On a Universal Potential Energy Function and the Importance of Ionic Structures for the Ground State of Molecules

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The Kratzer-Fues-Varshni-V-potential, applied to ionic dissociation energies, is shown to yield rather accurate potential energy curves in the bonding region for H_2, HF, LiH, Li_2 and LiF. Vibrational levels, calculated by this ionic approximation to the ground state of widely differing molecules, nearly coincide with RKR-data. At the repulsive side of the curve and up to $2r_e$, the agreement with RKR-curves is even better than for Morse's curve, also for the "covalent" molecules H_2 and Li_2. Calculated spectroscopical constants α_e and $\omega_e x_e$ are far better than those calculated with Morse's function. Even the existence of a maximum in the potential curve at larger r-values seems not in confict with an ionic approximation. From the universal character of the function used, it is concluded that a reasonable approximation for the ground state of all molecules considered is one in terms of ionic structures, even for H_2 and especially for Li_2. According to the present results, the term "covalent bonding" seems to be definitely superfluous, as the usually made distinction between ionic and covalent bonding is more appearant than real.

Introduction

Theoretical calculations of the spectroscopical behaviour of simple molecules, such as H_2 [1], are in nearly perfect agreement with experiment [2], especially around the equilibrium distance r_e. Still, there is a need for generally valid potential energy (PE) functions for more complicated systems [3, 4]. The ideal solution would be a single universal PE function, capable of accounting for the spectral data of a great variety of bonds. In a recent review of the question [5], the divergent behaviour of non-ionic and ionic molecules could be understood and accounted for if, in first approximation, the ground state of all bonds was determined by ionic structures, even for H_2. A universal PE function should therefore reproduce ionic dissociation energies in the first place.

The problem of finding such a universal PE function explicitly can temporarily be avoided, if the energy of the ionic structure is approximated by an oscillator function near r_e, with a proper behaviour at the limits. This is readily done using experimental ionic dissociation energies together with a basicly simple oscillator function, of which many forms can be found in the literature [4, 6]. In this way, the predictions of an ionic bonding approximation can be checked "in advance" against experiment. Results of such procedure are presented in this report for five molecules H_2, HF, LiH, LiF and Li_2, varying from homonuclear to very ionic.

Review of PE Functions in Oscillator Form

From the enormous amount of PE functions available in the literature, only two well-known functions were retained. Morse's function [7]

$$U(r) = U_e(1 - e^{-\beta(r - r_e)})^2 \qquad (1)$$

was chosen as a reference point for dissociation into atoms. For dissociation into ions, a more general form of the Kratzer [8] — Fues [9] potential, i. e. Varshni's fifth potential [4], was selected:

$$U(r) = U_e(1 - (r_e/r)^n)^2 \qquad (2)$$

although this function was shown to be completely out of order for non-ionic dissociation processes [4].

These poor performances of the Kratzer-Fues-Varshni function in comparison with (1) are however rather strange. In fact, both functions allow the wave equation to be solved, with similar results [7, 9]. Both are also very similar generalizations of the fundamental oscillator form, as readily inspected if $\beta = 1/r_e$ and $n = 1$. Both generalizing parameters are related through $n = \beta r_e$. So strictly spoken, there seems to be no obvious reason why Kratzer's function should be that bad for non-ionic bonds, if Morse's function behaves correctly. On

the contrary, a Kratzer-like potential has interesting pecularities, as amply shown in the literature [10]. For the present work, the following points are of interest. Relation (2) can readily be made "universal" by going over to reduced parameters $x = r/r_e$ and $E(x) = U(r)/U_e$. Hence

$$E(x) = (1 - (1/x)^n)^2, \qquad (3)$$

where the minimum in the PE curve lies invariantly at $x = 1$ and $E(x)$ varies between 0 and 1 for $r_e \leqq r \leqq \infty$, and between ∞ and 0 for $0 \leqq r \leqq r_e$. Also $U(0)$ is infinite in the Kratzer potential, whereas Morse's $U(0)$ is finite. By going over to another variable $\xi = (r - r_e)/r_e$ or $x = 1 + \xi$ equations (2) and (3) change into

$$U(\xi) = U_e(1 - 1/(1 + \xi)^n)^2$$

and

$$E(\xi) = [1/(1 + \xi)^{2n}][(1 + \xi)^n - 1]^2. \qquad (4)$$

As a first approximation of (4) one readily obtains the following oscillator form:

$$E(\xi) \approx n^2 \xi^2/(1 + \xi)^{2n} \qquad (5)$$

very analogous to Dunham's original expansion series [6], and, for instance, even allowing the use of Padé approximants in constructing PE functions [3]. While Dunham's $U(\infty) = \infty$, $U(\infty)$ in (2) is still finite, i. e. U_e. For $n = 6$, (2) moreover yields the Lennard-Jones potential [11], which is widely used.

The same equation also compares very well with results obtained by numerical integration of the wave equation [12].

Consequently, the bad results of a Kratzer-like potential for non-ionic molecules are really not understandable.

This discrepancy with Morse's function shows most clearly in the expressions obtained for F and G [4], related to the spectroscopical constants α_e and $\omega_e x_e$, written in terms of the Sutherland parameter Δ [13].

Equation (2) leads to

$$\Delta = n^2, \qquad (6)$$

$$F = n = \Delta^{\frac{1}{2}}, \qquad (7)$$

$$G = 8\Delta + 12\Delta^{\frac{1}{2}} + 4, \qquad (8)$$

whereas the Morse values are: $\Delta = (\beta r_e)^2$, $F = \Delta^{\frac{1}{2}} - 1$ and $G = 8\Delta$. For the same Δ-values, the corresponding F and G values completely disagree.

However, the simple Kratzer-potential $(n = 1)$ leads to the following "ideal" Kratzer-values, which should apply for all molecules:

$$\Delta = 1, \quad F = 1, \quad G = 24,$$

a rather improbable result [4]. However, the very strange situation now applies that several molecules are found with F and G values not too far from these idealized values (for a review see Ref. [5]), whereas the lowest Δ-value for non-ionic dissociation processes ever found is still larger than 2 for H_2 [4].

The consideration of ionic dissociation processes [5] however allows much smaller Δ-values for non-ionic bonds! Several Δ-values are then even very near to the ideal value of unity, exactly in the cases where the idealized F and G values also apply [5].

This is roughly why potential (2) was chosen to evaluate the behaviour of ionic structures in function of r, completely in agreement with Kratzer's original work on the HCl-molecule [8].

Moreover, it is known that Morse's function is systematically low in the attractive part of the PE curve at larger r-values when compared with RKR-curves [14]. For these negative deviations no direct explanation can be given in terms of simple bonding effects.
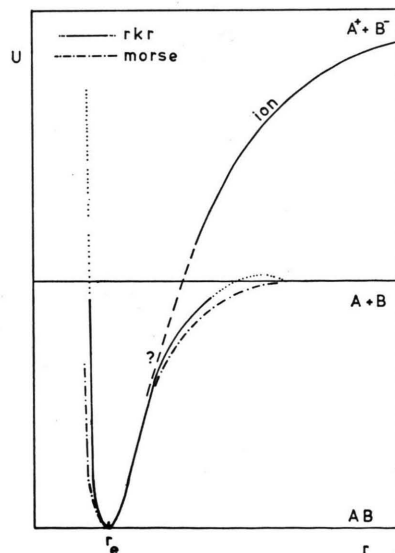

Fig. 1. General shape to be expected for the PE-curve according to an ionic approximation (line "ion"). The RKR is shown with possible extensions (see text), together with the general deviations of Morse's curve.

Table 1. Experimental data on H_2, HF, LiH, Li_2 and LiF[a].

Bond	U_e(ion) cm^{-1}	U_e(cov) cm^{-1}	r_e(Å)	$\Delta^{1/2}$	β(Å^{-1})	ω_e cm^{-1}
H_2	141878	38283.1	0.74144	0.74887	1.94455	4401.23
HF	131633	49405.5	0.916808	1.24583	2.21808	4138.32
LiH	57681	20291.5	1.5957	1.06765	1.12808	1405.65
Li_2	46908.8	8612.2	2.6729	0.98738	0.86374	351.43
LiF	64172.5	48122.2	1.563864	1.54916	1.14393	910.34

[a] All values taken from K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of diatomic molecules, Van Nostrand-Reinhold, New York 1979.

At the repulsive side of the PE curve, Morse's curve is in general low too.

On the other hand, an ionic approximation in oscillator form, starting from ionic structures at $r = \infty$, will "a priori" give positive deviations from an RKR as the non-ionic dissociation limit is approached. This situation is illustrated in Fig. 1, where the ionic approximation to the RKR is shown, together with the general trend found on Morse-curves.

The question is to see whether near r_e and at the repulsive side the ionic representation coincides with the RKR's, which can satisfactorily be done by calculating vibrational levels with (2) and comparing them with the experimental RKR-data.

Procedure

In this work, the behaviour of ionic structures in function of the internuclear separation r is approximated by the Kratzer-Fues-Varshni potential, relation (2). For its evaluation the following data are needed:

— the ionic dissociation energy
$$U_e = - (I E_A + E_{AB} - E A_B) + \tfrac{1}{2} h \nu_e, \text{ and}$$

— the ionic Sutherland parameter Δ calculated through $\Delta = n^2 = \tfrac{1}{2} k_e r_e^2 / U_e$.

The use of this definition of U_e for dissociation processes can however be questioned for bonds of intermediate polarity [5]. All data are collected in Table 1 for H_2, HF, LiH, LiF and Li_2. As an example, equation (2) is given for H_2:

$$U(r)_{cm^{-1}} = 141878 (1 - (r_e/r)^{0.74887})^2, \quad (9)$$

where $r_e = 0.74144$ Å.

RKR-curves are available for all of the selected molecules, except of course LiF, for which the general form of the PE curve can be calculated by various theoretical methods. $U(r)$ values are calculated directly for r_{max} and r_{min}, the turning points of each vibrational level determined by an RKR-analysis.

Table 2. Potential energy curve for the ground state of H_2[a] ($U(r)$ in cm^{-1}, r in Å).

v	r_{max}	Morse	Ion	exp.	Ion	Morse	r_{min}
0	0.883	2217	2134	2170	2242	2110	0.633
1	1.013	6443	6162	6331	6623	5911	0.571
2	1.120	10393	10020	10257	10873	9341	0.535
3	1.219	14008	13712	13952	15019	12501	0.509
4	1.316	17330	17308	17420	18890	15376	0.489
5	1.413	20349	20815	20662	22724	17984	0.473
6	1.513	23109	24297	23676	26201	20319	0.460

Mean deviation up to this level: Morse 5.51%, ion 4.59%

v	r_{max}	Morse	Ion	exp.	Ion	Morse	r_{min}
7	1.618	25625	27787	26458	29487	22457	0.449
8	1.730	27903	31315	29001	32777	24537	0.439
9	1.853	29974	34959	31294	35268	26073	0.432
10	1.992	31850	38799	33320	37926	27677	0.425
11	2.158	33566	43027	35057	39933	28867	0.420
12	2.370	35125	47916	36472	41608	29845	0.416
13	2.675	36521	54090	37521	42905	30594	0.413
14	3.260	37714	63710	38143	43790	31101	0.411

[a] Experimental RKR: S. Weissman, J. T. Vanderslice, and R. Battino, J. Chem. Phys. **39**, 2226 (1963).

Results

Vibrational levels, calculated with (1) and (2), are compared with experimental ones for H_2, HF, LiH and Li_2 in Tables 2 − 5. For LiH, the results of an adapted Hellman-potential are also given. Table 6 for LiF shows a comparison of the present results with those obtained through a Padé ap-

v	r_{max}	Morse	Ion	exp.	Ion	Morse	r_{min}
0	1.023	2176	2144	2047	1953	1904	0.836
1	1.115	6251	6163	6008	5883	5598	0.786
2	1.187	10041	9965	9798	9860	9210	0.755
3	1.253	13648	13682	13419	13605	12518	0.733
4	1.317	17104	17362	16878	17125	15556	0.716
5	1.379	20317	20919	20193	20753	18662	0.701
6	1.441	23342	24419	23351	24050	21357	0.689
7	1.503	26150	27831	26350	27093	23840	0.679

Table 3. Potential energy curve for the ground state of HF[a] (values in cm^{-1} for $U(r)$, r in Å).

Mean deviation up to this level: Morse 4.85%, ion 2.90%

v	r_{max}	Morse	Ion	exp.	Ion	Morse	r_{min}
8	1.567	28807	31240	29191	30081	26243	0.670
9	1.633	31287	34622	31875	32952	28519	0.662
10	1.701	33576	37958	34334	35244	30317	0.656
11	1.772	35692	41279	36705	37665	32194	0.650
12	1.847	37650	44609	38921	40218	34155	0.644
13	1.922	39348	47761	40973	42453	35853	0.639
14	2.009	41030	51204	42850	44314	37256	0.635
15	2.108	42620	54861	44543	46243	38698	0.631
16	2.223	44104	58786	46031	47734	39807	0.628
17	2.364	45498	63170	47292	49266	40938	0.625
18	2.555	46829	68445	48294	50510	41706	0.623

[a] Experimental RKR: R. J. Fallon, J. T. Vanderslice, and E. A. Mason, J. Chem. Phys. **32**, 698 (1960); **33**, 944 (1960).

v	r_{max}	Hellman	Morse	Ion	exp.	Ion	Morse	Hellman	r_{min}
0	1.779	714	708	693	698	699	677	675	1.447
1	1.938	2105	2082	2025	2058	2119	1994	2014	1.354
2	2.061	3446	3384	3296	3376	3538	3258	3320	1.297
3	2.173	4776	4648	4550	4643	4928	4456	4575	1.255

Table 4. Potential energy curve for the ground state of LiH[a] ($U(r)$ in cm^{-1}, r in Å).

Mean deviations: Hellman 2.26%; Morse 2.08%; ion 2.60%.
[a] Experimental RKR: R. J. Fallon, J. T. Vanderslice, and E. A. Mason, J. Chem. Phys. **32**, 1453 (1960).

Table 5. Potential energy curve for the ground state of Li_2[a] ($U(r)$ in cm^{-1}, r in Å, balance in %).

v	r_{max}	Morse	Ion	exp.	Ion	Morse	r_{min}	Balance ion [b]
0	2.84898	171	175	175	175	178	2.51723	100.00
1	2.99213	500	523	521	528	541	2.41389	99.04
2	3.09889	816	869	862	880	906	2.34761	98.72
3	3.19120	1122	1214	1198	1231	1271	2.29646	98.58
4	3.27546	1418	1557	1528	1581	1635	2.25414	98.43
5	3.35457	1705	1901	1853	1929	1998	2.21775	98.49
6	3.43021	1985	2244	2173	2275	2358	2.18570	98,57
7	3.50342	2257	2588	2487	2619	2715	2.15700	98.75
8	3.57495	2522	2933	2796	2960	3069	2.13099	99.03
9	3.64533	2781	3279	3099	3298	3419	2.10720	99.36
10	3.71501	3033	3626	3396	3633	3765	2.08529	99.79
11	3.78434	3280	3976	3687	3965	4107	2.06499	99.70
12	3.85365	3520	4328	3972	4293	4445	2.04609	99.12
13	3.92321	3756	4683	4252	4617	4777	2.02845	98.47
14	3.99331	3986	5043	4525	4936	5104	2.01193	97.64

Mean deviation for all $U(r)$ values: Morse 8.55%; ion 4.89%.
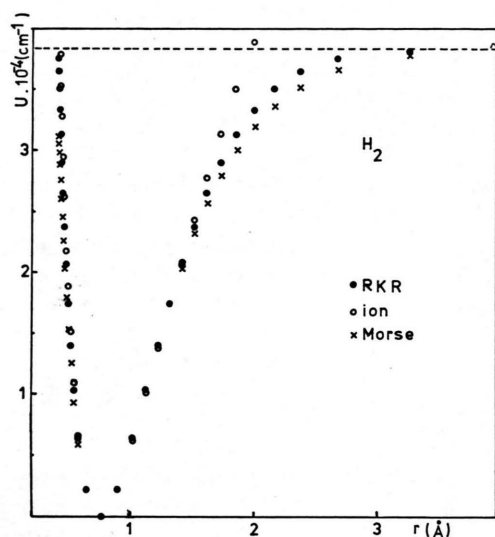[a] Experimental RKR: P. Kusch and M. M. Hessel, J. Chem. Phys. **67**, 586 (1977).
[b] Balance for the „ionic" levels, calculated as 100 $(1 - (U(r_{min}) - U(r_{max}))_{calc}/U_{exp})$.

Table 6. Potential energy curve for the ground state of LiF[a] ($U(r)$ in cm^{-1}, r in Å).

r	Morse	Ion	Padé
8	48061	54343	52957
6	47522	49182	47107
5	46251	44720	42434
4	42374	37710	35494
3	31306	25916	24367
2	7425	6443	6225
1.8	2696	2459	2408
1.4	2045	2245	2281
1.2	12825	16511	17000
1.0	39503	64063	64306

[a] Padé approximant PE curve: K. D. Jordan, J. L. Kinsey, and R. Silbey, J. Chem. Phys. **61** 911 (1974).

Fig. 3. Observed and calculated PE-curves for HF.

Fig. 2. Observed and calculated PE-curves for H$_2$ (only the vibrational levels are shown).

Fig. 4. Observed and calculated PE-curves for LiH.

proximant PE function, proposed by Jordan et al. [3], as no RKR analysis is possible for this molecule.

Graphical comparisons are made in Figures 2 – 6.
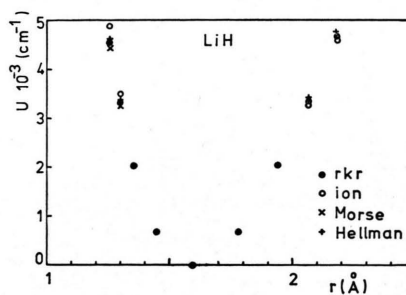
Table 7 shows calculated and experimental F and G values. In Fig. 7 a collection of $E(x)$ curves, · calculated by means of (3), is presented for different values of n or $\Delta^{1/2}$. A detail of this figure is

Table 7. Comparison of experimental and calculated F and G values[a].

Bond	F_{exp}	F_{ion} [b]	F_{Morse}	G_{exp}	G_{ion}	G_{Morse}
H$_2$	0.6066	0.749 (+ 23)	0.442 (− 27)	15.95	17.46 (+ 10)	16.63 (+ 4)
HF	1,253	1.258 (0)	1.034 (− 17)	34.30	31.37 (− 9)	33.08 (− 4)
LiH	0.885	1.067 (+ 21)	0.800 (− 10)	24.69	25.90 (+ 5)	25.90 (+ 5)
Li$_2$	0.9114	0.987 (+ 8)	1.332 (+ 46)	31.03	23.65 (− 24)	43.44 (+ 40)
LiF	1.701	1.549 (− 9)	0.79 (− 54)	47.14	41.79 (− 11)	25.6 (− 46)
Mean deviations		12.2%	30.8%		10.6%	19.7%

[a] See ref. [4] for the definition of F and G: $F_{exp} = \alpha_e \, \omega_e / 6 \, B_e^2$ and $G_{exp} = \mu \, r_e^2 \, \omega_e \, x_e / 2.1078 \cdot 10^{-16}$.
[b] Figures between brackets are rounded off deviations in %.
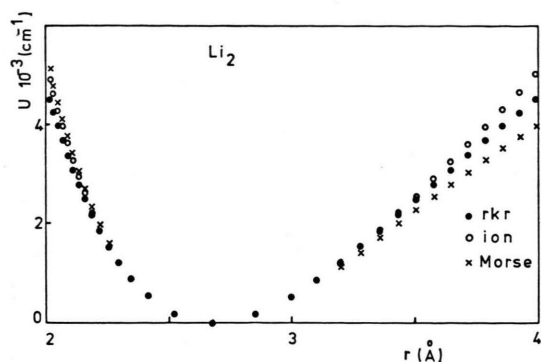
Fig. 5. Observed and calculated PE-curves for Li_2.
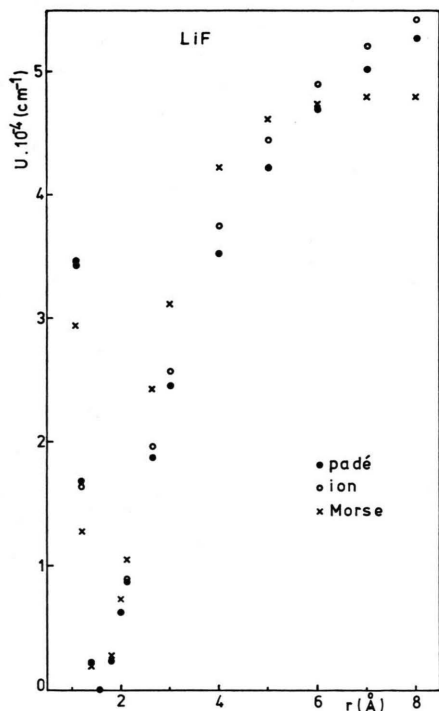
Fig. 6. Comparison of three calculated PE-curves for LiF The curves "ion" and "Padé" are bound to ionic dissociation, Morse's to atomic.
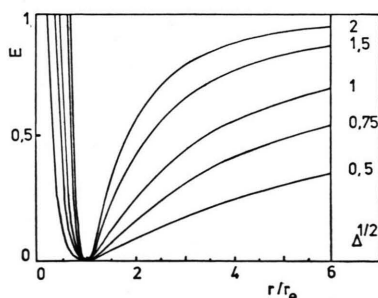
Fig. 7. Plot of different reduced PE-curves for different values of $\Delta^{1/2}$. There is no intersection of lines at the minimum.
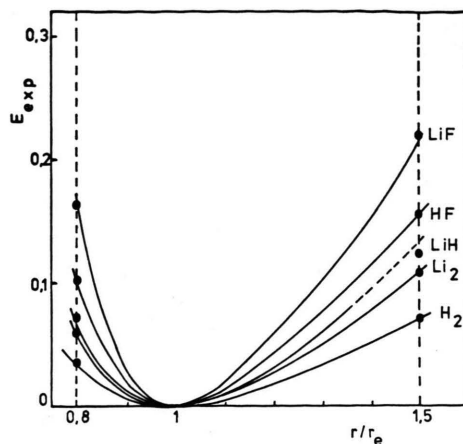
Fig. 8. Plot of experimental $E(x)$ curves for all molecules considered around r_e. The expectation values, according to theory at r/r_e equal to 0.8 and 1.5 are indicated by dots. There is no intersection at the minimum.

reproduced in Fig. 8 for x values between 0.8 and 1.5, where instead of the calculated curves, the experimental ones are shown. The theoretical expection values at x equal to 0.8 and 1.5 are indicated.

Discussion

The general trend predicted, as illustrated in Fig. 1, is confirmed: in all cases where RKR-curves are available, the ionic approximation indeed gives an upper limit, approaching the RKR-curve as r goes to r_e in the attractive region to a rather high degree of precision, in view of the approximations made. Morse's curve is by the same token a lower limit in this region, with nearly equal deviations, apart from sign, from the RKR.

At the repulsive side, the situation is not so clear: Morse's curve seems low again and the ionic seems high, although, especially at this side of the PE curve, dU/dr values are extremely large. Reminding however that $100\ cm^{-1}$ corresponds to a little bit more than 0.01 eV or 0.3 Kcal/Mole, the deviations on the whole are rather small, at least in the region between r_e and $2\,r_e$, where bonding effects become most pronounced.

H_2 (Fig. 2, Table 2)

Exactly in this molecule of extreme interest, the ionic Kratzer potential is seen to describe the experimental behaviour at least as good as the non-ionic Morse function in the bonding region. There,

the deviations of both functions are of comparable magnitude but of opposite sign. For vibrational levels up to 6 at both sides of the minimum, the ionic approximation is even better than Morse's function: the mean deviation for these levels is 4.6% for the ionic and 5.5% for the Morse curve.

For the positive deviations of the ionic curve at $r > 2 r_e$, the explanation is elementary (see above). For the negative deviations of Morse's curve in this region, the explanation is not straightforward at all, and has always been puzzling, especially in the context of an eventual maximum in $U(r)$ near 4 Å (see further).

It now turns out that these negative deviations of Morse's curve can be explained in terms of ionic structures, exactly in the case of H_2.

Furthermore, it is known that for H_2 bound states exist *above* the dissociation limit [15], a phenomenon also observed on other hybrides [16]. A possible explanation [15] for these states lies in the assumption of a very small maximum in $U(r)$ around 4 Å. This maximum is — in exaggerated form — indicated in Fig. 1 — 2 as an extension of the RKR-curve. Although the heigth of this maximum in the case of H_2 is very critical (a rotational band $J = 6$ at $v = 14$ is *not* observed [15]) the existence of such a maximum is perfectly allowed for in an ionic bonding approximation, imposing no restraints whatsoever on the behaviour of the non-ionic state, which might even be repulsive at larger r-values, when electron exchange has not yet come into play. The possible existence of such maxima is hardly understood in the usual non-ionic bonding approximation (as Heitler-London's theory [17]), where, by definition and through the wave equation imposed, the non-ionic structure should lead to bonding through all r-values $> r_e$ up to infinity. The existence of these maxima in the $U(r)$ potentials of ground states, amply supported by spectroscopic evidence, indicates that the range of electron-exchange contributions, allowed for through the VB wave function of non-ionic states, is largely overestimated. If, on the other hand, electron exchange comes in just around the critical distance in order to rearrange electrons according to the requirements of an ionic approximation to bonding, the observed maxima are even plausible (see below).

Anyhow, if it is agreed that, for H_2, Morse's function is a good covalent function — which it is

beyond doubt —, it must now be concluded that an *ionic* Kratzer-Varshni V-function is at least an equally good covalent function for distances up to $2 r_e$ and even offers a flexibility in interpretation a Morse function has not.

Nevertheless, closer examination of the situation around r_e shows that the present form of the ionic approximation yields values slightly lower than the RKR-curve, which in principle, is against the general trend expected. Although the deviations are small indeed, further work seems necessary. An inspection of the F-values for H_2, given in Table 7, points in the same direction: the deviations from the experimental value of the ionic and non-ionic functions are practically the same, but of opposite sign.

HF, LiH (Figs. 3 – 4, Tables 3 – 4)

For these heteropolar molecules, a situation is found, very similar to that of H_2. Remarkable seems here that on the repulsive side of the HF-PE curve, the results are quantitatively superior to Morse's. On the attractive side, the HF-RKR-curve is again quite symmetrically approached by the ionic and non-ionic potentials. For LiH, the ionic approach is the better at the first vibrational level, also in balance, but for the other levels, Morse's curve is superior. In this case, however, only a small portion of the PE curve is available. Moreover, both HF and LiH are bonds of intermediate polarity where the definition of U_e, used in the evaluation of the levels, is in need of revision [5].

For the alkalihydrides, the ionic Hellmann potential [18] is known to be one of the best functions available [19]. Values calculated by means of an adapted version of this potential are given for comparison. Table 4 shows that also in this case the observed divergences are rather small.

LiF (Fig. 6, Table 6)

For very ionic bonds, an RKR-analysis is impossible. One is therefore obliged to use other "calculated" curves, most of them being semi-empirical, but all yielding very similar results of reasonable quality [20]. It is typical that for these rather simple bonds more elaborate theoretical approaches [21] give rather poor results, which seems very strange.

Anyhow, the present approach is now compared with a curve constructed by means of a [2, 2] Padé

approximant [3], bound to Dunham's expansion (see above).

This potential is

$$U(\xi) = a_0 \xi^2 [1 - a_1 \xi + (a_1^2 - a_2) \xi^2]^{-1} \quad (10)$$

and is evaluated by means of the Dunham coefficients a_n and the equilibrium distance r_e and a U_e-value is not even needed [22]. A comparison with this function is readily done graphically.

Figure 5 shows that both curves are quite similar, although the ionic one is high. As indicated above for HF and LiH, this could be ascribed to the neglect of the other ionic structure, in this case, Li^-F^+. Morse's curve, bound to atomic dissociation, is seen to be out of order, even for intermediate r-values, at both sides of the minimum. At the repulsive side, the two ionic potentials are practically identical, as Table 6 reveals.

Li_2 (Fig. 5, Table 5)

A good approximation of the Kratzer potential can be expected "a priori" for Li_2, since most of its constants are very near to the ideal Kratzer values (see above), as inspection of Table 7 shows.

A confirmation of this rather "ideally ionic" behaviour of Li_2, a so-called non-ionic bond, is offered by the calculated vibrational levels in this case.

From a comparison of observed and experimental levels for Li_2, it is seen that an ionic approximation indeed sets a surprisingly narrow upper limit to the RKR-curve in the attractive part, even narrower than the lower limit, the Morse-curve.

In this context, it should also be reminded that the demands imposed on an ionic Kratzer potential near r_e are much larger than those imposed on a non-ionic Morse function. In fact, U_e for the ionic process is about 6 times larger than U_e for the non-ionic dissociation process. Errors in the ionic PE function are therefore expected to be 6 times more pronounced than similar errors in the Morse function. The deviations actually found on Li_2 are even smaller for the ionic function than for the non-ionic one.

Further aspects of the goodness of fit of the present approximation show in the balance of the energy levels, which can be expressed as $U(r_{max}) - U(r_{min})_{calc}/U_{exp}$ for each vibrational level. Deviations from a maximum of 100% balance are given in Table 5. The worst situation is found in the

highest vibrational level considered, where the balance is still over 97%. Above all, even the minor deviations from the RKR remain predictable in the ionic approximation, which is absolutely not the case for Morse's function.

It is only fair that, after all, Kratzer's function for non-ionic molecules now turns out to be at least as good as − if not better than − Morse's function with respect to experiment (see above). Moreover, its validity and applicability in these cases imply a rather elementary and classical solution to the question of chemical bonding.

It then appears that the long persistent dilemma between ionic and non-ionic bonding is, for the larger part, inexistent which finds a simple illustration in making the Kossel [23] and Lewis [24] representation of chemical bonds completely compatible [5]. Even H_2 is no longer to be considered as "the" stumbling block towards an ionic bonding approximation [25].

F and G values

The performances of both functions as to the calculation of spectroscopical constants, such as α_e and $\omega_e x_e$, characterized by F and G values [4], are compared in Table 7.

In comparison with other methods, usually restricted to a rather similar series of molecules, the present values for bonds varying from higly ionic to homonuclear are still reasonable. In this table, the superiority of the ionic Kratzer-Varshni function over Morse's appears: mean deviations found are about three times smaller for F and about two times smaller for G. The opposite deviations on H_2 for F although of comparable magnitude, also came out in the calculation of the vibrational levels. For ionic molecules, the "universality" of the ionic approximation is beyond doubt, since Morse's completely fails, as already observed in the general shape of the PE function.

Therefore, the question of the universal character [26] of an ionic function (2) is reconsidered.

A plot of

$$E(x) = (1 - (1/x) \Delta^{1/2})^2$$

for different values of $\Delta^{1/2}$ has been made in Fig. 7, showing the general shape of PE curves for all kinds of bonds. A detail of this figure is redrawn in Fig. 8, where, however, the curves now shown are the experimental RKR-curves for all molecules

considered above, in the region $0.8 \leq x \leq 1.5$, i. e. in the region where bonding effects are most pronounced. An exception is made for LiF, where the Padé approximant PE curve [3] is shown. In this figure, the expectation-values at x equal to 0.8 and 1.5 are indicated, as calculated from (11) with the use of the corresponding $\Delta^{1/2}$-values.

Not only is the analogy of this Fig. 8 with Fig. 7 very striking, but the theoretical expectation values are nearly in quantitative agreement with experiment.

So called ionic molecules are now characterized by large Δ-values, non-ionic ones have small Δ-values. Figure 7 could be completed by indicating also the non-ionic dissociation limits, which, as shown for Li_2 lies at about $E \approx 1/6$, but is much larger for LiF.

As expected, and confirmed by experiment, the gradation from homonuclear to heteronuclear bonds is very smooth, and there is no reason whatsoever to make a "spectroscopic" distinction between ionic and non-ionic molecules, as there is no intersection of curves in Figures 7 – 8. However, it is yet difficult to ascertain whether or not the present generalization of the Kratzer-potential through the exponent n leads to the best possible universality. Indeed, other generalizations are also possible with very similar results [27], both theoretically and practically.

Moreover, the rather satisfactory results for Li_2 indicate that an ionic Kratzer potential seems at its best when $n \approx 1$, i. e. when the generalizing impact of n is at its minimum.

Nevertheless, already in its present form, (2) has remarkable "universal" characteristics, which at least is one of the defaults of Morse's function. Indication of a possible improvement of the universality of a Kratzer-potential may be found in the nearly linear dependence of F in function of ionic $\Delta^{1/2}$-values found for over thirty diatomics of very different nature [5].

The whole question therefore remains constantly under review, since there are other criteria as well a genuine universal function should fulfil. Not the least is a reproduction of ionic dissociation energy values, a problem avoided in the present oscillator form. Hereto adds the question of the U_e-values for bonds of intermediate polarity, which, if solved, leads to an explanation of bond additivity, as shown before [28]. These are, however, results directly following from an ionic bonding approximation. This bonding theory should allow the reproduction of experimental molecular data, just by using atomic constants of the bonding partners, such as ionization energy and electron affinity. The present results strongly favour all these derivations.

Rescaling of the ionic PE-function for an atomic dissociation limit.

As shown above, the ionic Kratzer function behaves rather well at the repulsive side of the RKR's. This side of the PE-curve is often neglected, although it is at least equally important to account for the experimentally observed vibrational levels. Positive deviations, increasing as the non-ionic dissociation limit is approached, at the attractive side of the PE-curve, call for a correcting function. At least formally, this is a rather straigthforward matter.

For instance, if $U_1 = U_e - D_{\text{AB}}$, where D_{AB} is the atomic dissociation energy of the AB bond, one could put

$$U(r) = U_e(1 - (r_e/r)^n)^2 - U_1 f(r)$$

or

$$U(r) = U_e(1 - (r_e/r)^n)^2(1 - (U_1/U_e)F(r)), \quad (12)$$

where both $f(r)$ and the reduced equivalent $F(r)$ should obey the limiting values of 0, when $r = r_e$, and 1 when $r = \infty$.

These boundary conditions of course call for a function in terms of the Kratzer-variable $(r - r_e)/r$. In that case, (12) will not only lead to the atomic dissociation limit

$$U(\infty) = U_e - U_1 = D_{\text{AB}}$$

but, in the same time, will correct the positive deviations found for the uncorrected Eq. (2) at $r > r_e$ (see above). Preliminary tests [27] of (12) indicate that $f(r)$ seems bound to higher powers than 2 in the original or generalized Kratzer variable, indicating that around r_e, the corrections will be extremely small.

Thus far, however, an explicit form of $f(r)$, being valid for all molecules presented herein and improving the vibrational levels consistently, was not yet found. Although beneath the critical distance the corrections are of the expected order of magnitude, the main problem was that, for r-values larger than the critical distance, the cancellation of U-values was never perfect. Instead of approaching

the atomic dissociation limit asymptotically, fluctuations along the dissociation limit were obtained. In most cases, a maximum was obtained above the limit, eventually followed by a minimum, but, convergence is, in general, very slow. Similar difficulties are found in applying the Simons-Parr-Finlan potential [10], as pointed out by Jordan et al. [3]. An interesting detail shows at the repulsive side of the PE-curve, when a correction of this nature, inspired through the behaviour at $r = \infty$, is applied to $U(r)$. In fact, in this part also a maximum is automatically obtained which is rather sharp and suddenly leads to very negative $U(r)$ values, reaching, at least qualitatively, the united atom level at $r = 0$! An explicit study of this behaviour of PE-curves will soon be presented.

Anyhow, there is ample spectroscopic evidence for the existence of a maximum in the PE-curves above the dissociation limit at larger r-values [16, 30] and the existence of a maximum at very small r-values $(< r_e)$ is of course beyond doubt. These basic aspects of the PE-curve are not at all in conflict with an ionic approximation to chemical bonding [25].

The ionic or Coulombic nature of the Kratzer potential.

When not in oscillator form, a generalized Kratzer-potential may be rewritten as

$$V = -2\,^1A/r^n + B/r^{-n} \qquad (13)$$

showing the analogy with the Mie-Mecke-Sutherland potential [13, 29]. The original Kratzer potential has $n = 1$ and $A = e^2$. In that case, the U_e-values simply reduce to

$$U_e \approx e^2/r_e = 116140/r_e \,(\text{cm}^{-1}). \qquad (14)$$

The following U_e are calculated (in cm^{-1}): H$_2$ 156641, HF 126678, LiH 72783, Li$_2$ 43483 and LiF 74265. It is rather striking to see that the present approximation is "worst" for ionic bonds and that the seemingly bold assumptions in the Kratzer potential ($A = e^2$ and $n = 1$) are best obeyed for the non-ionic bonds Li$_2$ and H$_2$.

This strengthens the idea that for heteronuclear bonds the neglect of the other ionic structure in calculating U_e values is not at all justified (see above).

Moreover, with the U_e value given by (14), (2) may be rewritten as

$$U(r) = 116140/r_e (1 - r_e/r)^2 \qquad (15)$$

being valid as long as $n = 1$. For Li$_2$, (15) yields a first vibrational level of 187.67 and 166.96 cm^{-1}. Its mean value, i. e. 177.32 cm^{-1}, compares well with experiment, 175.032 cm^{-1}, with a deviation of only 1.3%. This level is obtained with just one parameter r_e.

Finally, other generalizations of the original Kratzer potential are possible (see above), in which the Coulomb force is explicitly showing [27].

Conclusion

The general demands imposed by an ionic approximation to chemical bonding on the spectroscopic behaviour of all bonds considered in this report seem nearly fulfilled. The variety in the bonds studied practically guarantees the universality of the approach. Especially appealing are the results obtained on Li$_2$, where Kratzer's original potential, for which the wave equation can be solved, is best obeyed. The generalized form of this function, due to Varshni, is distinctly better than Morse's function, at least if universality is the criterion.

Despite persistent prejudices in the literature against ionic bonding mechanisms, especially for so-called covalent bonds, it is beyond doubt now that an ionic approximation is also very suited to account for the spectroscopic characteristics of these molecules. Exactly in the bonding region, this theory yields a very narrow and rather exact upper limit to the RKR-curves, bound as these are to non-ionic dissociation. As soon as the influence of these different limits no longer plays a role, as at the repulsive side of the PE-curve, the superiority of the ionic function comes out clearly. This side is, strictly spoken, as important as the attractive side in reproducing vibrational levels.

The ultimate result of electron exchange near the critical distance seems to make it possible for the non-ionic structure to rearrange electrons according to the requirements of ionic structures (and vice versa for dissociation), even for H$_2$. At lower r-values, electron exchange allows for "resonance" between the two ionic structures describing the ground state of molecules.

The ionic approximation therefore provides one with a fundamental insight into the mechanism of bond formation, of which the details seem either to be lost or, at least, seem to be hardly retraceable in the complex apparatus of quantummechanical approximations.

Moreover, the efficiency of most of these methods for systems heavier than H_2 is still measured in about 0.1 eV or over 800 cm^{-1} [31], whereas the present approximation easily goes beyond this limit for a variety of molecules.

It seems worth while therefore to continue the search for a better universal PE-function than the one used in this report. However, even the present results show that earlier conclusions regarding ionic bonding [25] find ample confirmation from spectroscopic data.

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