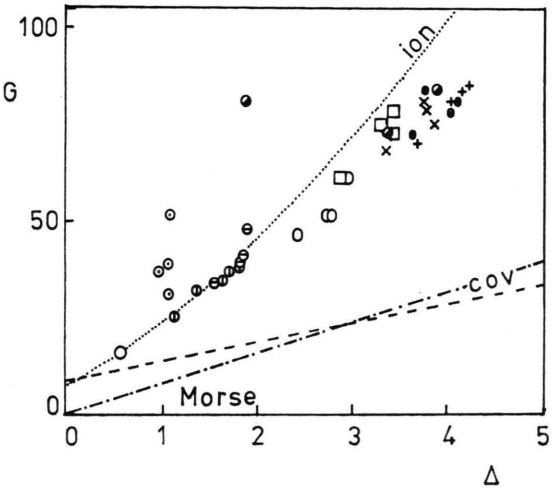

Fig. 4b. Plot of G versus the "universal" Sutherland parameter Δ. Same notation as in Fig. 1a [19].

D_{ion} values (for bonds with medium polarity) are still questionable.

The $F(\Delta)$ relation:

A regression analysis for F and Δ-values resulted in

$$F = 0.4945\,\Delta + 0.4577\,. \qquad (12)$$

Halogen-halogen molecules were excluded (see below). The goodness of fit (r^2) was over 0.96 for the remaining 34 molecules of Table 1. For these molecules, the rotational constant α_e can be calculated by means of (12) with a mean deviation of 5.47% only. For the alkalihalogenides allone, a mean error of 3.14% is obtained. For the "covalent" ones, the mean deviation is 8.8%. For some of the latter molecules, i.e. H_2, HX, Li_2, Na_2 and K_2, Varshni's empirical relation yields an average deviation of 20%. Moreover, as seen on Fig. 4a, the Born-Landé relation (1) still is a resonably good first approximation. Morse's prediction, and other non-ionic ones, is rather diverging as could be expected. Nevertheless, it can not be excluded that the final universal PE function could well resemble Morse's, since a plot of F versus $\Delta^{1/2}$, as in (2), was rather satisfactory. Approximate values of a and b in a relation $F = a\Delta^{1/2} + b$ were found to be 4/3 and -0.4.

The $G(\Delta)$ relation:

Also in this case, the spectroscopic gap has completely disappeared. The result shows a rather good similarity with the experimentally obtained $G(F)$ plot, shown in Figure 2. Exactly as in that figure, the M_2-series seems to be off-line. Part of this discrepancy, however, may be removed by introducing non-zero electron affinities for alkalimetals [14]. Amongst the halogens, especially F_2 falls out of the general trend. Since in this bond (and to a lesser extend in the other halogens) large extra non-bonding-electron repulsion is believed to be operative [15], this seems not unreasonable at all. In fact, such repulsion should be accounted for in the PE function, so that for these bonds slightly different $F(\Delta)$ and $G(\Delta)$ relations will be obtained.

Anyhow, the Morse's function is here definite lyout of order, for obvious reasons, whence the Born-Landé function again is the better approximation.

Due to the close similarity with the $G(F)$ plot and since a few D_{ion} values are still uncertain (see above), a further discussion is based upon the empirical $G(F)$ relation in Fig. 2, for which Eq. (10) has been evaluated. With the exception of the M_2-series, G-values, and hence $\omega_e x_e$-values, may be deduced with a mean deviation of 5.55%, including halogens. For the alkalihalide molecules separately, 6.17% error is obtained, whereas for the "covalent" molecules the mean deviation drops to 4.67%.

Conclusion

It is shown in this report that the spectroscopic gap between ionic and non-ionic molecules, as occuring in ordinary $F(\Delta)$ and $G(\Delta)$ plots, is easily removed by means of a standard or universal Sutherland parameter. For these "corrected" relations even the most elementary Born-Landé PE function seems to be an acceptable rationale. A consideration of an experimental $G(F)$ plot confirms the

validity of the modified Δ-formalism, although in this case all the different theoretical approaches seem to converge, which could be an interesting point [17], [18].

If the modified Δ-approach is valid, it must be concluded that the spectroscopic behaviour of all ionic and non-ionic species is very similar but also that it is governed primordially by ionic structures, even around r_e, the equilibrium distance of the bond. As this hypothesis seems to be confirmed by the spectroscopic data, this implies that somewhere, between $r = r_e$ and $r = \infty$, ionic attraction and non-ionic attraction always meet (crossing point), at which point the ionic attraction "takes over" to lead to the molecule's most stable ground state. Therefore, at $r = r_e$, spectroscopic evidence suggests that for all molecules considered, the wave function is best approximated by

$$\psi_{AB}(r_e) = a\,\psi_{A(1)}\,\psi_{A(2)} + b\,\psi_{B(1)}\,\psi_{B(2)} \qquad (13)$$

(with $a^2 + b^2 = 1$), even when A = B!

Speaking in terms of the Kossel and Lewis theories, this means that a Lewis structure H:H should be interpreted as an equivalent mixture of two ionic structures H^+H^- and H^-H^+, which would simply eliminate the dilemma inherent in the two theories.

After all, the behaviour of the spectroscopic constants is far more decisive with regard to the nature of the chemical bond than is an a posterio and subjective choice between D_{cov} and D_{ion}. The question of finding a universal PE function therefore will reduce to the question of reproducing D_{ion} values for all molecules. It is still uncertain if such a function will look like an "ionic" or "non-ionic" function, to remain in the older terminology. What seems more certain is that even a very simple Born-Landé function is acceptable in reproducing spectral parameters. Its capability of reproducing D_{ion} values for so-called covalent molecules is postponed to later work, where other and more sophisticated PE functions will be discussed. Other consequences of ionic bonding have been considered elsewhere [16].

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[18] For a further discussion of these data and of the constants β_e and γ_e, G. Van Hooydonk, Z. Naturforsch., submitted for publication.
[19] In this Fig. 4b, the points for halogens are incorrectly drawn. Correct positions can be obtained from the data in Table 1.