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Reduced *ab initio* theoretical internuclear potentials of diatomic molecules*

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Ab initio theoretical ground state potentials of diatomic molecules calculated with the use of the variational CI-MO (configuration interaction method based on molecular orbitals) are analyzed with the use of the RPC (reduced potential curve) method. It is shown on a series of examples that the following statement is true even for inaccurate *ab initio* calculations: in reduced form, the theoretical potential coincides to a high degree of accuracy with the reduced RKR (Rydberg-Klein-Rees) potential calculated from the spectroscopic data. Thus, with the use of the RPC method, even inaccurate *ab initio* calculations (in particular for heavier molecules) may be used for the construction of rather accurate internuclear potentials and hence obtain a practical significance. The statement also holds for excited states if strong perturbations are not present.

Key words: Diatomic molecules — Potential (internuclear) — Reduced potential curves

1. The RPC (reduced potential curve) method and its application

All fundamental concepts of molecular spectroscopy are based on the adiabatic approximation [1] and the concept of internuclear potential. Therefore, the study of molecular internuclear potentials is of fundamental interest. In this paper, we concentrate on the simplest case, i.e. the diatomic molecules. The number of diatomic systems including ions is of the order 10^4 and, for every molecule, a number of electronic states exist (ground and excited states). The potential curves for various molecules and the values of the corresponding molecular constants

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

are very diversified so that the study of molecular potentials rather reminds of a walk through a jungle. The method of reduced potential curve (RPC) [2] was conceived to permit a systematic comparative study of internuclear potentials of diatomic molecules in a unique scheme and thus facilitate the study of this rather complex domain. In this scheme, the potentials are expressed in the "reduced" form, i.e. in terms of dimensionless quantities: reduced energy, u, and reduced internuclear distance ρ. These quantities are defined by the following equations:

$$u = U/D_e, \tag{1}$$

$$\rho = \frac{r - [1 - \exp(-r/\rho_{ij})]\rho_{ij}}{r_e - [1 - \exp(-r/\rho_{ij})]\rho_{ij}} \tag{2}$$

$$\rho_{ij} = \frac{r_e - (\kappa D_e/k_e)^{1/2}}{1 - \exp(-r_e/\rho_{ij})}, \qquad \kappa = 3.96, \tag{3}$$

$$k_e = (d^2U/dr^2)_{r=r_2}. \tag{4}$$

For practical reasons, ρ vs $(u+1)$ is plotted in the figures (both quantities positive).

In the present paper, we shall deal only with the ground states. Figures 1 and 2 illustrate in a sufficiently pictorial way the meaning and significance of the RPC method: Fig. 1 shows the ground state Rydberg-Klein-Rees (RKR) potentials [3] of various molecules (calculated from spectroscopic data) where the potential curves have been moved to a common minimum in the r vs U diagram. The constants r_e and D_e of LiH were taken as units of distance and energy, respectively. Figure 2 shows the same potentials in the reduced form. Figure 1 clearly illustrates how diversified are the molecular constants and the form of the potential curves. In reduced form (Fig. 2), the potential curves of H_2, HF, LiH, CsH, Li_2, Cs_2, I_2, and Bi_2 practically coincide in the left limb and for all but the last three heavy molecules, they almost coincide also in the right limb. A crossing of the potential curves appears, for some molecules, in Fig. 1, whereas the RPCs in Fig. 2 do not cross and the ordering of the RPCs from left to right is the same in the left and the right limb (cf. Appendix A).

A systematic study of a large number of diatomic molecules has disclosed interesting regularities which we loosely call "a periodic system of diatomic molecules" (Appendix A). A warning is here in order: a superficial inspection of Fig. 1 might suggest that there already exists an ordering of the RKR potentials with respect to the force constant, which then might determine the ordering of the RPCs. This impression is, of course, false (not only because of the crossing existing in Fig. 1). This may be seen in comparing the RKR potentials of Cs_2, I_2, and Bi_2 with the corresponding RPCs in Fig. 2, where the ordering evidently is reversed in the right limb. One also observes that in spite of $\omega_e(I_2) > \omega_e(Bi_2)$ (Table 1), the RPC of I, lies to the right of the RPC of Bi_2 in Fig. 1. Moreover, whereas the ordering in Fig. 1 is different in the left and the right limb, it is the

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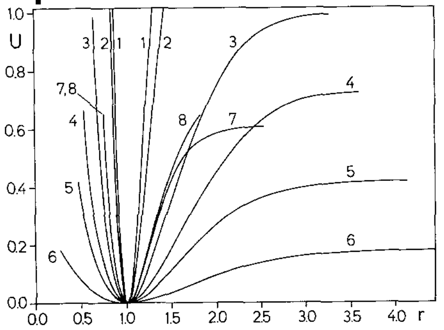

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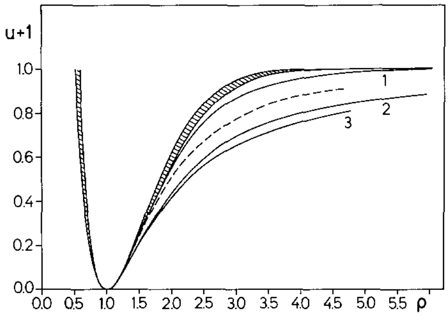

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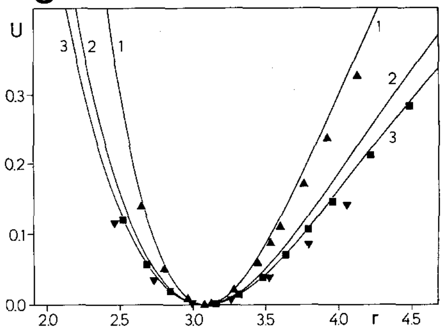

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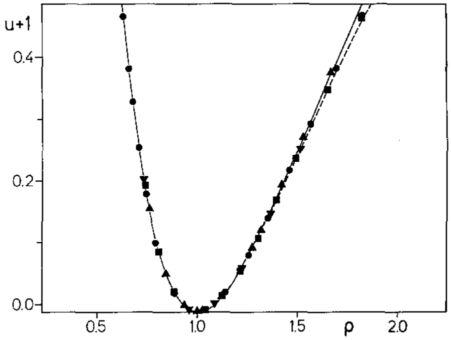


Fig. 1. RKR potentials. The values of r_e(LiH) and D_e(LiH) are taken as units of distance and energy, respectively. (References in brackets.) 1: HF [25]. 2: H_2 [25]. 3: LiH [13]. 4: CsH [22]. 5: Li_2 [35]. 6: Cs_2 [36]. 7: I_2 [37]. 8: Bi_2 [33]

Fig. 2. Reduced RKR and theoretical potentials to Fig. 1. Left limb: the hatched area contains the RPCs of H_2, HF, LiH, CsH, Li_2, Cs_2, I_2 and Bi_2 (the left and right boundary of this area are the RPCs Li_2 and Bi_2, respectively). Right limb: the *hatched area* contains the RPCs of all these molecules except Cs_2, I_2, and Bi_2. *Solid lines*: 1: Cs_2. 2: I_2. 3: Bi_2. The ordering from left to right is the same in both limbs. The RPCs do not cross anywhere. *Dashed line*: reduced theoretical potential curve of Bi_2 [32]

Fig. 3. Comparison of RKR and *ab initio* calculated theoretical potentials. 1: RKR curve of Na_2 [8]. 2: RKR curve of K_2 [9]. 3: RKR curve of Rb_2 [10]. ▲: theoretical potential of Na_2 [11]. ■: theoretical potential of K_2 [11]. ▼: theoretical potential of Rb_2 [11]. D_e (Na_2) is taken as unit of energy. Common minimum at r_e (Na_2)

Fig. 4. Reduced RKR and theoretical potentials [11] to Fig. 2. All potentials coincide in left limb in this format. Right limb: *Solid line*: reduced RKR potential of Na_2. *Dashed line*: reduced RKR potential of Rb_2. ●: reduced RKR potential of K_2. ▲: reduced theoretical potential of Na_2. ■: reduced theoretical potential of K_2. ▼: reduced theoretical potential of Rb_2. (Here and in Fig. 5, the errors in r_e or ω_e *alone* (Table 2) would lead to huge deviations, cf. Figs. 10 and 11)

same in both limbs in Fig. 2. This holds also for the lighter molecules, the RPCs of which are not explicitly shown in Fig. 2. Neither would the use of the reduced energy alone suffice to yield a reasonable scheme. For instance, $D_e(\mathrm{HF}) = 49\,383\ \mathrm{cm}^{-1}$, $D_e(\mathrm{H}_2) = 38\,297\ \mathrm{cm}^{-1}$, $\omega_e(\mathrm{HF}) = 4138.32\ \mathrm{cm}^{-1}$, $\omega_e(\mathrm{H}_2) = 4403.21\ \mathrm{cm}^{-1}$.

Hence HF is "more strongly bounded" than H_2. However, in the ordering of the RPC scheme (which corresponds to increasing atomic numbers and turns the curve to the right around the common minimum, cf. Appendix A) the RPC of HF comes after the RPC of H_2, i.e. is located nearer to the common RPC of the loosely bounded inert gases (cf. also Ref. [4]). In fact, the regularities observed in the RPC scheme are based on much more intrinsic relations [2] than just the value of a molecular constant (or constants).

The RKR (Rydberg-Klein-Rees) method [3] has now become a standard method for the calculation of the interatomic potentials from spectroscopic data. Its goodness may be verified in calculating back the energy levels from the RKR potential and comparing them with the experimental values. The potential may then be corrected by an iterative procedure like the IPA method [5]. Unfortunately, for many molecules, only the lower part of the potential well may be obtained. E.g. also for the simple and common molecules N_2 and O_2, the RKR potential could be constructed only up to about 50–60% of the depth of the minimum, D_e. For heavier molecules, the situation is still much worse, since the distance between the energy levels is smaller. Thus only a very small portion of the potential can be constructed from the experimental data, unless special methods of laser spectroscopy may be used in a particular case.

On the other hand, theoretical *ab initio* calculation of the interatomic potential for the all-electrons problem is a terrible task even for modern efficient computers. This has led to several simplified approximate methods (e.g. the method of effective atomic potentials, pseudopotentials etc.), however, for heavier molecules the errors in the calculated potentials and the molecular constants r_e, k_e, D_e etc. are still large, so that such calculations may rather be used only for a qualitative discussion, like the overall scheme of excited state potentials etc.

In Jenč's PhD Thesis and the subsequent publications [6] also *ab initio* calculated theoretical potentials of some diatomic molecules (including *ab initio* calculations of the author) were evaluated and the following hypothesis was formulated and demonstrated on a few examples (cf. also Ref. [2]):

The *ab initio* theoretical interatomic potential of a diatomic molecule calculated on the basis of the Raleigh-Ritz variational principle with the use of the CI-MO (configuration interaction method based on molecular orbitals) coincides in reduced form to high accuracy with the reduced RKR potential of the same molecule even if large errors in the molecular constants r_e, k_e, and D_e exist, if an approximation of at least about 75–80% is obtained for D_e and a sufficiently extended number of configurations is taken to take account of electron correlation. It was expected that, for heavier molecules, this hypothesis could hold also for pseudopotential calculations if account is taken of the electron correlation and of polarization in an adequate way. SCF calculations, which yield an essentially incorrect asymptotic behaviour of the potential, or too inaccurate simplified calculations do not yield any reasonable results and cannot be employed for the application of the RPC method [2, 6].

The meaning of this hypothesis is the following: although the variational method is not sufficiently accurate to yield correct values of the molecular constants, it still *reflects the fundamental structure of the physical problem.* This seems to be an important result, since from the point of view of the theory, the structure of the problem is more interesting than the values of individual constants.

Our hypothesis then leads to an interesting practical application of the RPC method. As a consequence of the hypothesis formulated above, even rather poor approximations could be used for a much more accurate determination of the internuclear potential as follows: Since, in reduced form, the RKR (IPA) potential and the theoretical potential practically coincide, one may obtain a very good approximation of the true potential if the experimental values of the constants r_e, k_e, and D_e are known. First, the reduced potential is calculated from the *ab initio* potential; the true potential is then calculated from this reduced potential inverting the RPC formulas with the use of the experimental values of r_e, k_e, and D_e. It may be obtained from the experimental data using the Dunham formula

$$k_e = 4\pi^2 c^2 \mu \omega_e^2 \tag{5}$$

which is commonly employed in molecular spectroscopy and in most cases (at least for the ground states) indeed represents a very accurate approximation. (Here μ is the reduced mass, c is the velocity of light, and ω_e is the "harmonic" spectroscopic vibrational constant.) Thus also *inaccurate* theoretical potentials could serve for a rather accurate approximation of the true potential and hence be of *practical use*, which certainly is an interesting application of the RPC method. It may also be used to extend RKR potentials from the bottom of the well to a wider range.

There has been a lot of scepticism about this hypothesis (including the author). However, it seems that, in general case, this hypothesis holds indeed which we would like to demonstrate in this paper on a series of examples, including heavier molecules. Problems connected with the calculation of theoretical values of the molecular constants r_e, k_e, and D_e, corresponding to the *ab initio* potentials, are discussed in Appendix B.

2. Results and discussion

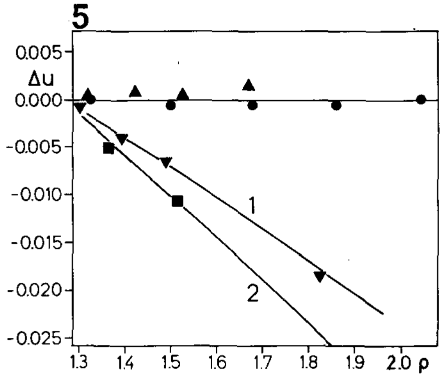
The RPC method is a graphical method, hence this paper must necessarily contain many figures. To keep the number of figures in reasonable limits, we can only show a certain choice of the material available, which we hope will nevertheless be sufficient to make our hypothesis plausible. It would be desirable to show in particular such examples, where both the RKR and the *ab initio* potential have been calculated up to the dissociation limit and where the experimental and theoretical values of the constants r_e, k_e, and D_e are known to sufficient accuracy.

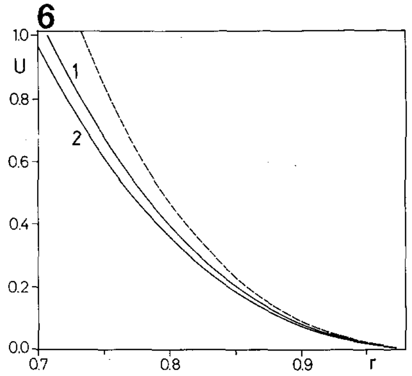
However, all these conditions are fulfilled only for a limited number of molecules [7]. Therefore, we show also examples where the potentials were calculated only in the lower portion of the potential well, which, however, nonetheless seem illustrative. Experimental values of the molecular constants are in Table 1. Figure 3 shows the RKR potentials of Na_2, K_2, and Rb_2 [8–10] and *ab initio* calculated potentials of these molecules [11]. The discrepancies are evidently large. Figure 4 shows the same potentials in reduced form. In the left limb, the differences between the RPCs are so small that they cannot be shown in this format. The coincidence of the reduced *ab initio* potentials with the reduced RKR potentials is also clearly seen in the right limb. The difference curves in Fig. 5 prove that this coincidence is, indeed, very accurate. One might, of course, suspect that more significant deviations could exist in the upper portion of the potential. Therefore, for comparison, Fig. 5 contains also the reduced theoretical potential of Na_2 corresponding to the *ab initio* potential of [12] which coincides here very accurately with the reduced RKR potential of Na_2. In [12] the potential of Na_2 was calculated in a very wide range of the internuclear distance, so that we can make a comparison of the whole potential curves of this molecule in Figs. 6–9 and discuss some interesting points in this context. Figures 6 and 7 show the RKR potential and the *ab initio* calculated potential of Na_2 of [12] in the left and right limb, respectively. The discrepancy is evidently again large. In both figures, the Morse potential function calculated with the experimental values of the molecular constants is also shown. As is well known, the Morse function is a rather poor approximation for most molecules (even the Hulburt–Hirschfelder potential function yields only a rather poor approximation [2]). Figures 8 and 9 show the same potentials in reduced form. Whereas the Morse potential, of course, still represents a very poor approximation, a very accurate coincidence

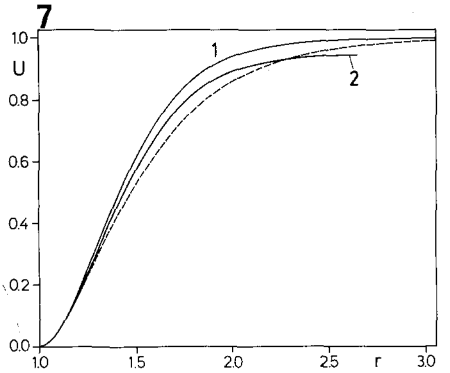
Table 1. Experimental values of molecular constants

Molecule	r_e(Å)	Ref.	ω_e(cm^{-1})	Ref.	D_e(cm^{-1})	Ref.
HF	0.91681	[40]	4138.32	[40]	49 383	[40]
H_2	0.74144	[40]	4403.21	[40]	38 297	[40]
OH	0.96966	[23]	3737.76	[23]	37 274	[40]
LiH	1.59558	[13]	1405.44	[13]	20 288	[13]
NaH	1.8890	[15]	1176.10	[15]	16 000[a]	[41]
KH	2.2401	[20]	986.65	[20]	14 776	[20]
RbH	2.3673	[21]	937.19	[21]	14 500[a]	[41]
CsH	2.4938	[40]	891.00	[42]	14 805	[22 (b)]
Li_2	2.67324	[35]	351.390	[35]	8516.78	[35]
Na_2	3.07908	[8]	159.177	[8]	6022.6	[8]
K_2	3.92443	[9]	92.3994	[9]	4440	[43]
Rb_2	4.20990	[10]	57.7810	[10]	3950[a]	[44]
Cs_2	4.64800	[21]	42.0203	[21]	3649.5	[21]
NaK	3.49680	[23(a)]	124.0124	[23(a)]	5274.9	[23(a)]
I_2	2.6655	[37]	214.5481	[37]	12 548	[37]
Bi_2	2.6609	[33]	173.062	[33]	16 407	[33]

[a] These values are not known with absolute certainty







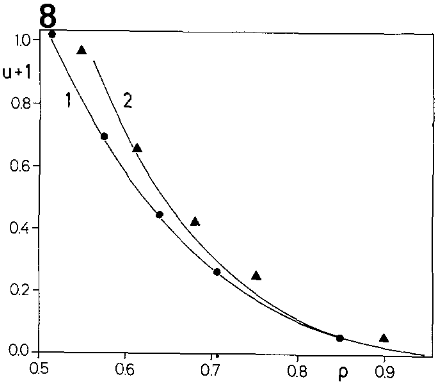


Fig. 5. Difference curves to Fig. 4. Differences in u from the reduced RKR curve of Na_2 (zero line) in the right limb. 1: reduced RKR potential of K_2. 2: reduced RKR potential of Rb_2. ●: reduced theoretical potential of Na_2 [12]. ▲: reduced theoretical potential of Na_2 [11]. ▼: reduced theoretical potential of K_2 [11]. ■: reduced theoretical potential of Rb_2 [11]

Fig. 6. RKR and theoretical potentials of Na_2 (left limbs). *Solid lines*: 1: RKR potential [8]. 2: theoretical potential [12]. *Dashed line*: Morse function (experimental values of molecular constants). Experimental values of $r_e(Na_2)$ and $D_e(Na_2)$ are taken as units for distance and energy, respectively. The r-scale is about seven times more sensitive than in Fig. 7. (Curves shifted to common minimum)

Fig. 7. RKR and theoretical potentials of Na_2 (right limbs). *Solid lines*: 1: RKR potential [8]. 2: theoretical potential [12]: *Dashed line*: Morse function. (cf. text to Fig. 6)

Fig. 8. Na_2. Reduced RKR and theoretical potentials to Fig. 6 (left limbs). 1: reduced RKR potential. 2: reduced Morse potential. ●: reduced theoretical potential [12]. ▲: reduced theoretical potential, where the experimental values of the molecular constants were used in Eqs. (1) to (3). The ρ-scale is about 8.5 times more sensitive than in Fig. 9

of the reduced RKR and the reduced *ab initio* potential is observed. Figures 8 and 9 also contain the reduced *ab initio* potential calculated not with the corresponding theoretical values of the molecular constants but with their experimental values, which now leads to a very large deviation from the reduced RKR potential. (For theoretical values of the molecular constants cf. Table 2.) Difference curves corresponds to Figs. 8 and 9 are shown in Figs. 10 and 11 for a wide range of internuclear distance and energy and prove the very close coincidence of the

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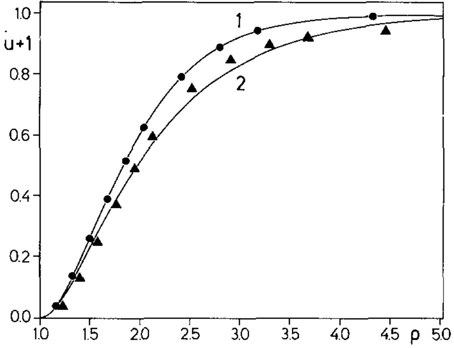

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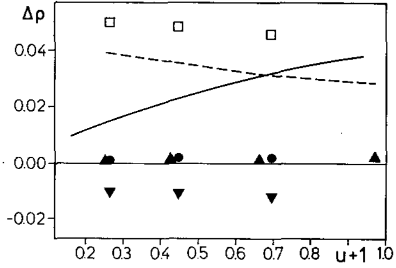

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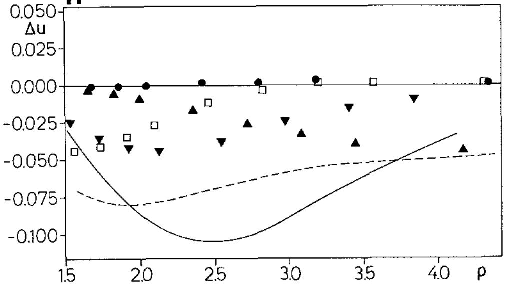

Fig. 9. Na_2. Reduced RKR and theoretical potentials to Fig. 7 (right limbs). 1: reduced RKR potential. 2: reduced Morse potential. ●: reduced theoretical potential [12]. ▲: reduced theoretical potential, where the experimental values of the molecular constants were taken in Eqs. (1) to (3)

Fig. 10. Na_2. Difference curves to Fig. 8. Differences in ρ from the reduced RKR potential (zero line) in the left limb. *Solid line*: reduced Morse potential. ●: reduced theoretical potential [12]. *Dashed line*: reduced theoretical potential where the experimental values of the molecular constants were taken in Eqs. (1) to (3). □: reduced theoretical potential with experimental value of r_e. ▼: reduced theoretical potential with experimental value of ω_e. ▲: reduced theoretical potential with experimental value of D_e

Fig. 11. Na_2. Difference curves to Fig. 9. Differences in u from the reduced RKR curve of Na_2 (zero line), right limb. *Solid line*: reduced Morse potential. ●: reduced theoretical potential [12]. *Dashed line*: reduced theoretical potential, where the experimental values of the molecular constants r_e, ω_e, and D_e were taken in Eqs. (1) to (3). ▼: reduced theoretical potential with experimental value of r_e. □: reduced theoretical potential with experimental value of ω_e. ▲: reduced theoretical potential with experimental value of D_e

RKR and *ab initio* potentials in reduced form in the whole range. At the same time, we also show in Figs. 10 and 11 the deviations which arise if the experimental value is used only for one of the three molecular constants, to characterize the influence of the various constants. Figures 8–11 clearly show that the coincidence of the RKR and the *ab initio* potential in reduced form is not due to a compensation of errors in the constants; rather the molecular constants corresponding to

Table 2. Theoretical values of the molecular constants in % of the experimental values[a]

Molecules	Ref.	r_e	ω_e[b]	D_e
HF	[26(GVB+1+2)]	100.38	100.25	93.45
HF	[26(GVB)]	99.99	99.72	79.92
HF	[27]	99.98	99.64	99.96
H_2	[25]	99.997	100.03	99.99
OH	[24(a)]	99.85	100.09	95.92
OH	[24(b)]	100.05	100.81	98.07
OH	[24(c)]	100.32	98.83	96.48
OH	[24(d)]	100.48	98.19	96.73
OH	[24(e)]	100.16	100.09	93.99
LiH	[15]	100.20	99.68	98.44
LiH	[16]	98.63	98.19	93.00
LiH	[17]	102.42	94.03	86.56
NaH	[18]	99.66	99.74	96.90[c]
NaH	[16]	98.54	99.48	95.29[c]
NaH	[17]	101.48	95.60	90.06[c]
NaH	[19]	100.04	99.61	99.29[c]
KH	[16]	99.09	100.44	98.05
KH	[19]	100.76	99.02	98.39
RbH	[16]	97.09	100.94	98.56[c]
RbH	[19]	101.31	97.14	105.52[c]
CsH	[16]	101.72	100.62	103.85
CsH	[17]	111.44	84.59	85.62
Na_2	[11]	103.45	94.05	93.33
Na_2	[12]	103.11	95.25	95.06
K_2	[11]	105.84	90.75	89.42
Rb_2	[11]	108.81	87.39	91.58

[a] Experimental values of the molecular constants for NaK^+, $NaRb^+$, KRb^+, and Li_2^+ are not known

[b] Theoretical value of ω_e is here calculated from k_e (cf. Appendix B) using Eq. (5)

[c] The experimental value of D_e is here not known with certainty

the theoretical *ab initio* potential have exactly such values that the differences between the RKR and the *ab initio* potentials shown in Figs. 6 and 7 compensate in the reduced form. Since, in the RPC scheme, some fundamental regularities in the potentials of diatomic molecules appear (depending on the fundamental parameters of the problem, namely, the atomic numbers Z_1 and Z_2 and the number of electrons n, where $n = Z_1 + Z_2$ for neutral molecules), we may say that the inaccurate approximate variational method still *preserves the fundamental structure of the physical problem.* The comparison with the Morse function in Figs. 6–9 certainly demonstrates quite convincingly that the degree of approximation of the potential obtained with the use of the RPC method cannot be challenged by any "empirical" potential function. (This also holds for the application of the RPC method where the potential of a molecule is calculated from RKR potential of another molecule of a group of affiliated molecules, cf. [2].)

Figures 12 and 13 show the RKR potentials of LiH and NaH ([13] and [14](a) and *ab initio* theoretical potentials calculated by different authors ([15–17] and [16–19], respectively), where quite different degree of approximation was obtained for the molecular constants in different papers (cf. Table 2). Figures 14 and 15 show the same potentials in reduced form. Whereas, in particular in Fig. 13, large discrepancies exist between the RKR potential and some of the theoretical potentials, these discrepancies again disappear in reduced form for all potentials.

Figure 16 shows the left limbs of the RKR potentials of KH, RbH, and CsH ([20, 21 and 22], respectively) and the *ab initio* potentials of these molecules calculated by different authors ([16, 19] for KH and RbH, and [16, 17] for CsH). The values of the molecular constants are in Table 2. Figures 17 and 18 show the same potentials in reduced form. An SCF basis of molecular orbitals was used in [19] and the potential curves do not have the correct asymptotical behavior (towards the dissociation products). We still use the values of D_e corresponding to the asymptotics of the curve (Table 2), since this value is consistent with its geometry (cf. the text below). Again a very good coincidence is obtained in reduced form, with the exception of the calculation of Karo et al. [17] for the heavy molecule CsH, where also only a poor approximation of D_e was obtained; in this case, the degree of approximation was not sufficient (relativistic effects were not included). In particular, the correlation effects probably were not adequately represented (cf. [17]). However, as may be seen in Figs. 17 and 18, the pseudopotential calculation of [16] seems to represent the core electron correlation adequately. In way of illustration, we also show in Fig. 18 the reduced *ab initio* potential of RbH of [19] calculated not with the value of D_e corresponding to the asymptotics of the potential curve but with the D_e value calculated by the authors for separated atoms (in this case, the two values do not agree). A deviation in the upper portion of the RPC then necessarily results, since the D_e value is not consistent with the geometry of the potential curve (cf. Appendix B).

The examples discussed above seem, indeed, to confirm our hypothesis which holds also in other cases not shown here. Hence the application of the RPC method for an acceptable approximation of internuclear potentials from *even rather inaccurate ab initio* potentials seems to be justified.

It is, however, to be noted that even quite accurate *ab initio* calculations are not accurate enough to reproduce correctly the regularities of the (very sensitive) RPC scheme. Figure 19 shows a comparison of the RKR potential of OH (from [23]) with five different *ab initio* calculated rather accurate potentials [24]. The values of the molecular constants are in Table 2. The differences are almost imperceptible in the current format of Fig. 19. However, the diperence curves of Fig. 20 reveal differences which are larger than the differences of reduced RKR potentials within a group of afflliated molecules (here nonmetallic hydrides). Unfortunately, there are evidently slight errors in the RKR potential of OH (possibly also in the experimental value of D_e (OH)) [4], since the RPC of OH

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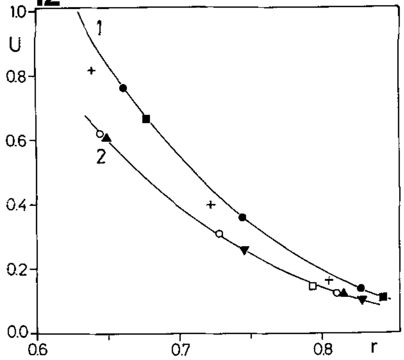

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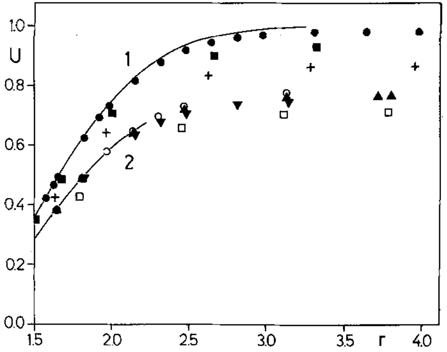

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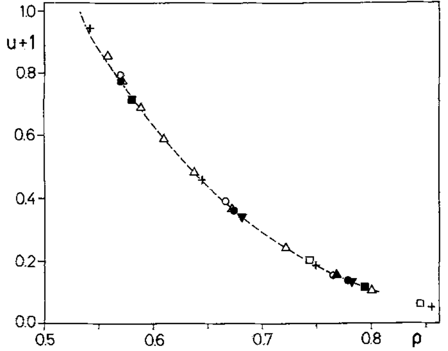

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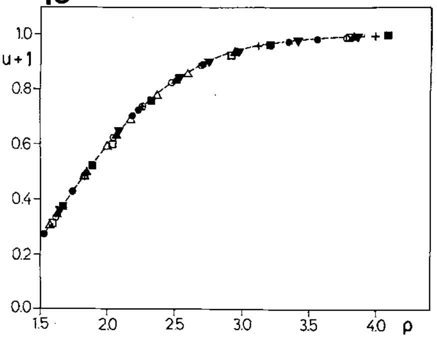

Fig. 12. RKR and theoretical potentials (left limbs). 1: RKR potential of LiH [13]. 2: RKR potential of NaH [14]. Theoretical potentials: ●: LiH [15]. ■: LiH [16]. +: LiH [17]. ▲: NaH [18]. ▼: NaH [16]. □: NaH [17]. O: NaH [19]. Experimental values of r_e (LiH) and D_e (LiH) are taken as units for distance and energy, respectively. The r-scale is about nine times more sensitive than in Fig. 13. (Curves shifted to common minimum)

Fig. 13. RKR and theoretical potentials (right limbs). 1: RKR potential of LiH [13]. 2: RKR potential of NaH [14]. Theoretical potentials: ●: LiH [15]. ■: LiH [16]. +: LiH [17]. ▲: NaH [18]. ▼: NaH [16]. □: NaH [17]. O: NaH [19] (cf. text to Fig. 12)

Fig. 14. Reduced potentials to Fig. 12 (left limbs). *Dashed line*: reduced RKR potential of LiH [13]. △: reduced RKR potential of NaH [14]. Reduced theoretical potentials: ●: LiH [15]. ■: LiH [16]. +: LiH [17]. ▲: NaH [18]. ▼: NaH [16]. □: NaH [17]. O: NaH [19]. The ρ-scale is about eight times more sensitive than in Fig. 15

Fig. 15. Reduced potentials to Fig. 13 (right limbs). *Dashed line*: reduced RKR potential of LiH [13]. △: reduced RKR potential of NaH [14]. Reduced theoretical potentials: ●: LiH [15]. ■: LiH [16]. +: LiH [17]. ▲: NaH [18]. ▼: NaH [16]. □: NaH [17]. O: NaH [19]

crosses the RPC of H_2. The probably correct form of the RPC of OH is indicated by the dashed line in Fig. 20. However, a comparison with the RPC of HF shows that the *ab initio* calculations often do not reproduce correctly the form of the potential in the upper portion of the potential well, even if they have a correct asymptotic behavior. (cf. also [4].)

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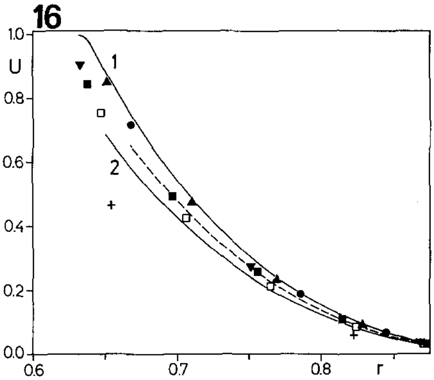

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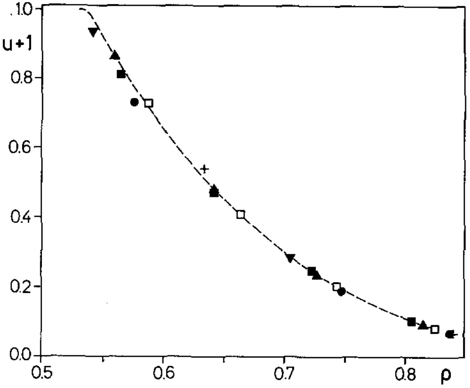

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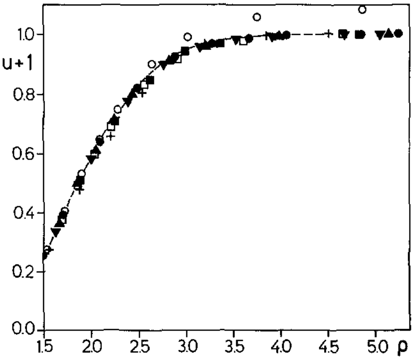

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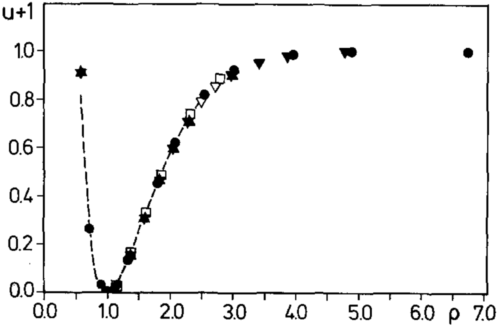


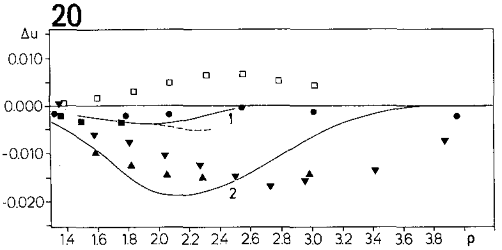
Fig. 16. RKR and theoretical potentials (left limbs). *Solid lines*: 1: RKR potential of KH [20]. 2: RKR potential of CsH [22(a)] *Dashed line*: RKR potential of RbH [21]. Theoretical potentials: ●: KH [16]. ▲: KH [19]. ▼: RbH [16]. □: RbH [19]. ■: CsH [16]. +: CsH [17]. r_e (KH) and D_e (KH) were taken as units of distance and energy, respectively (curves shifted to common minimum)

Fig. 17. Reduced potentials to Fig. 16 (left limbs). *Dashed line*: reduced RKR potential of KH [20]. Reduced theoretical potentials: ●: KH [16]. ▲: KH [19]. ▼: RbH [16]. □: RbH [19]. ■: CsH [16]. +: CsH [17]. The ρ-scale is 12.5 times more sensitive than in Fig. 18. The reduced RKR potentials of RbH and CsH of [22(a)] practically coincide with the reduced RKR potential of KH. There are slight inaccuracies in the RKR potential of CsH from [22(b)], which would be already noticeable with this ρ-scale (cf. [38])

Fig. 18. Reduced potentials to Fig. 16 (right limbs). *Dashed line*: reduced RKR potential of KH [20]. Reduced theoretical potentials: ●: KH [16]. ▲: KH [19]. ▼: RbH [16]. □: RbH [19]. ■: CsH [16]. +: CsH [17]. ○ RbH [19] for D_e corresponding to separated atoms. The reduced RKR potentials of RbH [21] and CsH [22(b)] practically coincide with the reduced RKR potential of KH in this format. In fact, the curve of CsH should lie slightly more to the right (cf. text to Fig. 17)

Fig. 19. Reduced RKR and theoretical potentials of OH. *Dashed line*: reduced RKR potential [23]. Reduced theoretical potentials (references): ●: [24(a)]. □: [24(b)]. ▲: [24(c)]. ▼: [24(d)]

Not every theoretical calculation reflects correctly the fundamental structure of the physical problem even though it may yield a very good approximation of the molecular constants. This is demonstrated in Fig. 21 on the example of the



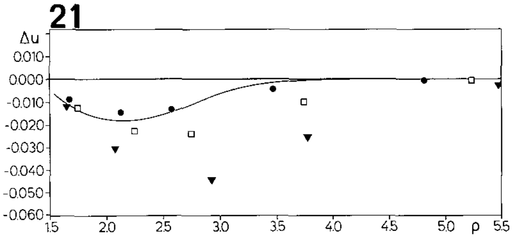


Fig. 20. Difference curves to Fig. 19 (right limbs). Differences in *u* from the reduced theoretical potential of H_2 [25] (zero line). *Solid lines*: 1: reduced RKR curve of OH [23]. 2: reduced RKR curve of HF [25]. Reduced theoretical potentials: ●: [24(a)]. □: [24(b)]. ▲: [24(c)]. ▼: [24(d)]. ■: [24(e)]. There are evidently slight errors in the RPC of OH. The *dashed line* indicates the probable correct continuation of this curve. The gap between the RPCs of OH and HF is relatively large, due to a slight anomaly of fluorine compounds (cf. Ref. 4); compare with the small gap between the RPC of H_2 and OH

Fig. 21. Difference curves for RPCs of HF (right limbs). Differences in *u* from the reduced theoretical potential of H_2 [25]. *Solid line*: reduced RKR curve of HF [25]. Reduced theoretical potentials: ▼: [27]. ●: [26] for the GVB+1+2 basis. □: [26] for the GVB method alone. The sensitivity of the *u*-scale is half of that in Fig. 20

potential of HF, where - in reduced form - the RKR potential [25] is compared with the *ab initio* CI calculations of Dunning [26] and the theoretical potential curve of Lie and Clementi [27] calculated by a semiempirical functional density method, where an excellent agreement with the experimental values was obtained for the molecular constants (cf. Table 2). Nevertheless, the deviation from the reduced RKR curve of HF is too large for the potential of [27] (the *u*-scale is twice less sensitive than in Fig. 20). On the other hand, the *ab initio* CI-calculation of [26] with the GVB+1+2 basis (cf. Table II [26]) almost coincides with the reduced RKR potential curve. The reduced *ab initio* potential calculated with the GVB method alone [26] is less accurate, however, still much more acceptable than the semiempirical potential of [27].

On the other hand, very primitive approximations, such as the one electron pseudopotential calculations are not accurate enough to reflect correctly the fundamental structure of the physical problem. This is demonstrated on the potentials calculated for the ions of alkali diatomic molecules by Valance et al.

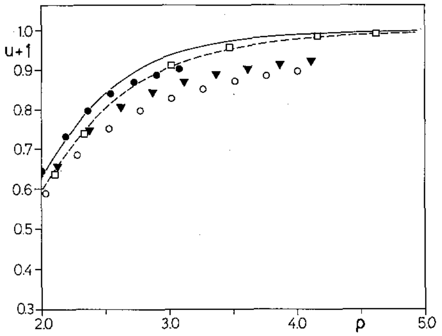


Fig. 22. Reduced RKR and theoretical potentials (right limbs). *Solid line*: reduced RKR potential of Li_2 [35]. *Dashed line*: reduced RKR potential of NaK [39]. Reduced theoretical potentials. ▼: NaK^+ [28]. ○: $NaRb^+$ [28]. ●: KRb^+ [28]. □: Li_2^+ [29]

[28]. These potential curves are evidently incorrect, as also a comparison with the theoretical *ab initio* calculated potential of Li_2^+ [29] shows. The method of Valance overestimates the D_e value; however, this alone is not the cause of the discrepancy, since this D_e value corresponds to the asymptotics and hence is consistent with the geometry of the potential curve.

In [28], only corrected D_e values obtained with the use of a correction for the electron correlation are given.. However, the corresponding potentials have not been and will not be calculated [30] and thus cannot be tested. There are a lot of papers using this method for molecular ions (cf., e.g. [31]), however, usually only the lowest portion of the potential well is calculated and, frequently, the tabulated potential has not been published. Although the method seems to give reasonable guesses of the molecular constants, it does not seem sufficiently accurate to yield a reliable potential curve.

For very heavy molecules, like, e.g. Bi_2, the all electron problem is too complicated even for modern computers. However, the method of effective potentials employed for such cases still does not yield reliable potentials, even if relativistic effects are included. This is illustrated by the reduced potential of Bi_2 corresponding to the theoretical potential of [32]. The discrepancy between this reduced potential curve and the reduced RKR potential [33] is unacceptably large (Fig. 2).

3. Conclusions

We have proved on a number of non-trivial examples (also for heavier molecules) that the statement formulated in the abstract is true. Thus even *inaccurate ab initio* calculations have a practical significance: with the use of the RPC method, one may obtain from the inaccurate *ab initio* potential a rather accurate estimate of the true potential, if the experimental values of the molecular constants r_e, ω_e, and D_e are known. This seems to be a quite interesting application of the RPC method since, for heavier molecules, the errors in the potential and in the molecular constants are still large even if quite extended theoretical calculations are made, and the knowledge of the potential is the fundamental information on the diatomic system.

Thus we have also shown that, in the framework of the RPC scheme, the configuration interaction variational method correctly reflects the fundamental structure of the physical problem (here the interatomic interaction). This property of the method (rather surprising at first sight) cannot be proved from the theory, neither with most sophisticated methods of modern mathematics. Hence, our statement has, in principle, empirical character. The same holds for the regularities of the RPC scheme, formulated in Appendix A. This "empirical" character of the method should not be a serious objection since, in reality, many methods of molecular physics have no solid theoretical (mathematical) foundations and in practice also have an empirical character. An important example is the calculation of expectation values of (in particular unbounded) observables for excited states with the use of the wave function obtained in the variational calculation (for literature cf. [34]).

Acknowledgement. The RPCs were calculated using the REDPOT program of D. Merdes. A rather violent discussion on the interpretation of quantum mechanics with Prof. Koutecký was the initiation of F. Jenč into the scientific life years ago. Together with this paper the author would like to present best wishes to the 65th birthday of Prof. Koutecký who also was a referee to the author's PhD thesis and was very interested in a proof of the hypothesis discussed in this paper. The author humbly hopes that he also will be satisfied by the justification presented here.

Appendix A

In Born-Oppenheimer approximation, the internuclear potential of a diatomic system is uniquely determined by three parameters: the two atomic numbers Z_1 and Z_2 and the number of electrons n (for neutral molecules, $n = Z_1 + Z_2$): The Coulomb repulsion of the nuclei depends only on Z_1 and Z_2, the electronic energy is obtained as the solution of the electronic Schroedinger equation (parametrized by the internuclear distance, r). The Schroedinger operator of electronic energy of different diatomics varies only according to Z_1, Z_2, and n. (In higher approximation of the adiabatic approach, the potential would also contain a small correction depending on the masses of the isotopes [1].) Therefore, in principle, any regularities existing in the family of ground state internuclear potentials of diatomic molecules might be expressed in terms of these three parameters as long as Born-Oppenheimer approximation is acceptable, which is the case for most ground states.

In the RPC scheme regularities are, indeed, observed. However, it appears that—in contradistinction to the earlier hypothesis (cf. [2]), the dependence on Z_1, Z_2, and n is rather complicated (monotonic dependence on Z_1 and Z_2 holds only as a rough rule for non-metallic molecules). The study of ground state potentials of a large number of neutral molecules revealed regularities that we loosely called "a periodic system of diatomic molecules", they may be characterized as follows: (1) By definition, the RPCs of different diatomics have a common minimum (1, 0). (2) There are groups of chemically related molecules (e.g. nonmetallic hydrides, alkali hydrides, hydrides of the IIa and IIb group, non-metallic homonuclear molecules of the fifth, sixth and seventh column of the periodic table, mercury halides etc.) in which the following rules hold: (a) the RPCs of different diatomics of the group do not intersect anywhere. (b) The shape of the RPC within the group changes with increasing atomic numbers as follows: The RPC turns to the right around the common minimum while becoming broader ("the reduced attractive force decreases"). (3) The noncrossing rule holds for all diatomics in the left limb and it also approximately holds for many molecules in the right limb. Nevertheless, *slight* crossings of the RPCs of different groups may appear in particular in the highest parts of the right limb. (4) The RPCs of the rare gases (ground states!) coincide approximately and form the right-hand boundary of the admissible RPC region in the ρ vs $(u+1)$ diagram (i.e., no ground-state RPC lies to the right of this curve.) For non-metallic molecules, the left-hand boundary of this region is formed by the RPC of H_2. (5) The differences in ρ between the RPCs are very small in the left limb, i.e., the "quasiparallel" RPCs of all diatomics lie close together in the left limb.

Molecular ions form a different scheme. The study of excited states is still more complicated [29]. For some excited states, the Born-Oppenheimer approximation (or even the adiabatic approximation) may not hold ("perturbations") so that the regular dependence on the fundamental parameters Z_1, Z_2, and n possibly may not hold quite accurately. Nevertheless, it certainly seems meaningful to compare excited states in a group of affiliated molecules, where the symmetries of the corresponding states are the same (like, e.g., the alkali diatomic molecules; for the spectral theory of Schroedinger operators including symmetry properties cf. [45]). Indeed, it appears [29] that the RPC method may be used to classify the excited states.

If not too strong perturbations are present, the hypothesis of this paper also holds for excited states [29].

Appendix B

The theoretical RPCs are calculated from the theoretical potentials with the use of formulas (1)-(3) and the theoretical values of the molecular constants r_e, k_e, and D_e. Therefore, the determination of the theoretical values of these constants accurately corresponding to the theoretical potential is essential. Since the methods frequently used for the calculation of k_e (even from expensive *ab initio* calculations) do not seem quite trustworthy, we considered this Appendix and Tables 3-6 worthwhile.

In a general case, the correct value of r_e, corresponding to the minimum of the theoretical potential may be rather accurately calculated by interpolation methods. The correct determination of D_e is a more complicated problem. The convergence of the variational CI-method depends on r, also the role of different configurations varies with r and some experience, feeling, and auxiliary tests are necessary for a satisfactory calculation (cf. [4]). When $U(r_e)$ is known, the dissociation energy may then be calculated in two ways which, in principle, should be equivalent:

(a) from the asymptotic value of the potential (value of potential energy for very large internuclear distance) or (b) from the energy of the dissociation products.

Both methods have some weak points: (a) for the reasons explained above, (b) the energy of the dissociation products should be consistently calculated "in the same approximation" as the molecular energy, however, this concept is in itself not quite exactly defined. In reality, in some cases both methods do not yield the same value of D_e; in some cases the difference is small in other cases (cf., e.g. [19]) the ~~difference is large~~. Anyway, the value of D_e calculated from the asymptotics of the potential should be preferred, since it is consistent with the geometry of the potential curve (cf. the discussion of the potential of RbH from [19] in the text and Fig. 18). Fortunately enough, the RPC method is not very sensitive to small errors in the value of D_e in the left limb and in the lower part of the right limb. It becomes highly sensitive in the upper tail of the potential curve; hence the use of theoretical potentials probably would not be meaningful for an estimation of D_e (cf. [34]).

The worst problem is the determination of the force constant k_e. One method employed is the calculation of the energy levels and the spectroscopic constants from the theoretical potential by numerical methods and calculation of k_e from $\omega_e(Y_{10})$ using Eq. (5). In many cases, only very few points of the potential are available, which makes also the application of this method somewhat dubious; moreover, if an approximate method must be used, it seems preferable to calculate k_e directly.

The k_e value is obtained in this case from interpolation, using Eq. (4). However, there is no mathematical criterion which could guarantee an accurate value of $(d^2U/dr^2)_{r=r_e}$ even if the interpolation function (polynomial) approximates the discrete points of the potential very accurately. An interpolation using three parameter "empirical" functions, like the Morse function (cf., e.g. [16]), does not seem reliable since, in a general case, these functions yield a rather poor approximation for the potential [2, 46]. In our opinion, it is necessary to use a *combined calculation* and only a *comparison of different approximative procedures* may give a certain guarantee for a reliable value of k_e. The procedure we use for the calculation of the theoretical value of k_e (and r_e and D_e at the same time) is the following (this procedure was also used in Jenč's PhD Thesis and the subsequent publications [6]): In the discrete points of the theoretical potential, we interpolate: (1) the potential function and (2) the (monotonic) electronic energy (subtracting the nuclear repulsion). These two calculations are two different numerical procedures. (3) Two different methods are used: (a) for $n+1$ points, a polynomial of degree n fitting these points is calculated and for a chosen number N of the points of the theoretical potential (in a reasonable range of r), this calculation is made for all $n < N$.

(4) For several chosen numbers N of points of the theoretical potential, the method of least squares is employed for all $n < N$. Thus four different numerical procedures are used and compared. The main criterion is the stability of the results with respect to the degree of the interpolation polynomial, n, and the agreement of the four different methods. (The depth of the minimum and the value of the mean deviation are further criteria.) It is found that, for the determination of k_e, only calculations with $N > 4$ are really meaningful: more points of the curve are needed to fix the curvature in the minimum. If no stability domain is found, or if an essential disagreement between the four different numerical procedures appears, the results cannot be trusted. However, if these criteria are fulfilled, the whole procedure is repeated including the value of r_e obtained in the first run and comparing the results; an agreement should be obtained.

The whole calculation is then parallelly repeated for a Morse potential calculated for the same r values with the theoretical values of the molecular constants (calculated from the theoretical potential), i.e., the procedure is parallelly simulated on a closely related potential function and the stability ranges and the deviations are compared. By this procedure, the discrepancies that might appear for some n or in some method may be explained and their significance cleared. This is a rather lengthy procedure, however, it seems to yield a certain guarantee for the value of the force constant, k_e. Experience shows that most reliable values of the molecular constants (in particular k_e) are obtained in the direct polynomial fitting for n between 7 and 10 (if the polynomial does not oscillate in the interesting range, which is currently checked on the monitor). The Morse function is used *only* for this auxiliary test. As an example we show a part of these calculations for the theoretical potential of KH from [16]:

It is, of course, not possible to present here all results of this voluminous calculation. Table 3 contains the interpolation without the point r_e. We show here calculations without any weighting of points to avoid the objection that the influence of some points might be practically eliminated through a small weight. The mean deviation

$$\left[1/(N-1)\cdot\sum_{i=0}^{N-1}(\Delta u)_i^2\right]^{1/2}$$

is of the order 10^{-7}–10^{-14} for the polynomial fitting and 10^{-1}–10^{3} for the least squares method. Since ω_e is always given in publications, we also show here the value of ω_e calculated from k_e with the use of Eq. (5) and not k_e itself. We do not show the calculation including r_e which gives slightly better (and more stable) results. Nevertheless, the results are quite satisfactory, the (accurate) stability range for the polynomial fitting ranges from $n = 6$ to $n = 12$. For $N = 13$, the least squares method naturally can give only for higher n accurate stable results that are in agreement with the polynomial fitting which is here $n \geq 9$. (For $N = 8$, the stability range would begin at $n = 5$.) In general the least squares method is less accurate than the polynomial fitting as a parallel calculation for the Morse function clearly proves. Better results are obtained in including r_e.

Table 4 is parallel to Table 3 and shows the same calculation for the Morse function corresponding to the values of the molecular parameters determined in the calculations of Table 3. The errors in ω_e (and r_e) resulting for small n in Table 3 are reproduced in Table 4 (though they are usually smaller for the analytic Morse function). The value of $\omega_e = 985.7$ in [16] is evidently by about 4 cm^{-1} in error.

A polynomial fitting of the Morse function for $N = 4$ including r_e gives $\omega_e = 1029$ for $n = 2$, and $\omega_e = 995$ for $n = 3$; a least squares interpolation gives $\omega_e = 960$ for $n = 2$.

A least squares interpolation of the Morse function (without r_e) gives, e.g., for $N = 6$ and $n = 3$: $\omega_e = 1004$ and for $n = 4$: $\omega_e = 994.3$. Including r_e, the values 1003 and 994.1, respectively, are obtained (corresponding results are obtained for the theoretical potential). Errors in r_e also result. This illustrates the insufficiency of calculations using too small a number of points and a low degree of the interpolation polynomial. (The next example shows that the errors may be much larger.)

This method may also be used to detect errors that are frequently found in the calculation of the force constant in many theoretical papers. In way of example we take the calculation of [32] for the Bi_2 molecule (we apologize at the same time to the authors: this certainly is no personal criticism, since such errors are frequent; we simply have to present a concrete example from a recent calculation).

In [32], nine points ($N = 9$) are interpolated using the least squares method by a polynomial of fourth degree ($n = 4$). The authors report the value of ω_e calculated from the force constant with the use of Eq. (5) as "about 170 cm^{-1}". However, this value is, in fact, by about 14% in error, as Table 5 shows—a too large error. Indeed, for the least squares method, the value $\omega_e = 168\ \mathrm{cm}^{-1}$ is obtained for $n = 4$, however, this value lies outside the stability range and the correct value is about 148 cm^{-1}. The parallel calculation for the Morse function with the value of k_e calculated with $\omega_e = 148\ \mathrm{cm}^{-1}$ clearly proves this statement, showing the same trend (though, for the analytic Morse function the results are more accurate and more stable). We would like to stipulate once more that a calculation of the force constant by a single method cannot be convincing and only a *comparative calculation yielding stable results* may guarantee a reliable result.

Table 3. Interpolation of the theoretical potential and the electronic energy of KH [16], $N = 13$ (r_e not included)

	1[a]		2[b]		3[c]		4[d]	
Polynomial order n	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})
4	2.21969	990.883	2.27618	997.292	2.22032	985.794	2.01004	1479.555
5	2.21971	990.742	2.22732	1016.923	2.21982	990.137	2.18136	801.954
6	2.21971	990.743	2.21974	991.847	2.21969	990.919	2.23477	916.172
7	2.21969	990.895	2.22028	987.259	2.21969	990.931	2.22461	986.791
8	2.21967	991.063	2.22009	987.457	2.21967	991.073	2.22038	990.714
9	2.21965	991.183	2.22019	988.204	2.21965	991.186	2.22011	988.693
10	2.21967	991.079	2.21988	990.508	2.21967	991.077	2.21987	990.471
11	2.21966	991.138	2.21966	99.917	2.21966	991.137	2.21966	989.907
12	2.21965	991.191	2.21967	990.030	2.21965	991.191	2.21967	990.003

[a] 1: polynomial fitting of the potential
[b] 2: least squares interpolation of the potential
[c] 3: polynomial fitting of the electronic energy
[d] 4: least squares interpolation of the electronic energy

Table 4. Interpolation for the Morse function for the values of internuclear distance of [16] (r_e not included) for KH[a]

	1		2		3		4	
Polynomial order n	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})
4	2.21988	991.999	2.27874	1006.810	2.22051	986.910	2.01662	1473.491
5	2.21998	991.096	2.22658	1030.787	2.22009	990.495	2.18232	822.750
6	2.22000	990.983	2.21816	1003.687	2.21998	991.158	2.23261	926.965
7	2.22000	990.997	2.21954	991.320	2.22000	991.033	2.22385	990.428
8	2.22000	990.999	2.21998	990.811	2.22000	991.008	2.22027	994.040
9	2.22000	990.999	2.22000	990.983	2.22000	991.003	2.21992	991.476
10	2.22000	991.000	2.22000	991.000	2.22000	991.001	2.21999	990.963
11	2.22000	990.999	2.22000	990.999	2.22000	990.999	2.22000	990.990
12	2.22000	990.999	2.22000	991.000	2.22000	990.999	2.22000	990.976

[a] Values of the molecular constants used: $r_e = 2.22$ Å, $\omega_e = 991.0\ \mathrm{cm}^{-1}$, $D_e = 14\,488.5\ \mathrm{cm}^{-1}$. The meaning of 1, 2, 3, and 4 as in Table 3

The molecular constants are, of course, needed also in the calculation of the RPCs from the RKR potentials. Here the same method may be employed for a verification of the validity of the approximation formula (5) (cf. [1]). The problem seems to be much worse, since, for the RKR potentials, the available points lie far from the minimum. Nevertheless, even here, the method gives very good results as the example of the RKR potential of LiH from [13] may illustrate. We have chosen the light molecule LiH, since here the points of the RKR potential lie sufficiently far from the minimum

Table 5. Determination of $\omega_e(\mathrm{cm}^{-1})$ from interpolation of the theoretical potential of Bi_2 [32] and the corresponding Morse function, $N=9(10)$

	Theoretical potential					Morse function[a]			
Polynomial order *n*	1[b]	2[c]	3[d]	4[e]	*n*	1[b]	2[c]	3[d]	4[e]
4	150.420	168.025	148.908	167.346	2	152.370	110.858	137.346	112.486
5	149.970	157.795	148.070	157.234	3	149.408	151.882	149.408	151.589
6	149.990	154.372	148.002	153.815	4	148.401	154.853	148.178	154.532
7	149.997	149.215	147.983	149.075	5	147.972	148.795	148.027	148.754
8	150.000	147.457	148.011	147.497	6	147.991	147.878	147.996	147.889
9			147.758	147.758	7	147.997	147.988	147.999	147.989
					8	148.000	148.000	147.999	148.000
					9			148.000	148.000

[a] The values of the molecular constants used: $r_e=2.788$ Å, $\omega_e=148.0\ \mathrm{cm}^{-1}$, $D_e=18\,483\ \mathrm{cm}^{-1}$

[b] 1: polynomial fitting (without r_e)

[c] 2: least squares interpolation (without r_e)

[d] 3: polynomial fitting (r_e included)

[d] 4: least squares interpolation (r_e included)

Table 6. Interpolation of the RKR potential and electronic energy of LiH [13] ($N=15$ Including r_e)[a]

	1[b]		2[c]		3[d]		4[e]	
Polynomial order *n*	r_e(Å)	$\omega_e(\mathrm{cm}^{-1})$	r_e(Å)	$\omega_e(\mathrm{cm}^{-1})$	r_e(Å)	$\omega_e(\mathrm{cm}^{-1})$	r_e(Å)	$\omega_e(\mathrm{cm}^{-1})$
4	1.59484	1408.99	1.59407	1477.18	1.59573	1404.46	1.59609	1385.49
5	1.59566	1404.05	1.59282	1415.95	1.59546	1406.04	1.59639	1403.26
6	1.59556	1405.15	1.59527	1402.50	1.59551	1405.46	1.59568	1406.95
7	1.59555	1405.24	1.59566	1404.83	1.59556	1405.10	1.59555	1406.17
8	1.59555	1405.23	1.59559	1406.06	1.59555	1405.21	1.59556	1405.99
9	1.59564	1404.34	1.59550	1406.06	1.59564	1404.36	1.59550	1405.99
10	1.59561	1404.78	1.59550	1405.22	1.59561	1404.78	1.59550	1405.21
11	1.59563	1404.53	1.59555	1404.99	1.59563	1404.53	1.59555	1404.99
12	1.59562	1404.73	1.59556	1405.10	1.59562	1404.73	1.59556	1405.10
13	1.59561	1404.88	1.59562	1404.81	1.59561	1404.88	1.59562	1404.81
14	1.59556	1405.39	1.59556	1405.36	1.59556	1405.39	1.59557	1405.33

[a] For experimental values cf. Table 1

[b] 1: polynomial fitting of the potential

[c] 2: least squares interpolation of the potential

[d] 3: polynomial fitting of the electronic energy

[e] 4: least squares interpolation of the electronic energy

($\Delta G_{1/2} = 705.8\ \mathrm{cm}^{-1}$). In Table 6, we show the calculation including the minimum point $r_e = 1.595584$ Å as given for the RKR potential in [13]. For all methods, the results are evidently, very accurate (maximal deviation from the experimental value of Y_{10} is smaller than 0.1% and hence practically irrelevant for the graphical representation of the RPC method). These results were fully confirmed by a parallel calculation for the Morse function. In this sense, the validity of the approximation (5) is verified for the ground states (it is possible that for some excited states, larger deviations might exist, in particular, if perturbations are present). The calculation without r_e is only *very* slightly worse, however, the differences are, indeed, minimal, the maximal difference in the ω_e values in the stability range being about 0.1%.

The troubles occurring most frequently in analyzing the theoretical potentials are first a frequently insufficient number of points, second a choice of points which is not suitable for the interpolation. It would be nice if the authors would pay more attention to these details of calculation which would make the value of k_e more reliable. Of couse, if, e.g. the configurations are not correctly chosen for corresponding values of r and the potential is not smooth enough, problems may occur (cf. the calculation for SH in [4]).

The interpolation of the RKR potentials is somewhat delicate for some older data where the calculation of the constants (analysis of the spectrum) was not done by the modern smoothing procedures. For the new data obtained by modern techniques and evaluated by appropriate computer methods, the method gives as a rule quite convincing results and is used for a verification of Eq. (5) in the calculation of the RPC curves from RKR potentials.

References and notes

1. Kolos W (1970) Adv Quantum Chem 5:99
2. Jenč F (1983) Adv At Mol Phys 19:265
3. For literature and a comprehensible presentation cf., e.g., Vanderslice JT, Mason EA, Maisch WG (1959) J Mol Spectrosc 3:17
4. Jenč F, Brandt BA (1987) J Chem Soc Faraday Trans 2, to appear
5. (a) Vidal CR, Scheingraber H (1977) J Mol Spectrosc 65:46; (b) Vidal CR (1986) Comments At Mol Phys 17:173
6. (a) Jenč F (1963) Collect Czech Chem Commun 28:2064; (b) Jenč F (1963) Collect Czech Chem Commun 28:2052; (c) Jenč F (1963) Collect Czech Chem Commun 29:2869
7. As explained above, reliable RKR curves up to the dissociation limit are known only for relatively few molecules. The accurate value of D_e is also frequently unknown. As for the theoretical potentials, it has now become a bad habit not to publish the tabulated potentials and present only figures in the publication. Neither is it possible to obtain these data from the authors even of recent papers in spite of much prayings. (It seems that some programs put out only the values of the molecular constants and the figures, which is good for the publication, however, not for further research.) For other calculations, reliable values of k_e and D_e cannot be determined (cf. Appendix B) or there are only very few calculated points of the potential
8. (a) Hussein K (1985) PhD Thesis. Université Claude Bernard, Lyon 1, No 06-85, Table II.6; (b) Barrow RF, Vergès J, Effantin C, Hussein K, d'Incan J (1984) Chem Phys Lett 104:179
9. Ross AJ, Crozet P, d'Incan J, Effantin C (1986) J Phys B 19:L145
10. Amiot C, Crozet P, Vergès J (1985) Chem Phys Lett 121:390
11. Partridge H, Dixon DA, Bauschlicher Jr CW, Gole JL (1983) J Chem Phys 79:1859
12. Konowalow DD, Rosenkrantz ME, Olson ML (1980) J Chem Phys 72:2612
13. Yat-Chen, Harding DR, Stwalley WC, Vidal CR (1986) J Chem Phys 85:2436
14. (a) Giroud M, Nedelec O (1980) J Chem Phys 73:4151; (b) Orth FB, Stwalley WC, Yang SC, Hsieh YH, Hsieh YK (1980) J Mol Spectrosc 79:314
15. Partridge H, Langhoff SR (1981) J Chem Phys 74:2361
16. Stevens WJ, Karo AM, Hiskes JR (1981) J Chem Phys 74:3989
17. Karo AM, Gardner MA, Hiskes JR (1978) J Chem Phys 68:1942

18. Olson RE, Liu B (1980) J Chem Phys 73:2817
19. Langhoff SR, Bauschlicher Jr. CW, Partridge H (1986) J Chem Phys 85:5158
20. Hussein K, Effantin C, d'Incan J, Vergès J, Barrow RF (1986) Chem Phys Lett 124:105
21. Hsieh YK, Yang SC, Tam AC, Verma KK, Stwalley WC (1980) J Mol Spectrosc 83:311
22. (a) Hsieh YK, Yang SC, Tam AC, Stwalley WC (1978) J Chem Phys 68:1448; (b) Yang SC (1982) J Chem Phys 77:2884; Unfortunately, the calculation for CsH by Laskowski and Stallcop (1981) J Chem Phys 74:4883 was carried out only for the right limb and cannot be used here, since the determination of a reliable value of k_e is not possible
23. (a) Foster SC (1982) PhD Thesis, Dalhousie University, Halifax; (b) Coxon A J, Foster SC (1982) Can J Phys 60:41; (c) Coxon JA, Foster SC (1982) J Mol Spectrosc 93:117
24. (a) Shih-I Chu, Yoshimine M, Liu B (1974) J Chem Phys 61:5389 (CI-method); (b) Stevens W J, Das G, Wahl AC, Krauss M, Neumann D (1974) J Chem Phys 61:3686 (OVC-method, basis IV); (c) Langhoff SR, Sink ML, Pritchard RH, Kern CW (1982) J Mol Spectrosc 96:200 (CI-method, basis $18\sigma 10\pi B\delta$); (d) Dishoeck van EF, Langhoff SR, Dalgarno A (1983) J Chem Phys 78:4552 (CI-method, basis I) (e) Meyer W, Rosmus P (1975) J Chem Phys 63:2356 (CEPA-method)
25. (a) Di Lonardo G, Douglas AE (1973) Can J Phys 51:434; (b) Huffaker JN (1977) J Mol Spectrosc 65:1. Since the RKR curve could not be calculated for very large values of the internuclear distance, we use the accurate theoretical potential of H_2 of the evaluation of the differences (cf. Kolos W (1986) J Chem Phys 84:3278). In the experimentally determined range, this curve coincides with the RKR curve of H_2 (cf. Spindler RJ (1969) J Quant Spectrosc Radiat Transfer 9:597)
26. Dunning Jr TH (1976) J Chem Phys 65:3854
27. Lie GC, Clementi E (1974) J Chem Phys 60:1275
28. Valance A, Bernier A, El Maddarsi M (1986) Chem Phys 103:151
29. Jenč F, Brandt BA, unpublished. The following reference was used for Li_2^+: Konowalow DD, Rosenkrantz MF (1979) Chem Phys Lett 61:489
30. Valance A, private communication
31. (a) von Szentpály L, Funtealba P, Preuss H, Stoll H (1982) Chem Phys 93:555; (b) Funtealba P, von Szentpály L, Stoll H, Fraschio FX, Preuss H (1983) J Mol Struct 93:213
32. Christiansen PA (1984) Chem Phys Lett 109:145
33. Effantin C, Topouzkhanian A, Figuet J, d'Incan J, Barrow RF, Vergès J (1982) J Phys B 15:3829
34. Jenč F, Brandt BA (1987) Phys Rev A, 35: 3784
35. Barakat B, Bacis R, Carrot F, Churassy S, Crozet P, Martin F, Vergès J (1986) Chem Phys 102:215
36. Weickenmaier W, Diemer U, Wahl M, Raab M, Demtröder M (1985) J Chem Phys 82:5354
37. (a) Tellinghuisen J, Keever MR, Abha Sur (1980) J Mol Spectrosc 82:225; (b) Tellinghuisen J, private communication
38. (a) Jenč F, Brandt BA (1985) J Chem Phys 83:5486; (b) Jenč F, Brandt BA (1986) J Chem Phys 85:3702
39. Ross AJ, Effantin C, d'Incan J, Barrow RF (1985) Mol Phys 56:903
40. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, constants of diatomic molecules, vol IV. van Nostrand, New York
41. Yang SC, Nelson Jr DD, Stwalley WC (1983) J Chem Phys 78:4541
42. Tam AC, Happer W (1976) J Chem Phys 64:2456
43. Ross AJ, Barrow RF, Effantin C, d'Incan J, Vergès J (1986) Indian J Phys 60B:309
44. Tsi-Ze N, San-Tsing (1937) Phys Rev 52:91
45. (a) Jörgens K, Weidman J (1973) Spectral properties of Hamiltonian operators. Springer, Berlin, Heidelberg, New York; (b) Žislin GM (1969) Izv Akad Nauk SSSR Ser Mat 33:590; (c) Žislin GM, Sigalov AG (1965) Izv Akad Nauk SSSR Ser Mat 29:835; Žislin GM, Sigalov AG (1965) Izv Akad Nauk SSSR Ser Mat 29:1261; (d) Žislin GM, Mandel EL (1969) Teor Mat Fiz 1:295
46. (a) Varshni YP (1957) Rev Mod Phys 29:664; (b) Steele D, Lippincott ER, Vanderslice JT (1962) Rev Mod Phys 34:239; (c) Spindler RJ (1965) J Quant Spectrosc Radiat Transfer 5:165
47. (a) Špirko V, Civiš S, Beran S, Čarský P, Fabian J (1985) Collect Czech Chem Commun 50:1519; (b) Špirko V, Civiš S, Ebert M, Danielis V (1986) J Mol Spectrosc 119:426

Note added in proof. The following remarks seem worthwhile: 1) The large deviations of the Morse function from the RKR potential (or, correspondingly, from the theoretical potential if theoretical molecular constants are used) suggest that a fit of the potential using Morse function cannot guarantee an accurate determination of the force constant. 2) It is interesting to note that the hypothesis discussed in the present paper (and formulted in Sect. 1) has proved efficient also in a succesful application of the RPC method to polyatomic molecules by Špirko et al. [47].