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 H2, HF, LiH, Li2 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 2rē, the agreement with RKR-curves is even better than for Morse’s curve, also for the “covalent” molecules H2 and Li2. Calculated spectroscopical constants 2ē and ωēx 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 conflict 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 H2 and especially for Li2. 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 apparent than real.

Introduction

Theoretical calculations of the spectroscopical behaviour of simple molecules, such as H2 [1], are in nearly perfect agreement with experiment [2], especially around the equilibrium distance rē. 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 H2. 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 rē. So strictly spoken, there seems to be no obvious reason why the wave equation to be solved, with similar results [7, 9]. Both are also very similar generalizations of the fundamental oscillator function, as readily inspected if β = 1/rē and n = 1. Both generalizing parameters are related through n = β rē. 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, results of such procedure are presented in this report for five molecules H2, HF, LiH, LiF and Li2, 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]

\[ U(r) = U_0 \left(1 - e^{-\beta (r-r_0)}\right)^2 \]  

(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:

\[ U(r) = U_0 \left(1 - (r_0/r)^n\right)^2 \]  

(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 function, as readily inspected if β = 1/rē and n = 1. Both generalizing parameters are related through n = β rē. 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, results of such procedure are presented in this report for five molecules H2, HF, LiH, LiF and Li2, varying from homonuclear to very ionic.

Reprint requests to Dr. G. Van Hooydonk, Centrale Bibliothek, Rijksuniversiteit te Gent, Rozier 9, B-9000 Gent (Belgium).
the contrary, a Kratzer-like potential has interesting peculiarities, 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

\[
E(x) = (1 - (1/x)^n)^2,
\]

where the minimum in the PE curve lies invariantly at \( x = 1 \) and \( E(x) \) varies between 0 and 1 for \( r_e \leq r \leq \infty \), and between \( \infty \) and 0 for \( 0 \leq r \leq r_e \). 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

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

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

\[
E(\xi) \approx n^2 \xi^2/(1 + \xi)^{2n}
\]

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 \( \omega_e \) and \( \omega_e x_e \), written in terms of the Sutherland parameter \( A \) [13].

Equation (2) leads to

\[
A = n^2,
\]

\[
F = n = A^3,
\]

\[
G = 8A + 12A^3 + 4,
\]

whereas the Morse values are: \( A = (\beta r_e)^2 \), \( F = A^3 - 1 \) and \( G = 8A \). For the same \( A \)-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:

\[
A = 1, \quad F = 1, \quad G = 24,
\]

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 \( A \)-value for non-ionic dissociation processes ever found is still larger than 2 for H2 [4].

The consideration of ionic dissociation processes [5] however allows much smaller \( A \)-values for non-ionic bonds! Several \( A \)-values are then 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.](image-url)
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

\[
U_e = - (I E_A + E_{AB} - E_{B}) + \frac{1}{2} \hbar \nu_e ,
\]

and

- the ionic Sutherland parameter \( \Delta \) calculated through \( \Delta = n^2 = \frac{1}{2} k_e r_e^2 / U_e \).

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 \( H_2 \):

\[
U(r) = 141878 \left( 1 - \left( \frac{r_e}{r} \right)^{0.74887} \right)^2 , \tag{9}
\]

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 1. Experimental data on \( H_2 \), HF, LiH, Li\(_2\) and LiF.**

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<tr>
<th>Bond</th>
<th>( U_e(\text{ion}) ) cm(^{-1})</th>
<th>( U_e(\text{cov}) ) cm(^{-1})</th>
<th>( r_e(\text{Å}) )</th>
<th>( \Delta^{1/2} )</th>
<th>( \beta(\text{Å}^{-1}) )</th>
<th>( \omega_e ) cm(^{-1})</th>
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**Table 2. Potential energy curve for the ground state of \( H_2^a \) \( (U(r) \) in cm\(^{-1}\), \( r \) in Å).**

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

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

a Experimental RKR:
S. Weissman,
J. T. Vanderslice, and
Results

Vibrational levels, calculated with (1) and (2), are compared with experimental ones for $\text{H}_2$, $\text{HF}$, 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-

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

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Mean deviations: Hellman 2.26%; Morse 2.08%; ion 2.60%

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Mean deviation for all $U(r)$ values: Morse 8.55%; ion 4.89%

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

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

Table 5. Potential energy curve for the ground state of Li$_2$ (U(r) in cm$^{-1}$, r in Å, balance in %).

Mean deviation for all $U(r)$ values: Morse 8.55%; ion 4.89%


$^b$ Balance for the ,,ionic" levels, calculated as 100 (1 — ($U(r_{\text{min}})$ — $U(r_{\text{max}})$)caic/$U_{\text{exp}}$).


$^b$ Balance for the ,,ionic" levels, calculated as 100 (1 — ($U(r_{\text{min}})$ — $U(r_{\text{max}})$)caic/$U_{\text{exp}}$).
Table 6. Potential energy curve for the ground state of LiF (U(r) in cm⁻¹, r in Å).

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*Pade approximant PE curve:
K. D. Jordan, J. L. Kinsey, and R. Silbey,

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 A¹/². A detail of this figure is

<table>
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Mean deviations 12.2% 30.8% 10.6% 19.7%

*See ref. [4] for the definition of F and G: F exp = xₑ oₑ/6 Bₑ and G exp = μ rₑ² oₑ xₑ/2.1078 · 10⁻¹⁶.

Fig. 2. Observed and calculated PE-curves for H₂ (only the vibrational levels are shown).

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

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

Graphical comparisons are made in Figures 2–6.
Fig. 5. Observed and calculated PE-curves for Li₂.

Fig. 6. Comparison of three calculated PE-curves for LiF. The curves "ion" and "Pade" are bound to ionic dissociation, Morse's to atomic.

Fig. 7. Plot of different reduced PE-curves for different values of $A^{1/2}$. 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 expectation 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 $r > 2r_e$, 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 hydrides [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 height 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 is not 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

\[ U(\xi) = a_0 \xi^2 \left[ 1 - a_1 \xi + (a_1^2 - a_2) \xi^2 \right]^{-1} \]

and is evaluated by means of the Dunham coefficients \(a_n\) and the equilibrium distance \(r_0\) 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.

\( \text{Li}_2 \) (Fig. 5, Table 5)

A good approximation of the Kratzer potential can be expected "a priori" for \( \text{Li}_2 \), 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 \( \text{Li}_2 \), 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 \( \text{Li}_2 \), 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 \( r_0 \) 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 \( \text{Li}_2 \) 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 \( U(r_{\text{max}}) - U(r_{\text{min}})_{\text{calc}}/U_{\text{exp}} \) for each vibrational level. Deviations from a maximum of 100\(^\circ\) balance are given in Table 5. The worst situation is found in the highest vibrational level considered, where the balance is still over 97\(^\circ\). 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 \( \text{H}_2 \) 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 \( \omega_n \) and \( \omega_n x_n \), 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 highly 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 \( \text{H}_2 \) 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

\[ E(x) = (1 - (1/x)A^{1/2})^2 \]

for different values of \( A^{1/2} \) 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 $A^{1/2}$ 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 $A$-values, non-ionic ones have small $A$-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 $A^{1/2}$-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 ionic dissociation.

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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 straightforward matter.

For instance, if $U_1 = U_e - D_{AB}$, 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

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

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

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

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

$$V = -2A/r^n + B/r^{-n}$$

(13)

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

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

(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

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

(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 \( \text{H}_2 \) 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 worthwhile to continue the search for a better universal PE-function than the one used in this report. However, even the present

7. P. M. Morse, Phys. Rev. 34, 57 (1929).
22. The ionic approximation offers a reasonable explanation for the fact that \( U_e \)-values can be calculated with a rather high degree of precision by a Padé-approximant function [3].
25. G. Van Hooydonk, Z. Naturforsch. 28a, 1836 (1973) and subsequent papers in that journal.
27. G. Van Hooydonk, unpublished results.
30. The possibility of multiple maxima and minima is not excluded, see f.i. A. G. Gaydon, in Ref. [16].