The reduced potential curve (RPC) method and its applications

F. Jenč[a]

[a] Fachbereich Physik, Philipps-Universität Marburg, Marburg, Germany

PLEASE SCROLL DOWN FOR ARTICLE

The reduced potential curve (RPC) method and its applications

by F. JENČ

Fachbereich Physik, Philipps-Universität Marburg, Renthof 7,
35032 Marburg, Germany

This paper provides a summary of the essence and the results of the author's reduced potential curve (RPC) method hitherto scattered in a large number of scientific papers, which he hopes may serve for the use and further development of this method by other interested scientists. The RPC method makes possible a systematic study of the internuclear potentials of the ground and excited states of diatomic systems in a unique RPC scheme. Interesting and so far unknown regularities and rules (laws suggested by the quantum mechanical background) appear in the RPC scheme. With the use of these 'RPC rules', the RPC formula and its parametrized generalization, the GRPC formula, may be used for various practical applications of the RPC method such as: (a) detection of (even small) errors in the potentials constructed from the spectral data or errors in the analysis of the spectrum of a diatomic system, (b) detection of errors in the values of the molecular constants, (c) detection of errors in the adiabatic potentials due to perturbations, (d) detection of anomalies, (e) estimation of the dissociation energy, (f) correction of errors in the potentials mentioned above, and (g) construction of the internuclear potential of a diatomic system and calculation of its spectrum from the spectral data of another diatomic system or from an *ab initio* calculated theoretical potential. The rules and the structure of the RPC scheme and the applications of the RPC method are demonstrated in numerous examples and further prospects are discussed.

Foreword

I first presented my formula of the reduced potential curve (RPC) defending my PhD thesis in 1962 [1]. The PhD thesis, where I compared *ab initio* and empirical potentials with the potentials calculated from spectroscopic data, was then published in three papers [2] and the study of the interesting regularities in the potentials and applications of the RPC method was continued up to 1968. The results of this period have been summarized in [3]. Being then engaged in research of a different type, I resumed the work on this subject as late as 1984, with the kind collaboration of B. A. Brandt. In the meantime, a lot of experimental work and interesting theoretical calculations had appeared suggesting further study and development of the RPC method. The work on the RPC method appeared to be quite fruitful; however, the results are scattered in a large number of papers published in different journals. I believe that my own work was just the beginning of promising research and I hope that this paper might be useful to anybody interested in the subject. In the meantime, several papers containing other definitions of a reduced potential of diatomic molecules have appeared [4]. It is not my intention to compare them with my own work, which would be difficult because of different basic conceptions and evaluations of the results and it would also lead to an impossibly bulky paper. In contradistinction to other such methods, my method is always referred to in this paper as 'the RPC method'.

References to experimental work and *ab initio* theoretical calculations may be found in the papers on the RPC method listed in the References to this paper. The only

other references given here belong to hitherto unpublished material on the RPC method or are necessary for the discussion.

The essence of the RPC method is a comparative study of the reduced potential *curves* of different molecules and states in a unified (RPC) scheme. Consequently, the results will be shown in a large number of figures.

1. Introduction
1.1. *The fundamental mathematical problem*

The number of different atoms of the elements is of the order of 10^2. The number of ground states of diatomic combinations is of the order of 10^4. Counting also excited states and different types of ions, one arrives at a figure in the order of 10^5. In contrast to the lucid periodic system of the atoms, the world of the diatomic systems represents a rather intricate jungle. Therefore, it is clear that any attempt to find an approach which would make a systematic study of diatomic systems possible would be worthwhile. As all properties of a diatomic system in a certain electronic state are determined by its internuclear potential, such an attempt entails a systematic study of the internuclear potentials of the diatomic systems.

The first attempt to find a general representation of these potentials was the idea of the 'empirical' potential functions [5]. Here the Morse function is the well-known example [6]. The idea was that the potential function $U(r)$ (where U is the energy, r is the internuclear distance) could be expressed in a unique functional form containing some molecular constants as parameters. In particular the 'geometric' constants were used: the depth of the minimum of the potential curve, D_e, the equilibrium internuclear distance, r_e, and the force constant, k_e, i.e. the second derivative of the potential at r_e. In the meantime, a large series of 'empirical' potential functions have been proposed (for reviews see [7(a), (b)], however, as is well-known, the results are rather modest. Relatively good results have recently been obtained by Zavitsas [8]).

When I started working on my PhD thesis, I was instructed by my tutor, Professor J. Pliva (who was just leaving for a two year stay with Professor G. Herzberg in Ottawa) to find some general relations for the diatomic molecules which were better than the empirical functions. Being free, and full of young enthusiasm, I began with a study of functional analysis, operator theory etc. in the hope of finding some approach to the underlying mathematical problem.

Indeed, a solution to the question mentioned above could be reduced to a solution of a mathematical problem in the theory of partial differential operators as follows:

The whole spectroscopy, its concepts, methods, and notations are based on the so-called 'adiabatic' approximation (see any textbook on quantum mechanics, and for a summary and references see Kolos [9]), in particular on the 'zero order' approximation of Born–Oppenheimer [10, 11]. The concept of the internuclear potential has proper meaning *only* in the framework of the adiabatic approximation.

In the Born–Oppenheimer approximation, the internuclear potential of a diatomic system is defined by

$$U(r) = E_{el}(r, N, Z_1, Z_2) + \frac{Z_1 Z_2}{r} \tag{1}$$

where $E_{el}(r)$ is the adiabatic electronic energy as a function of the internuclear distance r of the clamped nuclei. Z_1 and Z_2 are the atomic numbers of the two atoms, N is the

number of electrons. For a neutral molecule, $N = Z_1 + Z_2$. E_{el} is obtained as the r-dependent eigenvalue of the electronic Schrödinger operator which, as is well-known, results from the quasi-separation of the nuclear and electronic coordinates in the global Schrödinger equation of the problem. The 'ground state' of a diatomic system corresponds to the lowest electronic eigenvalue, the 'excited states' to the higher eigenvalues. The second term in equation (1) represents the Coulomb repulsion of the nuclei.

The structure of the electronic Schrödinger operator is completely analogous for all Ns, differing only in the number of variables and the number of terms in the kinetic and potential energy. Hence, from the mathematical point of view, the internuclear potential of a diatomic system is simply a function of the three fundamental parameters, N, Z_1, and Z_2. In the non-zero adiabatic approximation, a correction called the 'diagonal' term [9] should be added which would also bring in a dependence of the potential on the nuclear masses. In the majority of cases, the adiabatic approximation is very good and the 'diagonal' correction term may be omitted. (The correction for spin–orbit interaction and the relativistic correction may also be neglected in most cases, except for very large internuclear distances in some cases for the former and very heavy molecules for the latter.)

In the case of non-adiabatic perturbations, e.g. where the 'potential curves' of different electronic states of the same symmetry [5] lie close together, the adiabatic approximation is not a good one, and the concept of the internuclear potential loses its proper meaning. However, this concept and the approximation may be saved by employing 'deperturbation' procedures (with sufficient care!) if the potential is calculated from experimental (spectroscopic) data. (For a detailed account of these methods see Levebre-Brion and Field [12].)

Hence it would 'suffice' to find the dependence of $E_{el}(r, N, Z_1, Z_2)$ on the parameters N, Z_1, and Z_2 to obtain a general formulation of the diatomic problem in the Born–Oppenheimer approximation and, for the more general adiabatic approximation, the dependence on the two further parameters M_1 and M_2 (atomic masses) should also be known.

Let us recall: in the adiabatic approximation, all properties of a diatomic system are determined by its internuclear potential. In the Born–Oppenheimer approximation this potential is a function of the three parameters Z_1, Z_2, and N (and of the nuclear masses in the more general adiabatic approximation). The following interesting question now arises: does there exist a general scheme where the dependence on these fundamental molecular parameters could be visualized, in the same way as the dependence of the properties of the elements on the atomic number Z is systematically visualized in the Periodic System of Mendeleev? In particular, does there exist a scheme where some physical laws of the dependence of the *internuclear potentials* on these fundamental molecular parameters could be visualized?

I would like to emphasize that the aim of my research was primarily the search for the demonstration of such laws or regularities in the potentials.

Unfortunately, I soon found out that this problem in its generality cannot be solved by the methods of contemporary mathematics. One compares partial differential operators in functional Hilbert spaces of functions with different numbers of variables. Though all Hilbert spaces are unitarily equivalent and the spectrum of a self-adjoint operator (and all spectral properties) is an invariant of such transformations, the explicit construction of such a mapping leading to operational mathematical expressions would be a very complicated task as, for example, the

explicit construction of a Borel mapping between one- and n-dimensional Euclidean spaces (for a spectral correspondence of operators) already shows [13]. Moreover, one has here a correspondence of partial differential operators parametrized by the internuclear distance r.

Hence another indirect way had to be found, in an intuitive way, and the result was the RPC method to be discussed in this paper. However, let me first explain how the internuclear potentials are obtained. I shall deal only with systems for which the potential has a minimum.

1.2. Calculation of the internuclear potentials

The internuclear potential of a stable diatomic system (figure 1) may be calculated directly from the spectral data by the Rydberg–Klein–Rees (RKR) method [14] which has now become a standard method of spectroscopy. Although this method is in fact a Wentzel–Kramers–Brillouin–Jeffreys (WKBJ) type method [15] (i.e. a semi-classical approximation for the calculation of the 'turning points' on the potential curve for the measured vibrational energy levels), it gives surprisingly good results. For the lightest molecule, H_2, where the errors should be largest, a comparison of the RKR potential [16] with the extremely accurate ab initio calculation of Kolos et al. [17] shows practically negligible differences. In cases where the Born–Oppenheimer approximation holds, a coincidence of the RKR potential curves for isotopic molecules is found. The reliability of the RKR potential is checked by calculating back the spectrum (eigenvalues of the corresponding Schrödinger operator) by now standard methods [18]. If deviations from the measured spectrum are observed, the RKR calculation is iterated until the desired limit of error is obtained. In case of perturbations, a 'deperturbed', potential is calculated on the basis of the RKR potential [12] (see §1.1).

The accuracy of the RKR potential may be further improved by employing the Iterated Perturbation Approach (IPA) method [19] which permits a more accurate calculation, in particular of the higher portion of the potential near the dissociation limit. It is an iterative procedure which uses the RKR potential as the zero order approximation. In the framework of the adiabatic approximation, consistency with the spectroscopic data may be obtained with very high accuracy.

In cases where the spectral data do not exist or are insufficient, an ab initio theoretical calculation of the potential may be made using the well-known (variational) methods of quantum chemistry [20]. However, it has to be emphasized that, even with the use of modern computers and extended calculations, relatively large errors in the potential and the values of the molecular constants still result. It is significant that the use of the RPC method makes it possible to draw much more accurate information from such insufficiently accurate ab initio calculations if the experimental values of some molecular constants are known (see §§3.2 and 4.8).

1.3. The idea of the reduced potential curve (RPC)

The location of the potential curves of different diatomic systems and states in the r versus U diagram and their geometric form are, of course, very diversified. The original intention in the use of a 'reduced' potential was to obtain a representation of the potential curves of all diatomics by a unique potential curve (i.e. the (approximate) coincidence of all potentials) by using appropriate units for the internuclear distance
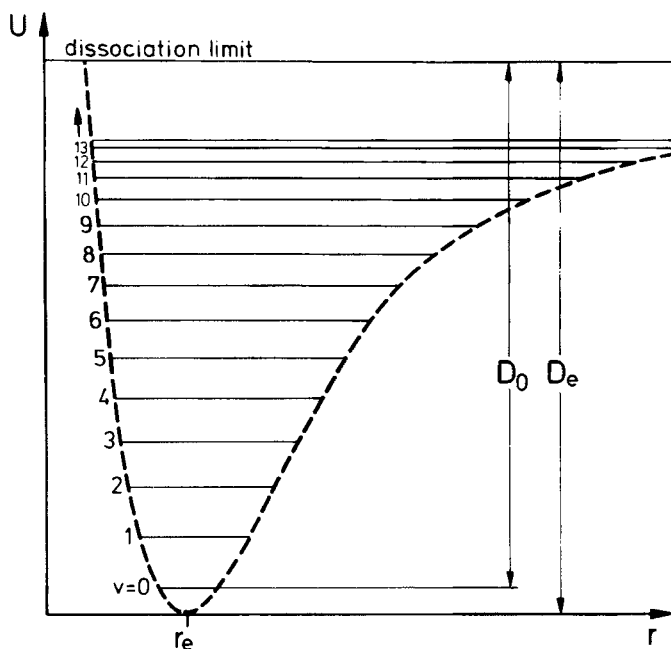
Figure 1. Typical example of a potential curve for a diatomic molecule. The horizontal lines indicate the levels of vibrational energy; r_e is the equilibrium internuclear distance; D_0 is the dissociation energy; D_e is the dissociation energy + zero point energy.

and the energy for different molecules. The natural units seem to be the coordinates of the minimum of the potential curve, i.e. the equilibrium internuclear distance, r_e, and the depth of the minimum, D_e, since the use of these molecular constants as units of r and U for different diatomics implies the coincidence of the minima and the dissociation limits of the potentials of all diatomic systems in the r versus U diagram. The reduced coordinates of the minimum are $(1, -1)$ if the zero of energy is taken at the dissociation limit. The reduced quantities are then

$$\rho = \frac{r}{r_e}, \quad u = \frac{U}{D_e}. \tag{2}$$

This natural idea of the 'reduced' potential is analogous to that of the reduced state equation of gases in thermodynamics and was first used by Puppi [21]. However, this primitive definition of the reduced potential does not by any means lead to a coincidence of the potentials of different diatomics and states. The differences are *very* large, they are in particular impossibly large in the repulsive limb. (Puppi [21] in fact also employed a different definition of the reduced internuclear distance, however, the results were no better.)

Nevertheless, it is worth noting that these reduced potential curves in principle do not intersect and there is a certain ordering with respect to the atomic numbers (different from that obtained in my RPC scheme, see below).

Frost and Musulin [22] tried to obtain smaller differences between the reduced potential curves by postulating a common 'reduced' force constant κ for all diatomics. This means, of course, that another molecular parameter has to be introduced (instead

of k_e). This parameter was denoted by ρ_{ij} (the index i and j denoting the two atoms in question) and the reduced potential was defined as follows:

$$\rho = \frac{r - \rho_{ij}}{r_e - \rho_{ij}}, \quad u = \frac{U}{D_e},$$ (3)

$$\rho_{ij} = r_e - \left(\frac{\kappa - D_e}{k_e}\right)^{1/2}, \quad \kappa = 3\cdot96.$$ (4)

(This definition is identical with that introduced later by Ferrante *et al.* [23] and Tellinghuisen *et al.* [24], see [25].)

As at that time the RKR method was still not developed, Frost and Musulin checked the validity of this definition in calculating molecular constants [22]. However, the results were not sufficiently good and they abandoned the project.

Indeed, the definition of equation (3)—which is in fact a limiting case ($\alpha \to \infty$) of my generalized reduced potential (§2.2)—does not sufficiently reduce the differences in the repulsive limb. It reduces the differences in the attractive limb but destroys completely the ordering of the potential curves which become an entangled mesh of intersecting curves, so that no regularities are observed [25].

2. The RPC and the generalized reduced potential curve (GRPC)

2.1. *The RPC formula*

I came across the paper of Frost and Musulin [22] while working on my PhD thesis in 1961. I studied the relation between the RKR and the *ab initio* potentials (which I also calculated by the CI-MO(SCF-LCAO) [20] method for some molecules [2(*b*)] and was disappointed by the still large differences between the RKR and the *ab initio* potentials and molecular constants. An appropriate definition of the reduced potential could not only mean the possibility of advancing towards a unified scheme for the study of the potentials of diatomics but also a possible means to reduce the differences between the RKR and the *ab initio* potentials. This could also make still inaccurate *ab initio* results interesting for a good approximation of the potential in cases where the spectral data were insufficient. It was clear that the definition of equation (3) was still too primitive. So I proposed a new definition of the reduced potential curve (RPC) and found that it satisfied both aims. The new definition was

$$u = U/D_e$$ (5)

$$\rho = \frac{r - [1 - \exp(-r/\rho_{ij})]\rho_{ij}}{r_e - [1 - \exp(-r/\rho_{ij})]\rho_{ij}},$$ (6)

which implies

$$\rho_{ij} = \frac{r_e - (\kappa D_e/k_e)^{1/2}}{1 - \exp(-r_e/\rho_{ij})}, \quad \kappa = 3\cdot96$$ (7)

$$k_e = (d^2U/dr^2)_{r=r_e},$$ (8)

where r_e and $-D_e$ are the coordinates of the minimum of $U(r)$.

In spectroscopy, the following approximation for k_e is currently used, which appears to be very accurate in most cases [5]:

$$k_e = \mu\omega^2 = C\mu\omega_e^2.$$ (9)

Here μ is the reduced mass of the diatomic system, ω is the 'harmonic vibration frequency' determined from the spectrum, ω_e is the 'harmonic' spectroscopic vibrational constant in cm^{-1} and the constant C depends on the choice of units for k_e.

For most cases, the approximation of equation (9) is indeed acceptable and is used in the RPC method (and checked by interpolation). ω_e is in a very good approximation equal to the Dunham coefficient Y_{10} (see Herzberg [5]). (The difference is determined by the quantity $B_e^2/4\omega_e^2$ where B_e is the 'rotational constant at r_e' [5]. For example, for NaK ($1^1\Sigma^+$), $B_e^2/4\omega_e^2 = 1\cdot47 \times 10^{-7}$.) The molecular constants r_e, D_e, and k_e are, of course, implicitly functions of Z_1, Z_2, and N.

(In the intuitive heuristics line, the value $\kappa = 3\cdot96$ followed from putting $\rho_{ij} = 0$ for H_2^+ (it does not accurately correspond to the new data) and the form of the second term in the numerator and in the denominator was considered to be related to the electronic repulsion effects.)

If we put

$$x \equiv \frac{r}{\rho_{ij}} \quad x_e \equiv \frac{r_e}{\rho_{ij}}, \tag{10}$$

we obtain from (5) the formula

$$\rho = \frac{x - 1 + \exp(-x)}{x_e - 1 + \exp(-x)}. \tag{11}$$

Hence the system parameter ρ_{ij} has in fact the function of scaling: it is the unit of length used for the internuclear distance, r, of a diatomic system if inserted into the formula of ρ. The parameter ρ_{ij} is calculated by iteration from the implicit equation (7).

For $0 \leqslant \rho_{ij} < r_e$, the reduced quantities fulfil the following conditions

$$\rho \geqslant 0$$
$$\rho = 0 \quad \text{for } r = 0$$
$$\rho = 1 \quad \text{for } r = r_e$$
$$\rho \to \infty \quad \text{for } r \to \infty$$
$$u \gtrless 0 \quad \text{for } U \gtrless 0 \tag{12}$$
$$u = 0 \quad \text{for } U = 0$$
$$u \to \infty \quad \text{for } U \to \infty$$
$$u = -1 \quad \text{for } U = -D_e$$

It is clear that these relations—which we naturally expect a reduced potential should fulfil—impose rather restrictive conditions on possible definitions of the reduced potential.

The reduced coordinates of the minimum of a potential curve are $\rho = +1$, $u = -1$ *if the zero of energy is taken at the dissociation limit*; in the figures, we always plot ρ versus $(u+1)$.

2.2. *The generalized reduced potential curve (GRPC) formula*

The definition of the reduced potential by means of equations (5) and (6) is a special case of the following more general definition of the reduced potential, the generalized reduced potential curve (GRPC) [25, 26]

$$\rho \equiv \frac{r - G(r, \rho_{ij}, \lambda_k)}{r_e - G(r, \rho_{ij}, \lambda_k)}, \tag{13}$$

$$u \equiv \frac{U}{D_e} \cdot g(r, \vartheta_n), \tag{14}$$

which implies an implicit equation for ρ_{ij}

$$G(r_e, \rho_{ij}, \lambda_k) = r_e - \left[\frac{\kappa D_e}{k_e\, g(r_e, \vartheta_n)} \right]^{1/2}, \tag{15}$$

if the minimum of the potential is chosen as the zero of energy, i.e.

$$U(r_e) = 0. \tag{16}$$

(Using the definition $U(\infty) = 0$, one obtains a slightly more complicated expression than (15).) λ_n and ϑ_n are auxiliary parameters.

With the special choice

$$G(r, \rho_{ij}, \lambda_k) = F(r, \rho_{ij}, \lambda_k)\, \rho_{ij} \tag{17}$$

equation (15) takes the form

$$\rho_{ij} = \frac{r_e - \left(\dfrac{\kappa D_e}{k_e\, g(r_e, \vartheta_n)} \right)^{1/2}}{F(r_e, \rho_{ij}, \lambda_k)}. \tag{18}$$

So far, the generalized definition of u, equation (14), has not been tested (in all previous publications we used the definition $U(\infty) = 0$).

Only a generalized definition of ρ with the choice (17) has as yet been tested, using for $F(r, \rho_{ij}, \lambda_k)$ a parametrized form of the basic RPC definition, i.e.

$$\rho = \frac{r - [f(r, \varphi_m)]^\eta \left\{ \beta - \gamma \exp\left[-\alpha \left(\dfrac{r - \xi}{\rho_{ij}} \right)^\sigma + \tau \right] \right\}^\delta \rho_{ij}}{r_e - [f(r, \varphi_m)]^\eta \left\{ \beta - \gamma \exp\left[-\alpha \left(\dfrac{r - \xi}{\rho_{ij}} \right)^\sigma + \tau \right] \right\}^\delta \rho_{ij}}, \tag{19}$$

which implies an implicit equation for ρ_{ij} in the form

$$\rho_{ij} = \frac{r_e - \left(\dfrac{\varepsilon \kappa D_e}{k_e} \right)^{1/2}}{[f(r_e, \varphi_m)]^\eta \left\{ \beta - \gamma \exp\left[-\alpha \left(\dfrac{r_e - \xi}{\rho_{ij}} \right)^\sigma + \tau \right] \right\}^\delta}, \tag{20}$$

if $\varepsilon \cdot \kappa$ is used for the reduced force constant instead of $\kappa = 3{\cdot}96$. Here, $f(r, \varphi_m)$ is a correction function which may contain further parameters, φ_m.

The GRPC is important for the applications of the RPC method described in §4, where the parameters λ_k, φ_m, and ϑ_n play the rôle of varied fitting parameters. Putting $\eta = 0$ simply switches off the correction function in the calculations.

The molecular constants r_e, D_e, and k_e may in principle also serve as fitting parameters. A change in the parameter ε is equivalent to a change in k_e and the variation of this parameter may serve to compensate for errors in the value of k_e (which is important in particular for the *ab initio* calculated values of the force constant).

The correction functions should, of course, be chosen in such a way that conditions (12) are fulfilled.

In working with the GRPC formula, one should have an idea about the effect of the change in the values of the parameters λ_k in equation (13). Figures 2–7 show the effect
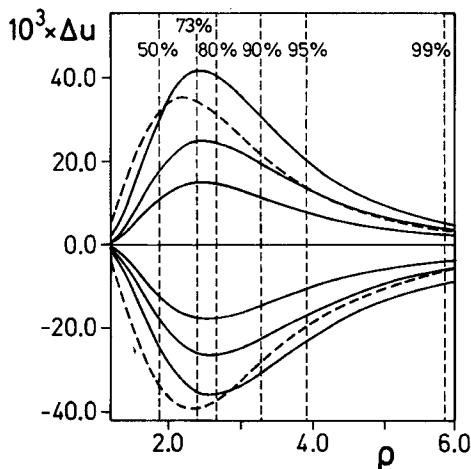
Figure 2.   Attractive limb of the ground state GRPC of Cs_2. Differences in u between the RPC and the GRPC for different values of the various parameters. Zero line: RPC. (———) from top to bottom: $\beta = 1.1$; $\alpha = 1.1$; $\xi = -0.2$; $\xi = 0.2$; $\delta = 1.1$; $\gamma = 1.1$. (- - - -) from top to bottom: $\varepsilon = 1.08$; $\varepsilon = 0.92$. The vertical lines denote the percentage of D_e (Cs_2).
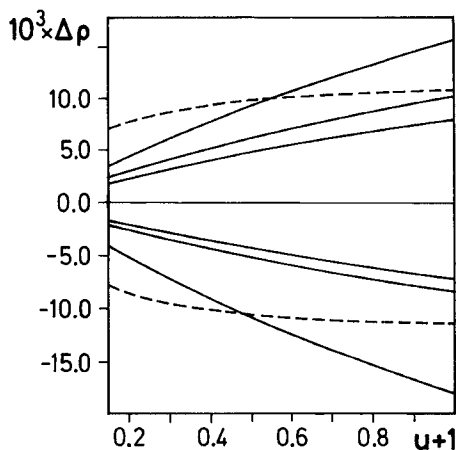

Figure 3.   Repulsive limb to figure 2. Differences in ρ. (———) from top to bottom: $\gamma = 1.1$; $\delta = 1.1$; $\xi = 0.2$; $\xi = -0.2$; $\alpha = 1.1$; $\beta = 1.1$. (- - - -) from top to bottom: $\varepsilon = 1.08$; $\varepsilon = 0.92$.

of a change in the parameters α, β, γ, δ, ε, ξ, τ, σ, and D_e in the attractive and the repulsive limb (equation (19)). An increase in the nominal value of α or β ($= 1$) turns the RPC to the right in both limbs whereas an increase in the nominal value of γ or δ ($= 1$) turns it to the left in both limbs. A corresponding decrease in the values of these parameters would turn the RPC in the opposite direction in an almost symmetric way. Negative values of α, β, or δ were not used. On the other hand, an increase in the nominal value of ε ($= 1$) must necessarily lead to a narrowing ('compression') and a decrease in ε to a broadening of the RPC (change in the 'reduced force constant'). Positive values of ξ turn the RPC to the right, negative values of ξ turn it to the left in a quite symmetric way (figures 2 and 3).
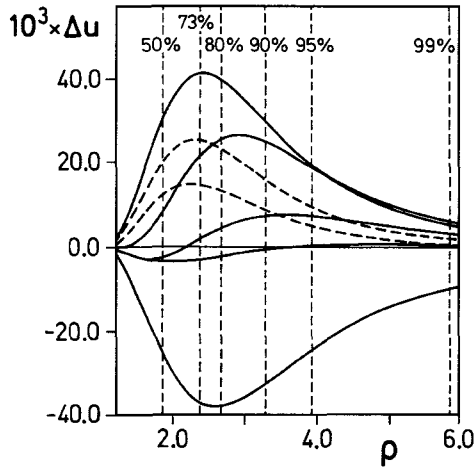
Figure 4.   The same as in figure 2 for the parameters σ and τ. (———) from top to bottom:
$\tau = -0\cdot2$; $\sigma = 1\cdot5$; $\sigma = 1\cdot3$; $\sigma = 1\cdot1$; $\tau = 0\cdot1$. (-----) from top to bottom: $\sigma = 0\cdot7$; $\sigma = 0\cdot8$.
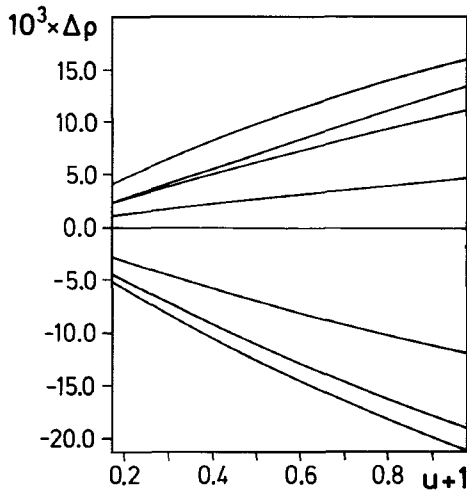
Figure 5.   The same as in figure 3 for the parameters σ and τ. (———) from top to bottom:
$\tau = 0\cdot1$; $\sigma = 1\cdot5$; $\sigma = 1\cdot3$; $\sigma = 1\cdot1$; $\sigma = 0\cdot8$; $\sigma = 0\cdot7$; $\tau = -0\cdot2$.

Positive values of τ turn the RPC to the right in both limbs, negative values turn it to the left but in a less symmetric way. The effect depends, of course, on the individual diatomic system (here shown for the ground state of Cs_2). The effect of the 'problematic' parameter σ (exponent in an exponent) is more complicated. An increase in the nominal value of σ ($= 1$) turns the RPC to the right in the left limb. It turns it first to the right in the attractive limb, then to the left after a boundary value of σ is reached. The increase in σ above a certain higher value has little effect in the attractive limb, since the exponential function then rapidly approaches zero. (The same holds, for example, for the parameter α. As already mentioned, in the limit $\alpha \to \infty$ ($\alpha = 10$ suffices), the Frost–Musulin formula results.) A decrease in the value of σ turns the RPC to the left in both limbs, up to negative values of σ (figures 4 and 5).

The effect of a change in the value of r_e and k_e was shown in [3]: the RPC is sensitive to a change of both constants in both limbs.
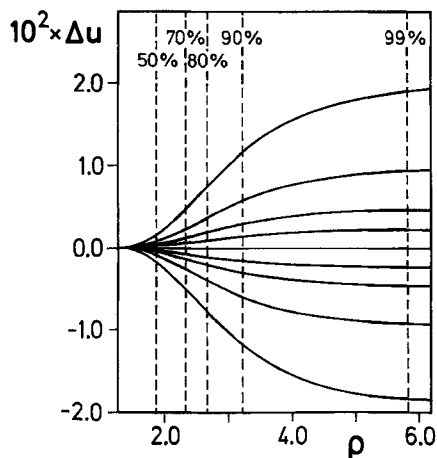
Figure 6. The same as in figure 2 for the parameter D_e. The different curves correspond to various changes in the value of D_e in % of D_e. (———) from top to bottom: -2; -1; -0.5; -0.25; 0.25; 0.5; 1; 2.
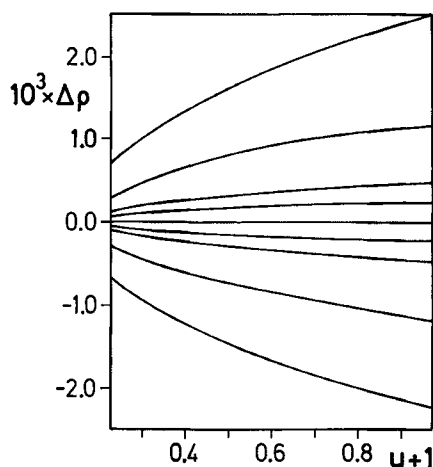
Figure 7. The same as in figure 3 for the parameter D_e. The different curves correspond to various changes in the value of D_e in % of D_e. (———) from top to bottom: -10; -5; -2; -1; 1; 2; 5; 10. The wiggles are corrected.

It is important to have in mind the effect of a change in the value of D_e in view of the applications of the RPC method (see below): up to 50 % of D_e, the RPC is rather insensitive to small changes in D_e in the attractive limb; it is, of course, very sensitive near the dissociation limit (figure 6) (which is important for the estimation of D_e, see §4.6). I shall return to these figures in discussing the applications of the RPC method in §4.

The RPC is quite insensitive to a change in D_e in the repulsive limb (figure 7) which is very important with respect to the application of the RPC method for the detection of errors in the construction of the potential or errors in the analysis of the spectrum, in cases where the value of D_e is not quite accurately known (which is often the case). Figures 6 and 7 show that an increase in the value of the parameter D_e turns the RPC to the right in the attractive limb and slightly to the left, in the repulsive limb, so that

it becomes broader. (In other cases, the RPC is turned *slightly* to the right in the repulsive limb. This change in the repulsive limb is not necessarily the same for all molecules and states because both p and u depend on D_e.)

The effect of a change in the value of a molecular constant is always a turning of the RPC in both limbs, i.e. a displacement of the limb as a whole, whereas a change in the sign of the curvature never appears in the repulsive limb. (It is important to keep this in mind with respect to the application of the RPC method for the detection of errors, see §§4.1–4.4.)

It is important to emphasize that different forms of the GRPC (values of the parameters or correction functions) may be taken in the repulsive and the attractive limb without violating the continuity of the RPC and its first derivative (and the condition of vanishing first derivative at $p = 0$, of course), and the reduced force constant also remains the same if the value of ε is the same for both limbs.

3. The RPC scheme

The RPC transformation (equations (5), (6)) makes it possible to compare and study the internuclear potentials in a unique scheme where all potentials have the same minimum, the same force constant, and the same dissociation limit. By definition, there is an asymptotic confluence of all RPCs at the dissociation limit, where the reduced energy equals 0 or 1, depending on the choice of the zero of energy.

Figures 8 and 9 show a comparison of the RKR potentials and the RPCs of some molecules, respectively. The differences in the repulsive limb are evidently strongly reduced in the RPC scheme. They are also considerably reduced in the attractive limb. The crossing of the potential curves disappears in the reduced form, and the RPCs of the heavy molecules I_2 and Bi_2 are markedly turned to the right of the RPC of the light molecule H_2.

Indeed, first results in the sixties (when there was still a lack of RKR potentials and the empirical Hulburt–Hirschfelder [27] function was partly used for orientation [3]) suggested that there could exist a monotonous dependence of the RPC on the atomic numbers in the following sense: the RPCs do not intersect and, with increasing atomic numbers, the RPC is turned to the right around the minimum in the p versus u RPC diagram. However, a more thorough investigation in the eighties (when much more experimental material was available) has shown that this is only a very rough rule for non-metal molecules and the real situation is more complicated. Nevertheless, it appears that, in the RPC scheme, some important rules hold which were called 'the RPC rules' and will be formulated below.

3.1. *The RPC rules for the ground state*

I shall not distinguish here between molecules and radicals, using only the term molecule.

It seems natural to begin with the study of the ground state of neutral molecules. In the RPC scheme, the following RPC rules have been observed which, however, also seem to hold for the excited states and for ions (with the exception of deviations from Rules II and III, for some special excited states):

I.   With the exception of some special cases, the RPCs of different diatomic systems do not intersect in the attractive limb and they never intersect in the repulsive limb, although they do lie very close together there.
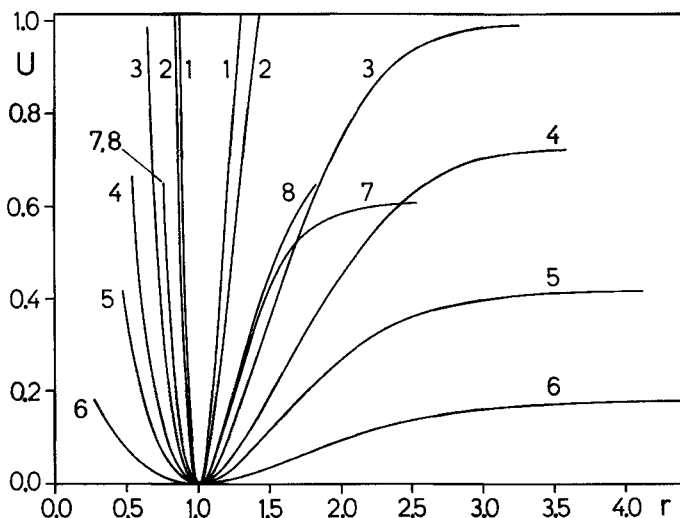
Figure 8. Ground state RKR potentials from [36]. The values of r_e (LiH) and D_e (LiH) are taken as units of distance and energy, respectively. Zero of U at the common minimum. 1:HF; 2:H_2; 3:LiH; 4:CsH; 5:Li_2; 6:Cs_2; 7:I_2; 8:Bi_2.
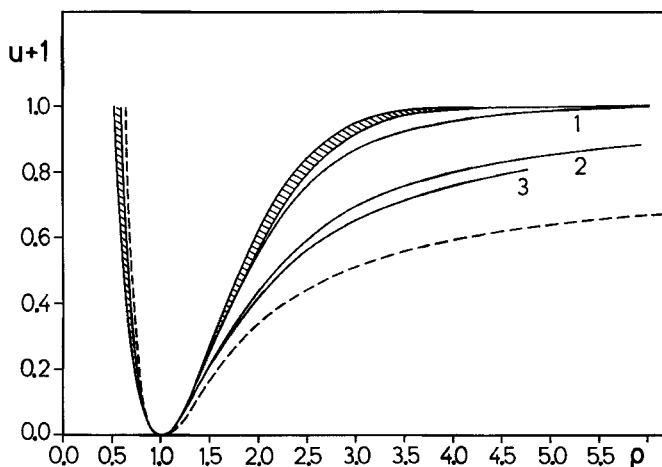
Figure 9. Reduced ground state RKR potentials to figure 8. Left limb: the hatched area contains the RPCs of H_2, HF, LiH, CsH, Li_2, Cs_2, I_2, and Bi_2 (the left and the right hand boundary of this area are the RPCs of Li_2 and Bi_2, respectively). Right limb: the hatched area contains the RPCs of all 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. Broken line: reduced *ab initio* potential curve of He_2.

II. The ordering of the 'quasiparallel' RPCs is the same in the attractive and the repulsive limb.

III. With the exception of some special cases, the left hand boundary of the admissible RPC region in the p versus $(u+1)$ diagram is the RPC of the Li_2 molecule. The right hand boundary is represented by the almost coinciding RPCs of the rare gases. (The only exception observed is the RPC of BeH which lies outside the left hand boundary. The RPC of H_2 represents the left hand boundary for non-metal molecules.)

Figure 10.   Ground state from [28]. Differences in reduced energy from the RPC of K_2 (zero line) in the attractive limb. (———) from top to bottom: RPCs of Li_2, LiNa, Na_2, NaK, KRb, Rb_2, RbCs, and Cs_2. (-----): GRPC estimate of the upper portion of the RPC of KRb (see §4.8.4). The right-hand energy scale refers only to 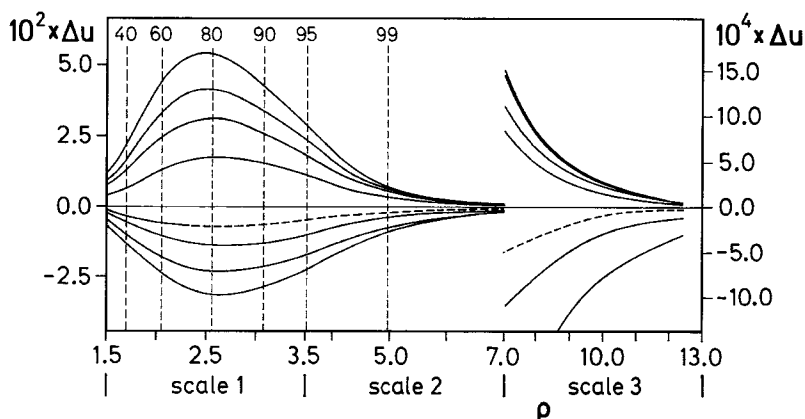the highest-p portion (third section). The vertical lines denote the levels of $100(u+1)$. Three different scales are used for the three intervals of p (1·5–3·5, 3·5–7·0, 7·0–13·0) on the p scale to make the figure more readable in the region of large differences. For large values of p (7·0–13·0), a hundred-times-more-sensitive scale is used for the energy differences to visualize the very small differences and illustrate the non-crossing rule. The LeRoy–Bernstein extrapolation for RbCs is not shown in scale 3 (see text).

IV.   As a rule, the RPCs of van der Waals type molecules lie close to the right hand boundary of the rare gases. (Note that this is not the effect of small D_e, since the RPC turns to the *left* with decreasing parameter D_e!!)

V.   There exist groups of affiliated (chemically related) molecules (see examples below) in which the following rules hold: (a) *The non-intersection rule*: the RPCs of different molecules of the group do not intersect anywhere; (b) *The ordering rule*: with increasing atomic numbers, the RPC turns to the right around the common minimum while becoming broader (the 'reduced' repulsive force *slightly* increases and the 'reduced' attractive force decreases, for heavier molecules).

As a rule, the effect of a small change in both atomic numbers is more pronounced than a large change in only one atomic number. The effect of a change in one atomic number is more pronounced for small atomic numbers than for high atomic numbers.

We shall illustrate rule V on a few groups of affiliated molecules in figures 10–14.

It should be mentioned that the possibility of calculating the RPCs of diatomics is still rather limited for the following reasons: (1) reliable spectroscopic data are not available or have been measured only up to a low energy level, and (2) the value of the dissociation energy is not known or is not known with sufficient accuracy.

I shall show here only the attractive limb which is, of course, more interesting. Figure 10 contains the RPCs of the ground state of alkali diatomic molecules [28] for which the RKR (IPA) potential could be constructed for very high values of energy and the value of D_e has been accurately determined using the LeRoy–Bernstein extrapolation method [29]. It can be seen that the non-intersection rule V(a) is obeyed very accurately up to the dissociation limit. (In the asymptotic portion, the RPC of RbCs is not shown since, for RbCs, the spectrum has not been measured for such high values of energy as for the other molecules and the value of D_e could not be so

Figure 11. Attractive limb from [25]. Differences in *u* of the ground state RPCs from the ground state RPC of ON (zero line). (——) from top to bottom: HN, CN, N_2, BrN; (▲) PN; (●) SiN. The dependence on the atomic number is much less pronounced for large atomic numbers.

Figure 12. Attractive limb from [25]. Differences in *u* of the ground state RPCs from the ground state RPC of CO (zero line). (——) from top to bottom: HO, BO, NO, ClO, SeO, TeO; (●) SO (see caption to figure 11).

accurately determined.) The RPCs are ordered with respect to the atomic numbers according to the ordering rule V(b). The left limbs may be seen in Jenč and Brandt [30], figure 4.

Figures 11 and 12 show the dependence on one atomic number of the RPCs of nitrides and oxides, respectively [25]. Although the value of D_e is not known to such accuracy and the RKR potentials could not be constructed for such high values of energy as for the alkali diatomic molecules, the data are sufficient for this qualitative picture. It is evident that the dependence on the atomic number is much less pronounced for high values of Z than for the light molecules. Figures 13 and 14 show the dependence on both atomic numbers for the halogen molecules and for the

Figure 13.   Attractive limb. Differences in u of the ground state RPCs of the halogens from the ground state RPC of F_2 (zero line). (——) from top to bottom: Cl_2, Br_2, I_2. (-----) from top to bottom: BrF, BrCl, ClI, BrI.
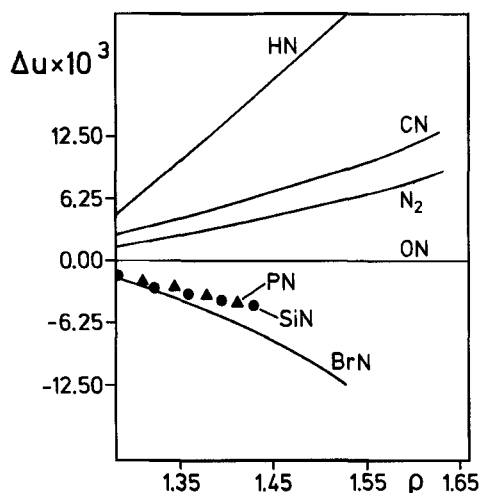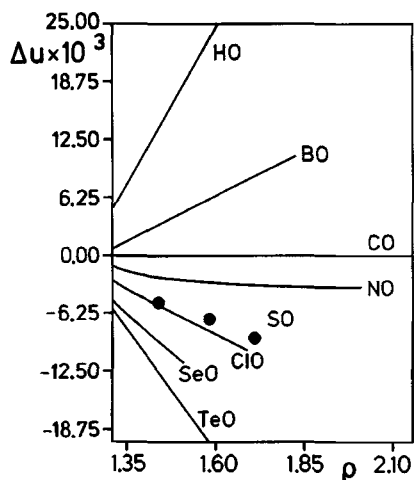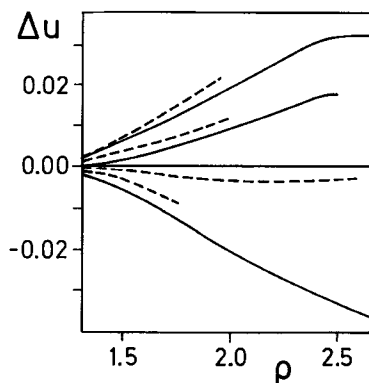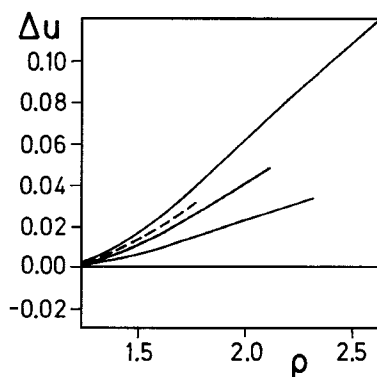

Figure 14.   Attractive limb. Differences in u of the ground state RPCs from the ground state RPC of Te_2 (zero line). (——) from top to bottom: O_2, S_2, Se_2. (-----) SO.

homonuclear molecules of the sixth column, respectively. (The molecule of SO is included. For other heteronuclear molecules, sufficiently reliable data were not available. The spectroscopic data and the RKR (IPA) potentials for BrF, Cl_2, BrCl, Br_2, ICl, IBr, I_2, F_2, O_2, SO and S_2, Se_2, Te_2, and the *ab initio* potential of F_2 may be found in [31(a)–(m)], respectively.)

Similar figures for non-metal hydrides, alkali hydrides, and for the hydrides of the Ib and IIb group have been shown in [32–34]. The following remark with respect to the hydrides is interesting: with the exception of the hydrides of the IIb group, the dependence on the atomic number is here relatively weak in the sense that the RPC is only slightly turned to the right of the RPC of H_2; this is also true, for example, for the very heavy hydrides PtH and TlH [34(b)]. For the hydrides of the IIb group, the RPCs are turned considerably more to the right, in particular for HgH, the RPC of which lies far to the right of the RPC of H_2, thus moving towards the region of weakly bound (van der Waals) molecules. In fact, HgH is, in a sense, an anomalous spectroscopic case presenting certain anomalies explained as being due to avoided crossing of the zero order potentials (5) (for details see Jenč and Brandt [34(b)]).

Generally speaking, the RPC scheme is useful for the demonstration of anomalies and deviations from the 'normal' behaviour of the potential. Thus in figure 13, the

anomaly of F_2 is observed, violating the ordering rule in a salient way: the RPC of F_2 is markedly turned to the right of the RPC of the heavier molecule Cl_2. (A similar anomaly is observed in comparing the RPCs of the molecules HCl and HF [25, 32].) Indeed, anomalies of F_2 and other fluorine compounds have also been observed with respect to other phenomena, e.g. with respect to electron ionization cross sections [35], and is also manifested in quantum chemical calculations for F_2 [25].

The anomaly of F_2 in the group of halogen molecules is also manifested by the value of D_e (F_2). The ordering of the RPCs of the halogen molecules in the RPC scheme according to increasing atomic numbers—with the exception of F_2—also corresponds to the ordering with respect to decreasing values of D_e (although a decrease in the value of the parameter D_e turns the RPC to the left!!). Thus the value of D_e of BrF, Cl_2, BrCl, ICl, Br_2, and I_2 is (in cm^{-1}) 20953, 20276, 18212, 17557, 16057, 14794, and 12547, respectively. The value of $D_e(F_2)$ is 12764 ± 100 [31(h)], though it is the lightest halogen molecule. (The ordering of the alkali diatomic molecules also corresponds to decreasing values of D_e. This, however, is not a general rule: e.g. for the oxides or nitrides, it does not hold at all (ordering in rows, not in columns of the Periodic Table).)

It is interesting to note that the ordering of the alkali diatomic molecules also corresponds to increasing values of r_e, increasing values of ρ_{ij} and decreasing values of the quantity $x_e = r_e/\rho_{ij}$. However, this regularity does not represent a general rule in the RPC scheme.

A crossing of the RPCs of different molecules is, in general, rare. It is well-known that the ground state of the alkali hydrides represents a special case where there is 'a change from the ionic to the covalent character of the bonding' (due to avoided crossing). This is manifested in the RPC scheme by the fact that there exists a slight crossing of the RPCs of the alkali hydrides with the RPCs of the alkali diatomic molecules and, much less pronounced, with the RPCs of H_2 and the non-metal hydrides. Apart from small differences due to the crossing, the RPCs of the alkali hydrides of Li_2, LiNa, and Na_2 lie to the left of the RPC of H_2. The differences between the RPCs of these molecules are almost invisible in the current format of the figures and difference curves are necessary for their visualization. The crossings of the close-lying RPCs of these molecules show the special effect of the ionic component in the alkali hydrides (mentioned above) on the one hand, whilst on the other hand they are due to the somewhat different character of the electronic structure of these molecules. (There is, of course, no crossing in the repulsive limb.) The RPCs of the alkaline earth diatomic molecules lie far to the right of the RPC of H_2.

The ground state of O_2 is a Π-state, in contrast to almost all other molecules where the ground state is a Σ-state. This anomaly is manifested in a slight crossing of the RPC of O_2 with the RPC of CO and CO^+.

Unfortunately, the experimental data available still do not permit the construction of RKR (IPA) potentials and the corresponding RPCs for a sufficiently large number of molecules. Therefore, one has to have recourse to *ab initio* calculated potentials and molecular constants discussed in the next section.

3.2. *Reduced* ab initio *calculated potential curves* (ab initio *RPCs*)

The RPC scheme evidently reflects certain physical laws governing the behaviour of the internuclear potentials of diatomics (related to the electronic structure). This can also be seen in more detail in the following sections. Therefore, we can say that an (perhaps not very accurate) *ab initio* method *reflects* (*preserves*) *the physical structure*

of the problem if the *ab initio* RPC approximates the RKR (IPA) RPC to a high degree of accuracy, in the RPC scheme.

For correctly conceived *ab initio* calculations this is, fortunately, the case and, as a rule, the RKR (IPA) RPC and the *ab initio* RPC of a molecule do not intersect ('quasiparallelity'). The following basic principle should be respected: the *ab initio* method should not aim to represent especially well a certain range of the potential or to calculate a certain molecular constant with high accuracy, rather it should reproduce the intrinsic relations of the problem in their correct proportion. The configuration interaction (CI) variational method (i.e. a one-electron approximation) is the most frequently used method suitable for computer programming. The trial function is constructed using a basis of one-electron wave functions according to the group symmetry of the problem, where the 'configurations' are the antisymmetric components (determinants) built up from different combinations of the one-electron functions of the basis [20]. Care should be taken in the choice of the configurations so as to represent the potential adequately over the whole range of r (so that the basic principle mentioned above is satisfied).

For heavier molecules, i.e. for large N, all-electron calculations would still lead to exceedingly extended and time-consuming computational effort. Therefore, simplifications in the construction of the trial functions are employed that are sometimes called the approximation of the 'effective core potential'. The essence of this method is that the trial function is built up only for the upper electron shells and the effect of the electron core is represented by an 'effective core potential' calculated separately [20]. The accuracy of the calculation depends, of course, not only on the choice of the one-electron basis but also on the calculation of the 'effective core potential' that should also correctly represent the polarization effects and the core–valence electron correlation [20].

The simplifications mentioned save a lot of computer time and are also justified by the fact that, for large N, in the all-electron calculation a certain limit of error cannot be reduced even if a very large number of terms in the trial function is used, which is, of course, the problem of convergence rate. (Numbers of configurations of the order of 10^4 are used in these approximations, anyway.)

The energy of the dissociation limit should also be calculated in the same approximation and the theoretical (*ab initio*) values of the molecular constants r_e and D_e can then be calculated by the interpolation of the potential as coordinates of the minimum, which poses no serious problems if sufficient points of the potential have been calculated. The calculation of the theoretical (*ab initio*) value of the force constant k_e, is a more difficult problem, since an accurate interpolation of the potential does not guarantee an accurate value of its second derivative at the minimum. I prefer a direct polynomial interpolation to the use of, for example, a Morse function, since few potentials are in fact of the Morse type. The method was described in [36] and the results are satisfactory if certain rules concerning the calculated points of the potential are obeyed:

(1) Points of the potential for sufficiently high energies must be included in the interpolation (up to 40 % of D_e, say). It does not suffice to use an accumulation of points in the vicinity of the minimum, and a broad range sampling is preferable.

(2) A sufficient number of points of the potential should be calculated in this range (at least 14–16).

(3) Points near the minimum should be calculated but the points used for the interpolation should rather be uniformly distributed in the interpolation range of energy (not partly accumulated around the minimum).
(4) Results for different polynomial order should be compared and a stability range for k_e looked for [36].
(5) Interpolation results of both the potential and the electronic energy should be compared.
(6) *For orientation*, a parallel calculation for a corresponding Morse potential may be performed [36].

Unfortunately, these requirements are often not fulfilled in existing *ab initio* calculations so that slight inaccuracies in the theoretical value of k_e may exist. (An insufficient number of points of the potential are currently calculated, in particular in the repulsive limb.) The use of the Dunham formula [37] may also lead to inaccuracies [38].

For instance, the method of effective core potential used by Meyer and co-workers for the calculation of the potentials of Li_2, $LiNa$, Na_2, and K_2 [39(a)–(d)] gave very good results in the RPC scheme, so that the differences between the RKR and the *ab initio* RPC are not seen in the current format of the figures and are only seen on difference curves. They may also serve for the illustration of the statement 'the *ab initio* method reflects the physical structure of the problem to a high degree of approximation': it is clear that with an increasing number of electrons, the correct description of the physical system is more difficult even if for the heavier molecules a more extended configuration interaction is used; although for the four molecules above, the error in the value of D_e was of the same order (50, 49, 77, and 56 cm^{-1} for Li_2, $LiNa$, Na_2, and K_2, respectively), the differences between the RKR and the *ab initio* RPC increased steadily from Li_2 (all-electron problem, where differences are almost negligible) to K_2, in particular in the high portion of the RPC above 80% of D_e. That is, in our language, the physical structure of the problem is not so well reproduced for the heavier molecules (see also [3], pp. 284–290). (As D_e (Li_2) = 8516·8 cm^{-1} and D_e (K_2) = 4451 cm^{-1}, the percentage error in D_e is larger for K_2 than for Li_2 which, however, cannot explain the relatively 'large' deviation for K_2. These errors can, of course, be seen only in difference curves.)

As the approximation of the RKR/RPC by the *ab initio* RPC is quite good, the *ab initio* RPCs may be used at least for the qualitative picture in the RPC scheme which will also be done in this paper in Figures 19–27. It is important that this approximation is relatively good even for rather inaccurate *ab initio* calculations. (Further applications will be shown in the corresponding sections.)

In figures 15–17, the comparison of the RKR potentials and *ab initio* potentials of Na_2, K_2, and Rb_2 in normal and reduced form is shown. The errors in the *ab initio* values of D_e were 4·94% and 6·67% for the two *ab initio* calculations for Na_2 and 10·58% and 8·42% for K_2 and Rb_2, respectively. Correspondingly large errors also resulted for r_e and k_e [36]. Although the differences between the RKR and the *ab initio* potentials are also large (figure 15), all RPCs almost coincide in the format of figure 16. The differences are better seen in detail in figure 17: although differences between the RKR/RPCs of different molecules still persist, the differences between the reduced RKR and the reduced *ab initio* potential of the same molecule are almost negligible (they would be somewhat larger in the upper portion of the potential). It should be noted that, for inaccurate *ab initio* potentials, the interrelation of the errors in the three
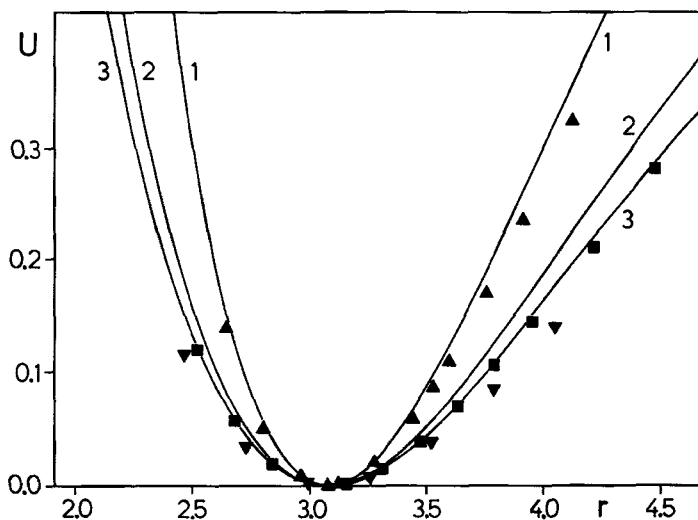
Figure 15. Comparison of RKR and *ab initio* ground state potentials from [36]. 1 : RKR curve of Na_2. 2 : RKR curve of K_2. 3 : RKR curve of Rb_2. (▲), *ab initio* potential of Na_2. (■), *ab initio* potential of K_2. (▼), *ab initio* potential of Rb_2. $D_e(Na_2)$ and $r_e(Na_2)$ are taken as unit of energy and internuclear distance, respectively. Common minimum at $r_e(Na_2)$. Zero of U at the common minimum.
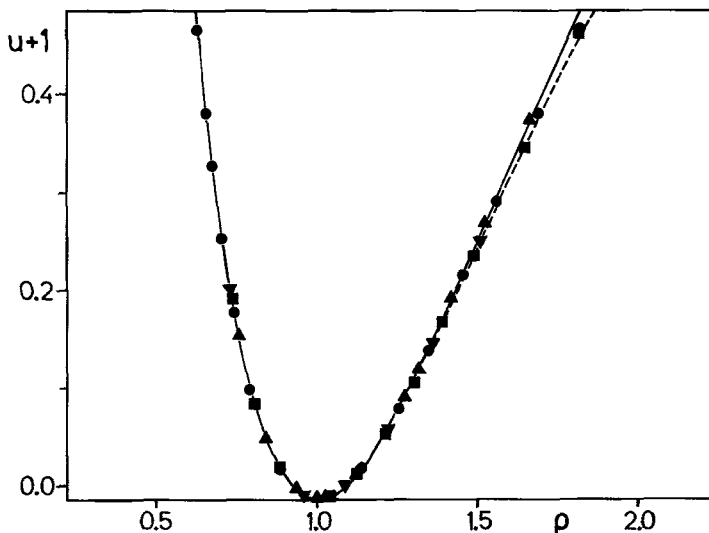
Figure 16. Reduced RKR and *ab initio* ground state potentials to figure 15 (from [36]). All potentials coincide in the left limb in this format. Right limb : Solid line : reduced RKR potential of Na_2. Broken line : reduced RKR potential of Rb_2. (●) reduced RKR potential of K_2. (▲) reduced *ab initio* potential of Na_2. (■) reduced *ab initio* potential of K_2. (▼) reduced *ab initio* potential of Rb_2.

ab initio calculated molecular constants, r_e, D_e, and k_e, must be of the type encountered in an adequate *ab initio* calculation if the *ab initio* RPC is to approximately coincide with the RKR (IPA) RPC (see equations (5) and (6)). Figure 18 may serve for illustration. For a more detailed discussion see [3], pp. 289–290. For example, for *semiempirical* calculations where the experimental values of r_e, D_e, and k_e are very well
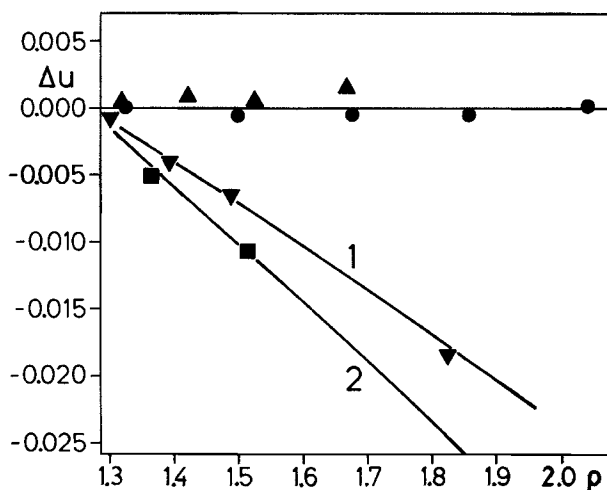
Figure 17. Difference curves to figure 16 (from [36]). Differences in u from the reduced RKR potential curve of Na_2 (zero line) in the attractive limb. 1: reduced RKR potential of K_2. 2: reduced RKR potential of Rb_2. (●) reduced *ab initio* potential of Na_2. (▲) less accurate (see text) reduced *ab initio* potential of Na_2. (▼) reduced *ab initio* potential of K_2. (■) reduced *ab initio* potential of Rb_2.
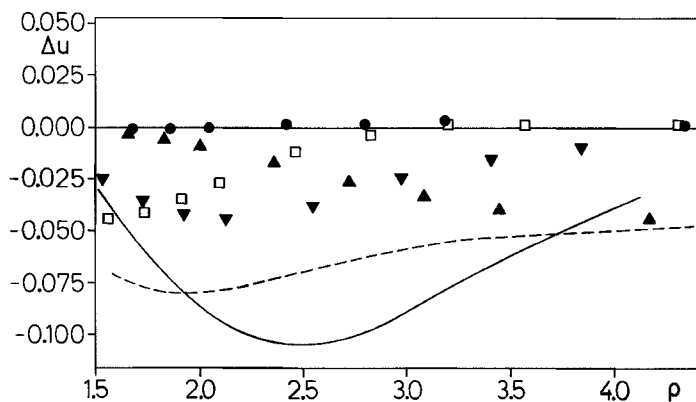
Figure 18. Differences in u from the reduced RKR potential curve of Na_2 (zero line), attractive limb (from [36]). Solid line: reduced Morse potential. (●) reduced *ab initio* potential. Broken line: reduced *ab initio* potential, where the experimental values of the molecular constants r_e, ω_e, and D_e were taken in equations (5) to (9). (▼) reduced *ab initio* potential with experimental value of r_e. (□) reduced *ab initio* potential with experimental value of ω_e. (▲) reduced *ab initio* potential with experimental value of D_e. The error in the *ab initio* value of D_e was about 4·94 %, i.e. 298 cm^{-1}.

approximated, a large deviation of the theoretical RPC from the RKR/RPC results [36], since, from the theoretical point of view, such a method is not consistently defined and does not reflect the physical structure of the problem correctly. For more details see [36] (pp. 418–419 and 422–423, and table 2).

Unfortunately, for heavy molecules, the *ab initio* calculations are often still unsatisfactory and it is quite difficult to obtain the tabulated potentials from the authors (all supplications being in vain, e.g. [40]).

A similar approximation of the RKR (IPA) RPC by the *ab initio* RPC may also be obtained for ions and for the excited states if the calculation is carefully performed.
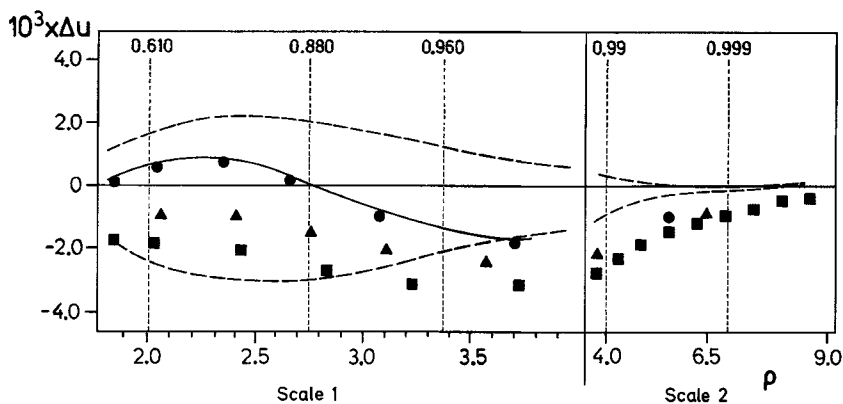
Figure 19.   Differences in reduced energy between the RKR/RPC of the ground state of Na_2 (zero line) and the other RPCs from [42]. (-----) ground state RKR/RPCs, from top to bottom: Li_2, K_2. (———) RKR/RPC of the A-state of Na_2. *Ab initio* RPCs for the A-state: (▲) Li_2. (●) Na_2. (■) K_2. The vertical lines denote the value of $(u+1)$ for Li_2 (X). The potentials of the A-state, though steeper in the potential well, approach the dissociation limit essentially more slowly than the ground state potential.

Increasingly large errors are usually obtained for increasing order of excitation (especially if the whole calculation was based on the approximation for the ground state).

3.3. *The RPCs of the excited states*

The results obtained so far show that the RPCs of the excited states obey the same RPC rules as the RPCs of the ground states (see §3.1) [41]. As for many excited states the value of D_e is not known, one has to have recourse also to the *ab initio* RPCs. Of course, not all theoretical calculations are suitable for this purpose (see §3.2). The RPCs of different excited states and of the ground state of a group of affiliated molecules in general do not cross. There are some exceptions similar to those found for the ground state of alkali hydrides in the general RPC scheme, i.e. in cases of 'avoided crossing' (§3.1). Such a situation is encountered, for example, in the first excited states of alkali diatomic molecules ($A^1\Sigma^+$) where the RPCs have an anomalous shape so that a slight crossing with the ground state RPCs occurs [42] as shown in figure 19. Nevertheless, it should be noted that the RPCs of the A-state do not intersect anywhere. The ordering rule is slightly violated here (the differences between the RPCs of different molecules are very small).

Of course, a crossing with the ground state RPC (and the RPCs of some other excited states) occurs for such states where the potential has a 'hump' in the attractive limb (e.g. the $^1\Pi_u(B)$ state of homonuclear alkali diatomic molecules, here also an effect of the ionic component [41]).

The normal case is shown in figures 20 and 21 on the example of the $1^1\Pi_g$ state of alkali diatomic molecules. It is clear that the non-crossing and the ordering rules are fulfilled.

As a rule, the RPCs of the excited states lie to the right of the ground state RPCs, thus moving towards the region of weakly bound molecules. This may be seen in figures 20 and 21. (The RPCs of the excited states of other molecules may also be seen in [3].) There are certain rare salient exceptions such as the $3^1\Sigma_u^+$ state of homogeneous alkali diatomic molecules (figure 3 of [41]) where the repulsive limb lies far to the left of the ground state RPC of H_2. A very small deviation of this type is also observed in
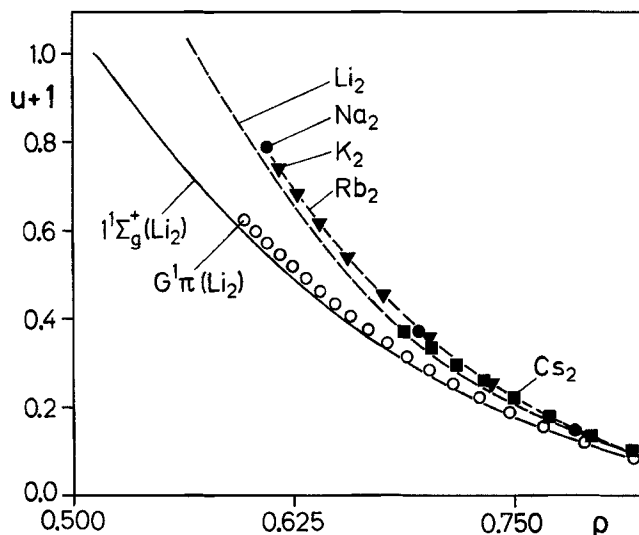
Figure 20. Repulsive limb from [41]. Comparison of the $1^1\Pi_g$ state RPCs of homonuclear alkali diatomic molecules. Broken lines from top to bottom: Rb_2, Li_2; ($\bullet$) Na_2; ($\blacktriangledown$) K_2; ($\blacksquare$) Cs_2. Solid line: ground state of Li_2. ($\bigcirc$) RKR/RPC for the $G^1\Pi_g$ state of Li_2. The ρ scale is about ten times more sensitive than in figure 21. (Note slight errors in the potential of Cs_2, see §4.)
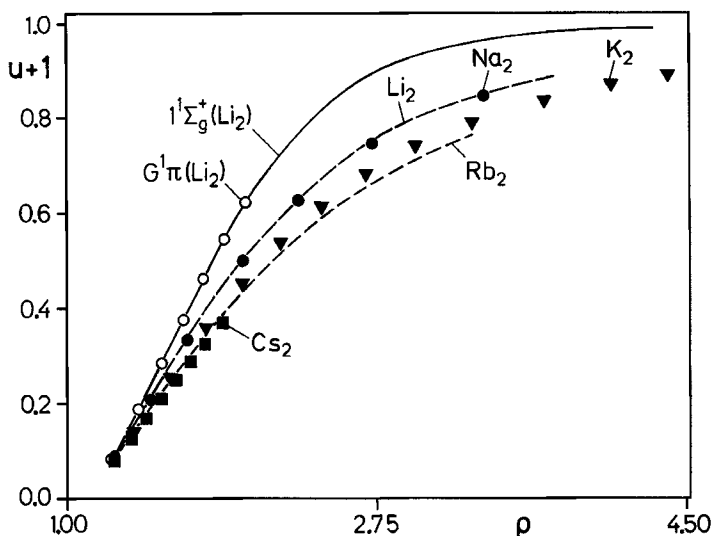
Figure 21. Attractive limb (from [41]). Comparison of the $1^1\Pi_g$ state RPCs of homonuclear alkali diatomic molecules. Broken lines from top to bottom: Li_2, Rb_2. ($\bullet$) Na_2; ($\blacktriangledown$) K_2; ($\blacksquare$) Cs_2. Solid line: ground state RPC of Li_2. ($\bigcirc$) RKR/RPC for the $G^1\Pi_g$ state of Li_2.

the lower portion of the repulsive limb of the RPCs of the slightly anomalous $A^1\Sigma^+$ state of alkali diatomic molecules mentioned above [41, 42].

Thus the RPCs of almost all excited states also lie inside the 'admissible' RPC region, i.e. between the ground state RPC of Li_2 and the ground state RPC of rare gases. So far only two cases have been found to lie below the RPC of the rare gases, i.e. the b- and the d-state of XeO (see §3.4).

F. Jenč

Figure 22.   Detailed picture of the lower portion of the repulsive limb for the $2^1\Sigma_g^+$ state (from
[41]). Broken line: RKR/RPC of Cs_2; ($\bullet$) *ab initio* RPC of Li_2; ($\blacksquare$) *ab initio* RPC of Na_2;
($\blacktriangledown$) RKR/RPC of Rb_2. The ρ scale is 2·2 times more sensitive than in figure 23.

Anomalies appear again as deviations from the RPC rules as, for example, the
violation of the ordering in the repulsive limb for the excited state $2^1\Sigma_g^+$ of Li_2 (*ab initio*
RPC) shown in figures 22 and 23. This anomaly appears to be due to the strong effect
of ion–ion interaction, as also confirmed by theoretical calculations [41] (§4.5).

Perturbation by other excited states [5] occurs for some excited states and has to be
eliminated in the calculation of the RKR (IPA) potential using the deperturbation
methods (see §§1.1 and 1.2). If this deperturbation is not sufficient, the resulting curve
is not a proper adiabatic potential and the error appears as a deviation from the RPC
rules. This error may also be demonstrated by comparison with an *ab initio* potential
(where the perturbation is not included) [38], see §4.4.

3.4. *RPCs of ions and weakly bound (van der Waals) molecules*

It has already been stated in §3.2 (and shown in §3.1) that the RPC scheme reflects
certain laws governing the potentials of diatomics that are related to their electronic
structure (including their number of electrons and atomic numbers). We hope that
this fact can be more clearly seen in this section and that one may realize that the
demonstration of these laws was the original aim of the RPC method (the applications
being a useful by-product).

In figures 24–27, we show the RPCs of positive and negative ions of non-metal and
metal containing molecules as well as the RPCs of weakly bound (van der Waals)
molecules and of some excimers. With a few exceptions, we employ their *ab initio*
potentials, since adequate experimental data were not available. As pointed out in
§3.2, only such *ab initio* potentials could be used where the calculation of the molecular
constants (in particular of the force constant, k_e) was possible. For heavy molecules,
the *ab initio* calculations are still not reliable (and, in fact, are rarely available, see
§3.2). It is obvious that only a small selection of diatomics can be shown here. In fact,
many of the *ab initio* potentials did not fulfil the requirements formulated in §3.2 so
that the calculation of k_e may not be very accurate. It is, however, sufficient for the
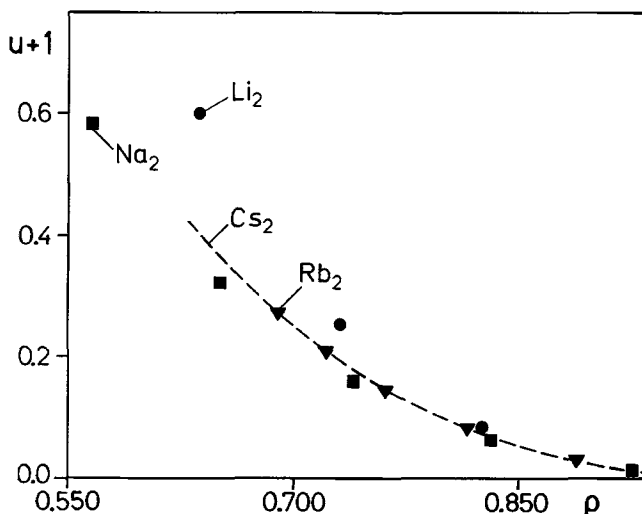qualitative picture in figures 24–27.
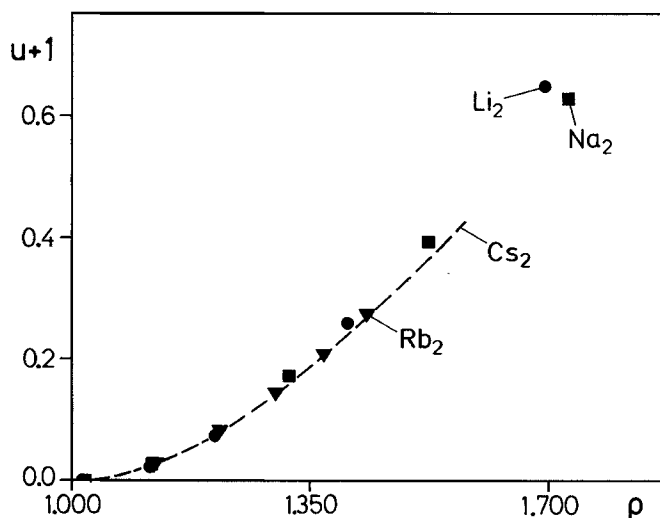
Figure 23. Detailed picture of the lower portion of the attractive limbs for the $2^1\Sigma_g^+$ state (from [41]). Broken line: RKR/RPC of Cs_2; ($\bullet$) *ab initio* RPC of Li_2; ($\blacksquare$) *ab initio* RPC of Na_2; ($\blacktriangledown$) RKR/RPC of Rb_2.
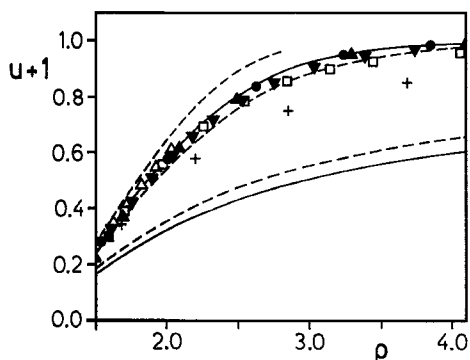
Figure 24. Attractive limbs of ground state RPCs. (——) from top to bottom: H_2, He_2. (-----) from top to bottom: BeH, H_2^+, the 2p excited state of H_2^+. ($\bullet$) BH; ($\square$) BH^+; ($\blacktriangle$) CH; ($\blacktriangledown$) CH^+; ($\triangle$) BeH^+; ($\blacksquare$) AlH; ($+$) AlH^+.

In figure 24, we compare the ground state RPCs of neutral molecules with the RPCs of their positive ions. As a rule, the effect of ionization appears as a turning of the RPC to the right. It can be seen that the effect of ionization is much more pronounced for the metal containing molecules than for non-metal molecules and that the ordering is in principle preserved after ionization. (There is a small discrepancy in the ordering of the RPCs of BH^+ and CH^+ that is not quite understood.) For the alkali hydrides, the differences between the RPCs of the positive ions are also much larger than the differences between the RPCs of the neutral molecules (Figure 25). One notes the anomalous case of BeH mentioned in §3.1 (also confirmed by *ab initio* calculations). (The potential was suspected to have a 'hump' [43(a)] which could not be confirmed by *ab initio* calculations [43(b), (c)].) Note that the value of D_e (cm^{-1}) is 17426 [43(a)], 38293·03 [17], and 26346 [2(a)] for BeH, H_2 and BeH^+, respectively.

It should be emphasized that, in general, the RPCs are not ordered with respect to decreasing values of D_e. If this were the case, the regularities observed in the transition
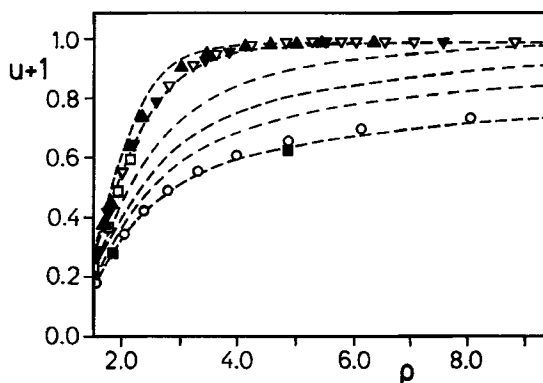
Figure 25.   Attractive limbs of ground state RPCs. (-----) from top to bottom: Li_2, HeH^+,
   LiH^+, NaH^+, KH^+, He_2. (■) Be_2; (○) HeH; (▲) Li_2^+; (▽) H_2^+; (▼) He_2^+; (□) Be_2^+.

from neutral molecules to ions could not exist. The behaviour of the RPC of a
diatomic system in the RPC scheme is not determined only by one parameter, rather
it reflects the global structure of the physical problem. We also show here the striking
effect of the 2p-excitation in the H_2^+ molecule which brings the RPC very close to the
ground state RPC of He_2.

   In figure 25, the interesting difference in the effect of positive ionization in normal
molecules and in weakly bound (van der Waals) molecules is shown. As the RPCs are
accumulated in the left part of the RPC scheme, the number of molecules shown
explicitly in the figure had to be limited. The ground state RPCs of Na_2, H_2, and K_2
(in this order) and the ground state RPCs of LiH, NaH, and KH (in this order) lie
between the ground state RPCs of Li_2 and HeH^+ in figure 25 (whereby the RPCs of the
alkali hydrides slightly cross the RPCs of the other molecules in the upper portion of
the curve above $(u + 1) = 0.9$, see §3.1). The ground state RPCs of Na_2^+ and K_2^+ almost
coincide with the ground state RPCs of Na_2 and K_2, respectively. Not all these RPCs
are shown in figure 25, where only the ground state RPCs of Li_2 and Li_2^+ may be seen
(the effect of ionization is strongest for the lightest molecule). For the positive ions of
the alkali diatomic molecules, the value of D_e is larger while for the positive ions of the
alkali hydrides it is an order of magnitude smaller than for the neutral molecule. (Let
us, however, recall again that a decrease in the value of D_e turns the RPC to the left!)

   At any rate, it is clear that the effect of the ionization of the alkali diatomic
molecules is very small and is *essentially* smaller than for the alkali hydride molecules.
(The ordering of the RPCs according to increasing atomic numbers is here preserved.)
The difference in the electronic structure, already observed for the ground state (§2.2),
here becomes more apparent.

   In figure 25, the RPCs of the weakly bound and van der Waals molecules HeH, He_2,
and Be_2 are shown, which nearly coincide at the lower border of the admissible RPC
region, ordered according to increasing atomic numbers. The ionization has here a
quite different effect than for the normal molecules: the RPC is turned far to the left
so that the RPCs of HeH^+, He_2^+, and Be_2^+ lie in close vicinity to the ground state RPC
of H_2^+ (nearly coinciding but in the same order as the RPCs of the neutral molecules).
The *ab initio* value of D_e (cm^{-1}) is 16455.6, 19972.3, 15891.5, 22525.7, and 13.347 for
HeH^+, He_2^+, Be_2^+, H_2^+(1s), and H_2^+(2p), respectively, whereas it is 5.3767, 7.6058, 827.0,
and 38293.03 for HeH, He_2, Be_2, and H_2, respectively.

   It is clear that for He_2, the 'noble gas configuration' disappears through the
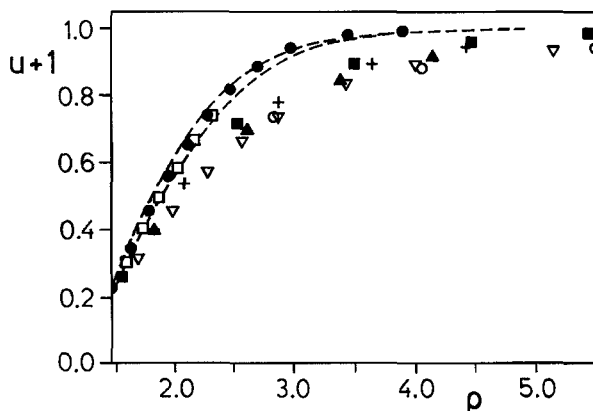
Figure 26. Attractive limbs of ground state RPCs. (------) from top to bottom: Li_2, HCl. (●) LiH; (□) CsH; (■) Li_2^-; (+) LiH^-; (▲) NaH^-; (▽) CsH^-; (○) HCl^-.

ionization and a similar effect occurs also in Be_2 and HeH. The following remark seems worthwhile in this context: it has been shown [33(a)] that the ground state RPCs of alkali hydrides practically coincide with the ground state RPCs of noble gases if, instead of the true value of D_e, a value of D_e is used which would correspond to dissociation of the molecule into ions $M^+ + H^-$ (M = alkali metal) where the atoms have a closed shell structure.

In figure 26, the ground state RPCs of negative ions are compared with the ground state RPCs of the neutral molecules. The effect of the formation of a negative ion is again a turning of the RPC to the right. However, the situation is somewhat different from that observed for the positive ions in figure 25: (1) The differences between the RPCs of the negative ions of the alkali hydrides are much smaller than for the positive ions, and the differences between the RPCs of the negative ions and the neutral molecules may be compared to the difference between the RPCs of LiH^+ and LiH; (2) The RPC is now turned about by the same amount for the alkali diatomic molecules as for the alkali hydrides or for the non-metal molecule, HCl. The ordering of the RPCs of the negative ions is the same as for the neutral molecules. For the negative ions, the value of D_e is here smaller than for the neutral molecules, however, it is of the same order, i.e. essentially larger than for the positive ions.

Let us now look at figure 27, which should also be compared with figure 26. It is certainly interesting to observe that the excitation of the molecules He_2 (a-state) and HeH (A-state) has approximately the same effect as the formation of the negative ion: the RPCs are markedly turned to the left and lie in the vicinity of the RPC of H_2. The RPCs of the ground state of He_2^- and the a-state of He_2 practically coincide and have the same 'hump' (i.e. a maximum above the dissociation limit). (D_e (cm^{-1}) = 16639·3 and 15800·8, respectively.) We further show here RKR/RPCs of the excited $b^1\Pi$ and $d^1\Sigma^+$ states of XeO which are the only two cases found so far where the RPC lies below the RPC of the rare gases (although the dissociation energies are not too small (D_e (cm^{-1}) = 461·0 and 693·0, respectively). It does not seem probable that this is due to errors in the RKR potentials.

It is also interesting to observe the difference between the ground state RPCs of the combinations of the rare gases with non-metal molecules and with the alkali metals: for $ArCs^+$ and $XeCs^+$ (D_e (cm^{-1}) = 680·3 and 878·0, respectively), where the alkali atom also has a closed shell structure, the RPCs almost coincide with the RPC of He_2,
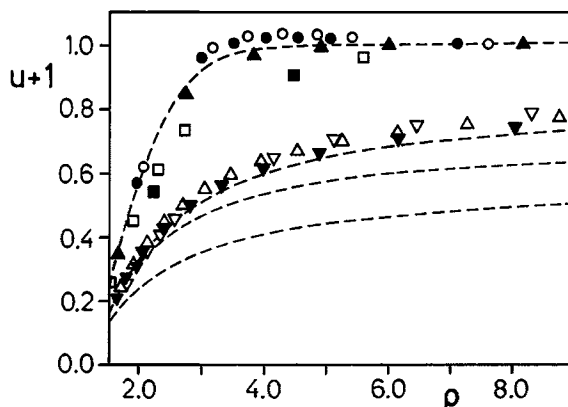
Figure 27. Attractive limbs of ground and excited state RPCs. (-----) from top to bottom: ground state of H_2, ground state of He_2, b-state of XeO, d-state of XeO. Ground states: (●) He_2^-; (▼) HeH; (△) ArCs$^+$; (▽) XeCs$^+$; (■) ArB$^+$; (□) ArC$^+$. Excited states: (○) He_2(a); (▲) HeH(A).

which is not the case for the combination of the rare gases with non-metal atoms, ArB$^+$ and ArC$^+$ (D_e (cm^{-1}) = 2832·7 and 9506·8, respectively. (These two RPCs are not very accurate and serve only for the qualitative picture.) The RPCs of the pairs, ArB$^+$, ArC$^+$ and ArCs$^+$, XeCs$^+$ are ordered according to increasing atomic numbers, respectively. For all figures, the ordering of the RPCs is also the same in the repulsive limb.

The ground state RKR (IPA) potentials and molecular constants of BeH, BeH$^+$, LiH, NaH, KH, CsH, HCl, Li_2, Na_2, K_2, and the b$^1\Pi$ and d$^1\Sigma^+$ excited states of XeO were taken from [43(a)] and [44(a)–(j)], respectively. (See also [45] and [33(c)] for the D_e values of BeH$^+$ and the alkali hydrides.) The RKR potentials for the alkali hydrides are those recommended in [44(k)] with values of D_e corresponding to the RPC estimates of [33(c)]. The ground state *ab initio* potentials of H_2^+, BH, AlH, CH, and BeH, were taken from [46, 47(a)–(c)] and [43(c), 47(b)], respectively and for BH$^+$ and AlH$^+$, and CH$^+$ from [48(a), (b)], respectively. The ground state *ab initio* potentials of He_2, He_2^+, He_2^-, HeH, HeH$^+$, Be_2, and Be_2^+ were taken from [49(a)–(g)], respectively. The excited state *ab initio* potentials of H_2^+(2p), HeH(A$^2\Sigma^+$), and He_2(a$^3\Sigma_u^+$) were taken from [46], [50], and [49(c)], respectively. The ground state *ab initio* potentials of LiH$^+$, NaH$^+$ and KH$^+$, K_2^+, Li_2^+, and Na_2^+ were taken from [51(a)–(c)] and [39(a), (c)], respectively. The ground state *ab initio* potentials of LiH$^-$ and CsH$^-$, and Li_2^- were taken from [52(a)–(c)]. The ground state *ab initio* potentials of ArB$^+$, ArC$^+$, and ArCs$^+$ and XeCs$^+$ were taken from [53(a)–(c)], respectively.

We hope that we have given in §3 a sufficient illustration of the possible use of the RPC method for a systematic comparative study of the potentials of different diatomic systems in a unified RPC scheme where the RPC rules (representing certain physical laws) are valid. (In [30], the RPC scheme was, therefore, somewhat poetically called 'a periodic system of diatomic molecules'.) The number of examples is naturally limited in a publication where only some typical cases can be shown.

This was the intended aim of the RPC method. In the next section, we show some applications of the method which follow from the RPC rules.

4. Applications of the RPC method

The main practical applications of the RPC method are listed below:

(1) Detection of errors in the construction of the RKR (IPA) potentials;
(2) Detection of errors in the molecular constants;
(3) Detection of errors in the analysis of the spectrum;
(4) Detection of errors in the RKR (IPA) potential due to perturbations;
(5) Detection of anomalies;
(6) Estimation of D_e;
(7) Correction of errors in the RKR (IPA) potential caused by the factors listed in (1)–(4);
(8) Extension of RKR (IPA) potentials by the GRPC method using *ab initio* potentials of the same molecule, or the RKR (IPA) or *ab initio* potential of another molecule;
(9) Calculation of the spectrum of a molecule from the spectrum of an affiliated molecule or from an *ab initio* potential by the GRPC method.

In cases (1)–(5), salient deviations from the RPC scheme and the RPC rules appear. Let us discuss them in detail.

4.1. *Detection of errors in the construction of the RKR (IPA) potentials*

The spectroscopic data are often known only up to a certain energy level and one frequently attempts to extrapolate the RKR potential above this energy limit. So far the only reliable extrapolation has been found in the GRPC extrapolation method described in §4.8.

(a) Extrapolations using an empirical potential function lead to large errors. This is illustrated in [54] on the example of mercury halides where the Morse function [6] was used in [55] for the extrapolation. An anomalous deviation of the RPC leading to a crossing of the RPCs of other molecules appears, in particular, in the repulsive limb. Deviations in the repulsive limb are here decisive, since they cannot be caused by an error in the value of D_e (due to the insensitivity of the repulsive limb to errors in D_e, see §2.2). Errors following from an extrapolation of the RKR potential using the Morse function [6] or the Hulburt–Hirschfelder function [27] (repulsive and attractive limb) and other potential functions in the repulsive limb have been shown in [56] (figures 3 and 4).

(b) Large errors (deviations from the RPC scheme) also appear if one attempts to extrapolate the RKR potential using the RKR formulas beyond the limits of their validity (i.e. outside the domain of the known spectroscopic data). This has been illustrated in [33(c)], [34(a), (b)], and [57(a), (b)] on the example of extrapolated potentials of RbH, the halogen hydrides, TlH, CuH, and CO (anomalous bending and crossing of the RPCs of other molecules in the repulsive limb). We do not show here any figures (see the references quoted), since it should be *a priori* clear that such extrapolations of necessity lead to large errors.

4.2. *Detection of errors in the molecular constants*

In the experimental values of r_e and ω_e, large errors are improbable. (Deviations in the RPC scheme resulting from errors in these constants have been shown in [3] figures 16–18.) However, one should realize that one has to be cautious in calculating the force
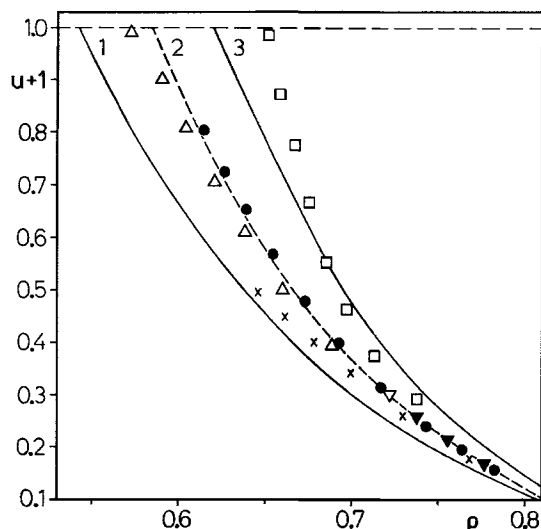
Figure 28.   Repulsive limbs of the RPC (from [64]). Curve 1, the RPC of H_2; curve 2, the RPC of I_2; curve 3, the RPC of rare gases. ($\blacktriangledown$) the RPC of Pb_2; ($\bullet$) the RPC of Bi_2; ($\times$) incorrect RPC of Bi_2; ($\triangle$) the RPC of Cl_2; ($\square$) incorrect RPC of Cl_2.

constant k_e from the value of ω_e, since in the case of anomalous potentials a unique Dunham formula does not accurately represent the spectrum up to high energy values or the value of ω_e in such a formula does not correspond to the force constant [33(c)]. (Errors in the *ab initio* calculated value of ω_e or k_e sometimes occur and may be detected by the RPC method (figure 3 of [38], see also §3.3.)

Errors in the value of D_e are more frequent. They cannot be seen in the repulsive limb because of its insensitivity to errors in the value of D_e. Very small errors in D_e may be detected only if the potential is known up to sufficiently large values of energy where the RPC is sufficiently sensitive to a difference in the value of D_e in the attractive limb (see §2.2, figures 6 and 7). Larger errors may be also seen in the lower portion of the attractive limb of the RPC (say, above $(u+1) = 0.7$). This is illustrated in [30(b), 34(a)], where large errors in the value of D_e, proposed by the experimenters for Rb_2 and MgH, respectively, led to a salient crossing of the RPCs. We shall discuss this topic in more detail in §4.6.

4.3. *Detection of errors (or insufficiencies) in the analysis of the spectrum*

Errors in the analysis of the spectrum sometimes occur due to insufficient resolution and incorrect assignment of the lines, omission of a weak line, etc. Such errors occurred for the ground state of Cl_2 [58], through the use of the data of Rao and Venkateswarlu [59] with an incorrect assignment, and for the ground state of Bi_2 [60(a)], where the spectroscopic data of Aslund *et al.* [60(b)] were used. These errors were detected using the RPC method in [61] and [54] (see also [3]) and were corrected by the experimenters in [62] and [63], respectively (see also [64]). The deviations may be seen in figure 28: the 'quasiparallelity' of the RPCs in the repulsive limb is violated and an intersection with the RPCs of other molecules results.

Small errors also seem to exist in the RKR potential of the ground state of NaCs [30(a)]. Further cases of this type are the ground state of RbCs [65] and LiNa [66(a)] and the excited $1\,{}^1\Sigma_u^+(A)$ state of Na_2 [67] for which the errors were detected by the RPC
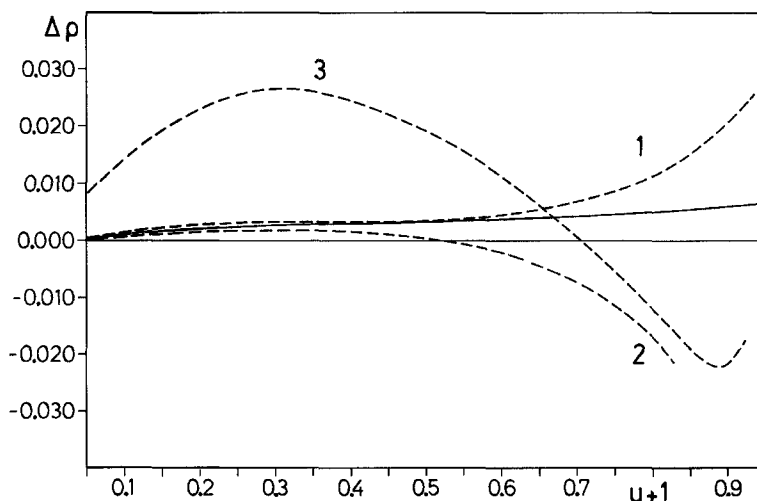
Figure 29. Repulsive limb (from [30(*a*)]). Differences in *p* from the ground state RPC of Li$_2$ (zero line). (———) ground state RPC of Cs$_2$; (- - - -) incorrect ground state RPCs of LiNa, LiK, and RbCs. Curve 1, LiNa; curve 2, LiK; curve 3, RbCs. All RPCs should lie between the RPC of Li$_2$ and the RPC of Cs$_2$.

method (figure 1 of [30(*a*)], figures 13 and 14 of [25], and figure 8 of [42]). The errors were confirmed and corrected by other spectroscopists for RbCs (false assignment) and LiNa in [68] and [69], respectively. It has also been found that the RKR potential for the A-state of Na$_2$ calculated in an unpublished PhD thesis [70] did not present the deviation found for the RPC corresponding to [67], thus confirming the RPC analysis. Further accurate measurements for the A-state of Na$_2$ are in progress [71], however, no results have so far been published. The deviations were again an anomalous bend and a crossing of the RPCs of other molecules in the repulsive limb, as may be seen in figure 29, for RbCs and LiNa.

In addition to false assignment, the error in the ground state RKR potential of LiNa was also partly caused by the use of the data of the B–X transition in LiNa. A strong perturbation of the B-state by higher excited states exists in LiNa [39(*b*), 72], however, no deperturbation procedure was used by Engelke *et al.* [66(*a*)] (see §1.1). Hence a similar error was also found [30(*a*)] in the RKR potential of the B-state in the RPC scheme. On the other hand, Fellows [69] used the data of the A–X transition which yielded a correct RKR potential (with the exception of the highest portion where a very strong 'wiggle' appears [28], probably due to an error in the rotational analysis, see below). All such errors may also be demonstrated by a comparison of the RKR (IPA) RPC with an *ab initio* RPC (§§3.2 and 3.3) as has also been done for Na$_2$ and LiNa [25, 30, 42]. Perturbations will be further discussed in §4.4.

Small errors in the rotational analysis are often due to insufficiently extended rotational data or an insufficiently accurate rotational analysis where the centrifugal distortion is often represented by an inaccurate approximation term. Such errors lead to 'wiggles' in the upper portion of the repulsive limb of the potential (for an analysis of this phenomenon, see Wells *et al.* [73]). These 'wiggles' are sometimes quite large and represent certain problems in more sophisticated applications of the RPC method (see §4.9 and also figure 4 of [30(*a*)], figure 2 of [28], and [42] p. 50). Difference curves must be used for the study of such errors.

An error in the evaluation of the centrifugal distortion may also lead to a displacement of the whole repulsive limb. This was the case with the $1^3\Sigma_u^+(a)$ state of Na_2 [74] which was detected by the RPC method (figure 3 of [41] and was essentially corrected by the spectroscopists in [75]. The error was identified through comparison with an *ab initio* potential where an impossible large discrepancy appeared.

It is also worth emphasizing that errors in the potential which are due only to errors in the rotational analysis imply a (horizontal) displacement of the potential of the same amount in both limbs (while the width of the potential well remains correct [14, 73]). Hence if a deviation is thought to be due *only* to errors in the rotational analysis, then the differences evaluated in the repulsive limb may be also compensated in the attractive limb (correction of the potential, §4.7). Such an error also appears in the highest vibrational level of the RKR ground state potential of KH [44(d)] where both turning points of the potential are shifted 'to the left' (see figure 2 of [33(b)] and figure 1(a) of [33(c)]). However, the difference in r is much larger in the attractive limb than in the repulsive limb so that some major error or mistake must be involved.

4.4. Detection of errors in the RKR (IPA) potential due to perturbations

It has been shown in §2.2 and in [3] that errors in the molecular constants, r_e, k_e, and D_e lead only to a turning of the repulsive limb of the RPC as a whole. Anomalous bends and crossings of the RPCs such as shown in figures 28 and 29 may be caused by errors in the construction of the potential or in the analysis of the spectrum as discussed in §§4.1 and 4.3. If such errors can be excluded, the anomalous bends and crossings in the repulsive limb may also be due to the fact that the molecular state in question is strongly perturbed and the effects of the perturbations have not been eliminated by letting out the strongly perturbed lines, or by a deperturbation procedure [12] (see §1.1).

The $1^1\Pi(B)$ state of the heteronuclear alkali diatomic molecules, LiNa, LiK, LiRb, and NaK, NaRb may here serve as an example. (It is well-known that there is an essential difference between the B-state of the hetero- and homonuclear alkali diatomic molecules which must be considered as two distinct groups of affiliated molecules in this state [41]; the potential of the latter has a significant 'hump'.)

We shall discuss here the case of LiNa, although the cases of LiK and LiRb are similar. In [39(b)], an incorrect assignment in the analysis of the spectrum of LiNa in [66(a)] was suspected, which has been confirmed by the new analysis of the spectrum of the B-state of LiNa [72]. As in [66(a)], strong rotational perturbations were here reported that had already led to an erroneous assignment in [66(b)]. In [66(a)], a discrepancy between the experimentally determined value of the centrifugal distortion constant D_v [5] and the Kratzer formula, $D_v = B_e^2/\omega_e^2$ was also reported (B_e = 'the rotational constant in the equilibrium position' [5]). On the other hand, an interaction of the B-state with the $2^1\Pi(D)$ state (avoided crossing) should exist [39(b)] and a strong perturbation by the $3^1\Sigma^+(C)$ has been found [72]. The ΔG_v sequence of the B-state is quite anomalous, having a maximum which is thought to be due to these interactions (the Dunham fit [5, 37] does not seem to converge even for lower energies). Therefore, a special procedure of fitting was employed by Fellows *et al.* [72]. The rotational data were not sufficient for the calculation of the centrifugal distortion constant, D_v, for which the Kratzer relation $D_v = 4B_e^2/\omega_e^2$ was used. However, for this calculation the *ab initio* value of ω_e and B_e from [39(b)] were used. A deperturbation procedure using a simple phenomenological Hamiltonian was employed taking into account only the interaction with the C-state. These facts seem to indicate that the rotational data were

not quite sufficient to guarantee an accurate RKR potential and moreover, an incorrect value of the centrifugal distortion constant was used: we have shown [38] that the *ab initio* value of $\omega_e = 191\cdot78$ cm^{-1}, determined by a Dunham fit [5, 37] of the *ab initio* energy levels in [39(*b*)] does not correspond to the force constant of the *ab initio* potential where the value $\omega_e = 182\cdot76$ cm^{-1} should be used (see table 23 and reference 16 of [30(*a*)]). However, Kratzer's relation is based on the assumption that the value of ω_e corresponds to the force constant k_e (see equation (9)).

This means that the representation of the centrifugal distortion in [72] is erroneous, which may lead to a similar deviation and violation of the RPC rules (§3.1) in the RPC scheme as observed, for example, for the potential of the a-state of Na$_2$ [74] (see §4.3). At the same time, it appears that the very simple deperturbation procedure is not sufficiently efficient so that the deviation is also due to this factor. This hypothesis is supported by the fact that, in figure 30, deviations of the same type and almost of the same size also appear in the RKR potentials of the B-state of LiK and LiRb [76(*a*), (*b*)] where analogous perturbations exist. No deperturbation procedures were employed in [76(*a*), (*b*)], nor were perturbations reported, so they evidently have not been sufficiently taken into account. It appears that the rotational perturbation of the B-state induced errors in the rotational analysis of the spectrum of the B–X transition which also caused errors in the potentials of the B-state of LiK and LiRb shown in figure 30. It is clear that an extrapolation of these potentials to higher energy levels would lead to very large errors.

The erroneous B-state potential of [66(*a*)] is also shown in figure 30. As already mentioned in §4.3, the errors in the analysis of the B–X transition led here also to errors in the ground state RKR potential of LiNa [66(*a*)] (see figure 29) whereas the use of the A–X transition data yielded an essentially correct IPA potential [69].

In the analysis of the spectra of the B–X transition of NaK and NaRb [77(*a*), (*b*)], no deperturbation procedures were employed but the lines thought to be perturbed were omitted in the Dunham fitting [5]. An impossible bend to higher energies in the repulsive limb of the RKR potential of NaK still appeared which was then replaced by an analytic potential in the highest portion. However, the final correction had to be made with the use of the GRPC method (see §4.7) and a similar GRPC correction was also necessary for NaRb [38]. For the Na-containing molecules, the deviation had the opposite direction to that found in the Li-containing molecules. It should be emphasized that these deviations cannot be caused by errors in the value of D_e (see §2.2). The correct reduced potentials for LiNa, NaK, and NaRb in figure 30 were calculated using the GRPC method and the *ab initio* potentials (see §4.8; for details see [38]).

Rotational perturbations in the AO_u^+ state should also have partly caused [63] the errors in the ground state potential of Bi$_2$ in [60(*a*)] based on the data of [60(*b*)] (see figure 28).

Similar deviations to those described above were also observed, for example, in the RPCs of the $B^2\Pi_{1/2}$ and $B^2\Pi_{3/2}$ excited states of NO and the $c^1\Pi_g$ excited states of C$_2$ [78] (in [78], the c-state was inadvertently denoted as a state of CO). Both states are perturbed by a higher excited state of the same symmetry ($C^2\Pi$ and $B^3\Pi_g$, respectively) and a crossing of the RKR potential (and the RPC) with the RKR potential (RPC) of the perturbing state occurs (i.e. there is no efficient deperturbation).
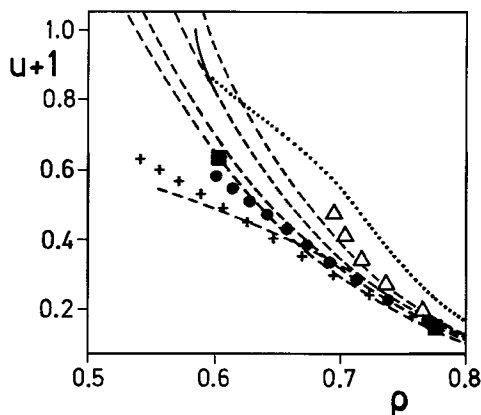
Figure 30.   Repulsive limb of the RPCs of the B state (from [38]). The broken lines from top
   to bottom are, respectively, the GRPC for NaRb, the GRPC for NaK, the GRPC for
   LiNa (see text), the RKR/RPC of Li_2, and the RKR/RPC of LiNa [72]. The solid line is
   the erroneous portion of the RKR/RPC of NaK [77(a)]. The dotted line is the erroneous
   RKR/RPC of LiNa [66(a)]. (■) ab initio RPC of Li_2 [39(a)]; (+) erroneous RKR/RPC
   of LiK [76]; (●) erroneous RKR/RPC of LiRb [76(b)]; (△) erroneous RKR/RPC of
   NaRb [77(b)].

4.5. Detection of anomalies

If errors or perturbations can be excluded, salient deviations from the RPC scheme
may be interpreted as anomalies. So far in all such cases anomalous features have been
disclosed when analysing also other data of such cases. We have shown the case of the
ground state of F_2 as an example (§3.1).

A comparison of the RKR (IPA) RPC with an *ab initio* RPC (if available) is, of
course, very important for the detection of anomalies, since the *ab initio* potential
should represent the adiabatic (Born–Oppenheimer) case and adequate *ab initio*
methods have been found to represent the physical structure of the problem correctly
(even if the approximation of the molecular constants is not very accurate; see §3.2).
So the deviation of the ground state RPC of F_2 has also been confirmed by its very
good approximate coincidence with the *ab initio* RPC (the *ab initio* potential from
[31(m)]). The same holds for the $2^1\Sigma_u^+$ excited state of Li_2 (§3.3), whereas, for example,
the errors in the RKR potential (and the analysis of the spectrum) of the $1^3\Sigma_u^+(a)$ excited
state of Na_2 were proved, demonstrating its *difference* from the *ab initio* RPC which
fulfilled the RPC rules (§4.3). Avoided crossing or strong influence of an ionic
component may lead to certain anomalies in the geometry of the RPC as is the case of
the ground state of the alkali hydrides and the A-state of the alkali diatomic molecules
(see §§3.1 and 3.3).

For the very anomalous $A^1\Sigma^+$ excited state of LiH, the nominator in equation (7)
is negative and no positive solution exists for ρ_{ij} [79(a), (b)]. It has been shown that the
Born–Oppenheimer approximation does not hold in this case (anomalous isotope
shift) [79(c)] (which was also shown in [79(b)], see [3]). This is, however, not the cause
of the anomalous ΔG_v sequence (which has a maximum) nor of the RPC anomaly,
since the same anomalous ΔG_v sequence and negative ρ_{ij} are also found for the *ab initio*
potentials of [79(d), (e)] (Born–Oppenheimer approximation). The cause is again, of
course, the avoided crossing of the zero order curves [5, 79(c)], one covalent and one
of ionic character, the interaction here being extraordinarily strong [79(f), (g)]. The

numerical reason for the non-existence of a positive solution for ρ_{ij} is the unnaturally small value of the force constant with $\omega_e(\text{exp}) \approx 240\ \text{cm}^{-1}$ (a flat bottom of the potential curve). A value of k_e approximately three times larger would be necessary to yield a positive solution for ρ_{ij}.

4.6. *Estimation of D_e*

Whereas the repulsive limb of the RPC is essentially used for the detection of errors in the analysis of the spectrum or in the construction of the RKR (IPA) potential, or of perturbations, it cannot be used for the detection of errors in D_e (§4.2). Its insensitivity to differences in the value of D_e (§2.2) is on the other hand the reason for its use for the detection of other errors, since small errors in the experimental value of D_e may frequently occur. The effect of a change in the value of D_e has been shown in figures 6 and 7.

The RPC method may serve for the determination of the lower and upper limits for the value of D_e of a molecule and state if the potentials of molecules of the same group of affiliated molecules are known, in particular of the molecules with neighbouring atomic numbers. Values of D_e which already lead to a crossing of the RPCs of the other molecules may be considered as limits for the values of D_e. Thus, in figure 1 of [30(*b*)], the value of D_e (cm^{-1}) for the ground state of K_2 was estimated to lie within the limits 4300 and 4600. The correct value is 4451·0 [44(*i*)]. For Rb_2, the RPC limits of D_e were 3870 and 4100. The correct value is 3994·4 [80]. Both ground state potentials of K_2 and Rb_2 were then only known up to 83 % of D_e.

In figure 2 of [33(*c*)], the limits for D_e (cm^{-1}) of NaH and RbH were estimated as 15 900–16 250 and 14 230–14 680, respectively. The ground state RKR potentials were only known up to about 55 % of D_e (the correct values of D_e are still not known).

These limits for the values of D_e followed from the RPC non-crossing rule. However, the RPC picture suggested that, for example for D_e (RbH), the limits could be 14 380–14 580 cm^{-1}.

Similarly, for the ground state of KRb, the value of D_e (cm^{-1}) was estimated, using the RPC non-crossing rule, to lie between 4100 and 4320, and from the comparison with the RPCs of other alkali diatomic molecules, the limits were estimated as 4200–4220 [81(*a*)]. (The RPCs of the heteronuclear alkali diatomic molecules lie approximately in the middle between the RPCs of their homonuclear neighbours [56].) In extending the KRb potential by the use of the GRPC method (§4.8) the estimate could be improved, following from the RPC non-crossing rule, to 4160–4280 [81(*b*)]. The final estimate was 4200–4240 which was then reduced to 4210–4230 [56]. Our RPC estimate of the D_e value was 4220 cm^{-1} (the RKR potential [82] was only known up to 68 % of this value). The experimental value still has not been determined.

Accurate estimation of D_e for a molecule, the spectrum of which has been measured over 95 % of D_e, is possible in some cases where, in a group of affiliated molecules to which the molecule belongs, the RKR (IPA) potentials have been constructed up to very high energy values for two neighbouring molecules (in the sense of atomic numbers). In figure 31, we illustrate the case of the ground state of RbCs by way of example. Here, the RKR potential of RbCs was constructed up to about 99 % [68], and a linear fit of the last few points to $V(r) = D_e - C_6/r^6$ was made. The value D_e (RbCs) $= 3845 \pm 1\ \text{cm}^{-1}$ resulted, however, the authors suspected that 'the error limits were misleadingly small' (in fact, LeRoy's criterion [29(*b*)] for the use of this extrapolation was not quite fulfilled). They surmised that this value may be considered as the upper limit of D_e (RbCs).
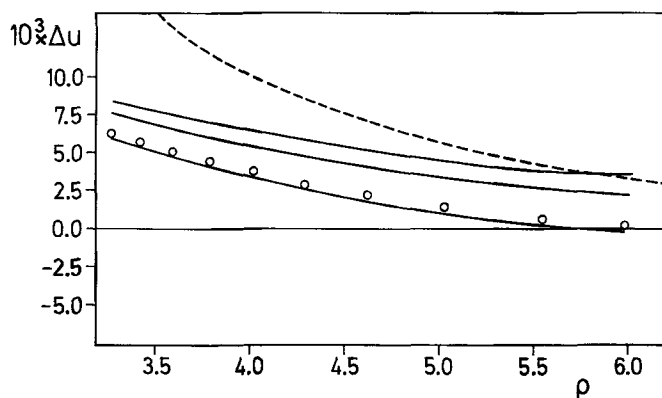
Figure 31. Attractive limb (from [84]). Differences in reduced energy, u, from the RPC of Cs_2 (zero line) of the RPCs of RbCs calculated for different values of $D_e(RbCs)$. (——) from top to bottom: $D_e = 3830$ cm^{-1}, $D_e = 3835$ cm^{-1}, $D_e = 3845$ cm^{-1}; (O) $D_e = 3843$ cm^{-1}; (-----) RPC of Rb_2.

Figure 31 shows the ground state RPCs of RbCs, and of Rb_2 and Cs_2. For the latter, the IPA potential curves could be constructed up to 99·6% and 99·44% of D_e, respectively [80, 83(*a*)] and the LeRoy–Bernstein extrapolation [29] led to very accurately determined values of D_e. The tail of the respective RPCs may be trusted.

Assuming that the RKR potential of RbCs is, indeed, correct, it follows from figure 31 that the value D_e (RbCs) $= 3845$ cm^{-1} is too large, since the RPC of RbCs then already crosses the RPC of Cs_2. On the other hand, the value 3835 cm^{-1} is too small, since, for this value, the RPC of RbCs would cross or just touch the RPC of Rb_2 (a salient crossing occurs for the value 3830 cm^{-1}). The upper limit appears to be 3843 cm^{-1} so that the RPC limits for the D_e (RbCs) are 3835–3843 cm^{-1}. Unfortunately, some doubts arose about the correctness of the upper portion of the RKR potential of RbCs in [68] when the GRPC procedure (§4.8) was applied for the construction of the potentials of alkali diatomic molecules [28], where this potential exhibited a slightly different behaviour than all the other molecules. The differences are smaller than $10^{-3} \times D_e$ (i.e. 4 cm^{-1}) however, they could, of course, make our rather accurate estimate uncertain. Nevertheless, this case may certainly serve for a good illustration of the possibilities of the RPC method [84]. If the RKR potential of RbCs had been determined only up to a somewhat lower energy level, the GRPC extensions of this potential would have been employed (using the potentials of Rb_2 and Cs_2) as in the case of KRb [81(*b*)].

The value of D_e of the ground state of NaCs could not be estimated, since there appear to exist small errors [30(*a*), 81(*a*)] in the RKR potential of [83(*b*)] (see §4.3).

As has been shown ([56], p. 574) the value of D_e may also be quite generally estimated with the use of the GRPC method (see §§4.8 and 4.9).

4.7. *Correction of errors in an RKR (IPA) potential caused by the factors described in §§4.1–4.4*

Errors in the RKR (IPA) potential caused by the factors described in §§4.1–4.4 may be corrected if at least the lower portion of the potential can be considered correct. This correct repulsive limb of the portion of the potential may then be extended with the use of the GRPC method described in §4.8. If the errors are thought to be due only to errors in the rotational analysis, the attractive limb may also be

corrected by the same amount as differences in the internuclear distance so that the width of the potential well remains the same [14]. Such a two-sided correction of small errors was attempted [38] for the potential of the B-state of NaK, and one-sided for NaRb [77(a), (b)]. Correction of the repulsive limb was carried out for the ground state RKR potential of CO in [57(b)] (see §4.1).

The GRPC method may also be used to eliminate the unpleasant 'wiggles' in the repulsive limb caused by small errors in the rotational analysis [73] (see [56] where these corrections were necessary for the calculation of the spectrum). RKR (IPA) potentials of other molecules or *ab initio* potentials or even empirical functions may be used for these corrections within the RPC scheme [56] (see §4.8.1).

If none of the potential is considered to be correct, one may at least obtain an approximation of the potential by the primitive GRPC method if an *ab initio* potential has been calculated (see §4.8.1). In [30(a)], the RPC method (§4.8.1) was also used to obtain limits for a correct repulsive limb of the ground state and the B-state potentials of LiNa and LiK, where the RKR potentials of these molecules were altogether discarded as incorrect.

4.8. *Construction and extension of RKR (IPA) potentials and the use of the GRPC method*

4.8.1. *Simple inversion of the RPC formula*

It has been shown in §3, figures 10–12, that the RPCs, for example of light alkali diatomic molecules or heavier nitrides or oxides, i.e. heteronuclear molecules such as CO and NO or SO and ClO or PN and SiN, lie very close together (there is only a difference of one unit in the atomic number of one atom). It has further been shown (figure 17) that an *ab initio* RPC of a molecule (calculated by an adequate method) also yields quite a good approximation of the RKR (IPA) RPC of the same molecule and state. The corresponding differences in r are, of course, much smaller in the repulsive limb than in the attractive limb since, in the repulsive limb, all RPCs lie close together (figure 9). One can use this fact for the construction of approximations of potentials.

If the values of the molecular constants r_e, $k_e(\omega_e)$, and D_e are known, one may then calculate an approximation of the potential of a molecule and state A from a close-lying RPC of another molecule and state B by inverting the RPC functions $\rho(r)$ and $u(U)$, using the values of the molecular constants of A. It is clear, from §3, that the approximation will be much better in the repulsive limb than in the attractive limb and that the RKR (IPA) potential of an affiliated molecule and the same state should be used if available, and that the rules of §3.2 should be respected if an *ab initio* RPC is used. It is also clear from the preceding text that a close-lying *ab initio* RPC of another (possibly affiliated) molecule could be used.

The fact that r_e and ω_e are known means that the corresponding spectroscopic data must be available. In most cases, the RKR (IPA) potential can then be constructed at least up to a certain (possibly not very high) energy so that one calculates an approximate extension of this potential. However, in some cases, accurate values of ω_e and r_e are known but the rotational analysis does not yield enough data for the construction of the RKR potential. In this case an approximation of the whole potential is calculated.

The molecular constant D_e poses more problems: if only a small portion of the potential is known, then the value of D_e, of course, cannot be calculated from the spectroscopic data (estimates using an extrapolation by empirical functions are highly inaccurate, see figure 3 of [56]). However, the value of D_e may often be obtained

from the value of D_e of another state if the dissociation limits are known, from predissociation or by other methods. (This point has been discussed in more detail on p. 1325 of [28]), where examples are quoted.) Approximation of the repulsive limb is easier since (not too large) errors in D_e are irrelevant in the calculation due to the insensitivity of the repulsive limb to D_e (§2.2, figure 7). As has already been mentioned, errors in the rotational analysis cause the same shift in r in both limbs whereas the width of the potential well depends only on the vibrational analysis [14, 73]. Thus in a case of insufficient rotational data, an estimate of the repulsive limb alone suffices and is a great help. Indeed, this application of the RPC method has been used in this way by some spectroscopists for the ground state potentials of halogens and alkali diatomic molecules [31(d), 85].

We have employed this method for the calculation of the limits for the repulsive limb of the ground state and the B-state of LiNa (using RKR ground and B-state potentials of Li_2 and NaK) and for an estimate of the repulsive limb of these potentials using *ab initio* potentials [33(b)] (see figures 9 and 11 of [30(a)]). For the ground state, these estimates have been fully confirmed by comparison with the later published ground state IPA potential of LiNa [69] (for the B-state, the RKR potential is still not known, see the discussion in §§4.3 and 4.4). It is clear that the use of the *ab initio* potential yielded a better approximation, lying between the limits calculated from the potentials of Li_2 and NaK. This method has further been demonstrated on the example of CN and CO where the ground state potential of CO was calculated from the ground state potential of NO in the repulsive limb. The errors in r were only of the order of 10^{-4} Å (up to 70 % of D_e, where the potential of NO is known; see figure 5 of [25]).

In the attractive limb, only an adequate *ab initio* potential should be used if acceptable approximations are to be obtained (see figure 14 of [30(a)]). This figure clearly shows how the large differences between the (relatively accurate) *ab initio* potentials and the RKR potentials could already be reduced by many orders with the use of this primitive RPC method. This fact gives a new meaning and importance to *ab initio* calculations of the potentials.

On the other hand, the GRPC method (next section) was not conceived for simply acceptable approximations of potentials. The intention was to develop a special method that might give very accurate approximations and also serve for the calculation of the spectrum of a molecule, either from the spectrum of another molecule or from an *ab initio* potential.

4.8.2. *The GRPC method*

The non-crossing and the 'quasiparallelity' of the RPCs in the RPC scheme (§3) suggests that it might be possible, by a suitable choice of the values of some GRPC parameters (§2.2), to deform and at the same time move, in the RPC scheme, the RPC of a molecule (and state) A so that it should coincide to a high degree of accuracy with the RPC of another molecule (and state) B. However, our task is more difficult and the question may be formulated as follows: (a) If one chooses the values of the GRPC parameters in such a way that a coincidence of the two RPCs in a lower portion of the potential (up to 40 % of D_e, say) is obtained, would then the coincidence in the upper portion of the RPC (say, up to the dissociation limit) follow? That is, can one define in this way a method for the calculation of an accurate extension to higher values of energy of the potential of A from the potential of B? (b) Can one also use in this way *ab initio* calculated potentials?

It seems *a priori* clear that, in the attractive limb, this task may possibly be feasible for the same state within a group of affiliated molecules (e.g. for the ground state potentials of the alkali diatomic molecules) where this 'quasiparallelity' indeed holds, and that it might be more difficult for two cases which differ in their physical structure where this 'quasiparallelity' is to some extent violated, e.g. the ground state and the A-state potentials of the alkali diatomic molecules (see figure 19 and §3.3).

It is also clear that this task will be much easier in the repulsive limb than in the attractive limb of the potential because of the simple geometric form of the former (figure 3) and the general validity of the non-crossing rule (§3.1) and its insensitivity to small errors in the value of D_e. Evidently, the choice of the GRPC parameters and the fitting should in general be made *separately* for the two limbs of the potential because of their different geometry.

It has been shown that the GRPC method may, indeed, be successfully used for this purpose, at least for some groups of affiliated molecules and *ab initio* calculations in the attractive limb, and quite generally in the repulsive limb.

The essence of the GRPC method is the following [25, 28, 56]. Let the RKR (IPA) potential of a molecule (and state) A be known only up to $x\%$ of D_e and the potential of a molecule (and state) B be known up to $y\%$ of its own D_e, $y > x$, and let the molecular constants, r_e, ω_e (k_e), and D_e, be known for both A and B. Then the GRPC of B is fitted to the known portion of the potential of A by varying a chosen set of GRPC parameters (and chosen correction functions, see equations (14) and (19)) and the extension of the potential of A is calculated from this GRPC of B by inversion of the RPC formula (equations (5) and (6)) using the molecular constants of A. Exchanging the roles of A and B, the procedure is repeated *mutatis mutandis* (i.e. varying the parameters in the GRPC of A and inverting the GRPC formula) and the average of the two extensions of the potential of A so obtained is then used to extend the potential of A. (Only one (one-sided) procedure is often sufficient for a good approximation [28].)

The same calculation may be performed using instead of B an *ab initio* potential of A or an *ab initio* potential of another suitable (affiliated) molecule.

Other variants are also possible, e.g. moving, in the RPC scheme, the RPC of A towards the RPC of B (and vice versa) by a change in the nominal value of a GRPC parameter before the variation of the chosen GRPC parameters in the case of problems with distant RPCs (see figure 12 in [25] for excited states of NaK).

It is also possible to make a fit of the (extended) potential of A itself by inverting the GRPC formula in each step of the fitting procedure and minimizing the difference between the result and the (fitted) potential [42]. Nevertheless, the results obtained with the use of the method described above have so far been satisfactory and we shall discuss them briefly in the following.

4.8.3. *One-parameter GRPC approximation*

Intuitively, the parameter α in equation (19) appears to be the most important. Indeed, it has been shown that, using only this parameter in the GRPC method, one can obtain a very good approximation of the extended potential, particularly in the repulsive limb.

In [25] 'empirical rules' were used to reduce the error limit by about 50%. These rules were based on the regular behaviour of the GRPC in the RPC scheme in both limbs. However, the errors were also very small without the use of these 'empirical rules' which were then abandoned in the further development of the method. The limit

of error in extensions from 40–45% up to the dissociation limit were generally less than 0·002 Å in the repulsive limb [25]. It was not necessary to use potentials of the same state and of an affiliated molecule (e.g. the repulsive limb of the ground state potential of I_2 was used to extend the repulsive limb of the ground state potential of HF from 40% of D_e up to the dissociation limit with error limit in p of 2×10^{-4}, i.e. about 4×10^{-4} without the use of the 'empirical rules' (figure 9 of [25])). The use of the repulsive limb of the (weakly bound) excited d-state of XeO (§3.4) for the extension of the repulsive limb of the ground state of I_2, in the same limits of energy, led to an error limit in p of about 2×10^{-4}, i.e. about 4×10^{-4} without the use of the 'empirical rules' (this was, of course, a special case). The ground state potentials of Rb_2 and RbCs (which were then known only up to 72% of D_e) were *predicted* by this method in [30(*a*)] and the limit of error was later verified to be smaller than 0·001 Å (see figure 11 of [25]).

In a sense, the GRPC extension of the repulsive limb of an RKR (IPA) potential may be more accurate than the potential itself, since one may avoid the 'wiggles' which often lead to an error *much larger* than 0·002 Å. This may be achieved using a potential of some affiliated molecule which has no significant 'wiggles' [42] or an *ab initio* potential or an analytic function like the Morse function (which gives as such only a miserable approximation to the true potential). For example, the use of a Morse function of Rb_2 led in general to limits of error less than 0·002 Å. It was employed, for example, for the extension of the repulsive limb of the ground state potentials of the alkali hydrides [33(*c*)] and the B-state potentials of alkali diatomic molecules [38]. The advantage of the use of *ab initio* potentials or the Morse function is the fact that the 'wiggles' are completely avoided. The disadvantage of the *ab initio* potentials is the small number of points, while the advantage of the empirical potential functions is the unlimited number of points and the continuation above the dissociation limit (easy calculation).

The attractive limb of the ground state potentials of Rb_2 and RbCs was a more difficult problem, since the values of D_e were not accurately known (the values $D_e(Rb_2) = 3950$ cm^{-1} and $D_e(RbCs) = 3833$ cm^{-1} were recommended by the experimenters, see table 1 of [30(*a*)]). The GRPC fit was calculated for different values of D_e and it was suggested that the value of $D_e(Rb_2)$ should be larger than 3950 cm^{-1} (see table 20 of [30(*a*)], the correct value is 3994·4 cm^{-1} [80]). Unfortunately, a too small value of $D_e(Rb_2)$ was still used (3960 cm^{-1}) so that the extension up to the dissociation limit was inaccurate.

The value $D_e(RbCs) = 3843$ cm^{-1} was proposed on the basis of GRPC calculations as the most probable value in table 22 of [30(*a*)]. This value was then also confirmed by the RPC estimation in [84] (with the assumption that the potential of [68] was, indeed, correct, see §4.6). For the (one-sided) GRPC prediction of the attractive limb of the potential of RbCs in [30(*a*)] using this value of D_e, the limit of error was less than 3 cm^{-1} (this is shown on p. 408 and in figure 7 of [25]).

Figure 6 of [25] shows the extension from 30% of D_e up to the dissociation limit of the ground state potential of HCl in the attractive limb (using an inaccurate *ab initio* potential of HF) with an error limit of 5×10^{-4} D_e(HCl). As the value of D_e(HCl) is large, the error was about 18 cm^{-1}. Further examples may be found in [25].

A further application of this one-parameter method was the extension of the RKR potentials of the A-state potentials of the alkali diatomic molecules LiNa ($2^1\Sigma^+$) and K_2 ($1^1\Sigma_u^+$) for which the RKR potentials were known only up to 60% of D_e [42]. Unfortunately, the ground state RKR (IPA) potentials were used for the (one-sided) GRPC fit which may have led to errors (only) in the attractive limb because of the

slightly different geometry (and crossing) of the RPCs (figure 19). Indeed, the differences between the (not quite accurate) RKR potential of the A-state of Na_2 [70] and the GRPC approximation in the high portion of the attractive limb (above 90% of D_e) of the potential (limit of error ≈ 10 cm^{-1}) might be caused by this difference between the geometry of the RPCs of these two states (compare figures 6 and 10 of [42] and figure 19 of this paper). A better strategy might have been to use the *ab initio* potentials of the A-state from [39(b), (c)] for the LiNa and Na_2 molecules which, however, contained only a small number of points (no adequate potential was available for K_2).

This simple one-parameter method was further used for the construction of the RKR ground state potential of NaRb [86] for which the value of D_e could be determined from the predissociation of the excited B-state to be 5030 ± 2 cm^{-1} [87]. Unfortunately, the RKR potential could be constructed only up to 13% of D_e [87] which is too small a value of energy for an accurate extension. Moreover, the RKR potential appeared to be slightly in error and was, therefore, not used for an extension. The repulsive limb was calculated (ignoring the RKR potential) using an α-GRPC approximation with a Morse function (see above), the ordering rule and the close-lying RPCs of the other alkali diatomic molecules (§3.1) for an estimate. The limit of error was estimated as 0·004 Å. A larger limit of error certainly exists in the calculation of the attractive limb (estimated to be about 60 cm^{-1}) where a *rough* estimate of the attractive limb was calculated using the fact that the ground state RPCs of heteronuclear alkali diatomic molecules are located around the mean of the RPCs of the respective homonuclear molecules (here Na_2 and Rb_2). An α-GRPC approximation with the ground state potential of K_2 was used.

The one-parameter approximation is better than the majority of the known methods, however, in the attractive limb it is too inaccurate. Here, the multi-parameter GRPC method should be employed.

4.8.4. *The multi-parameter GRPC method*

It is *a priori* clear that the multi-parameter GRPC method could in principle yield better results than the simple one-parameter method. It is also clear that more parameters would lead to a better fit, however, not necessarily to a better extension (extrapolation) of the potential (which has also been confirmed in the calculations).

As has been explained and repeated many times in the preceding sections, slight differences in the geometry of the RPCs of different groups of affiliated molecules and also between the RKR (IPA) RPC and an *ab initio* RPC may exist. Therefore, if *very* accurate results are to be obtained, the most suitable ensemble of GRPC parameters (and correction functions) should in principle be chosen for a certain group of affiliated molecules or for an *ab initio* method. Such a choice is, of course, only possible if accurate potentials and values of the molecular constants are known for several (at least two) molecules of the same group or if a certain *ab initio* method has been tested on a series of cases. The experimental values of the molecular constants are obtained from the spectroscopic data and the *ab initio* values from the *ab initio* potential. The method of their determination may sometimes lead to slight errors or uncertainties which must be taken into account. This problem has been discussed in [56] and will not be commented on here.

The multi-parameter GRPC method was thoroughly tested on the ground states of the alkali diatomic molecules, Li_2, LiNa, Na_2, NaK, K_2, Rb_2, RbCs, and Cs_2 [28] since,

for these eight affiliated molecules, the RKR (IPA) potentials had been determined from the spectra for very high energy values and the value of D_e could be accurately determined with the use of the LeRoy–Bernstein extrapolation [29] (a slightly less reliable upper portion of the potential and D_e value was obtained for RbCs, §4.6). The method was then used for the estimation of the dissociation energy of KRb [81(*b*)] (§4.6) and the prediction of the ground state potential of KRb and its spectrum above 68 % of D_e [81(*b*), 56] (see §4.9).

As has been emphasized in the preceding section, the use of the exponential parameter α in the GRPC fit (up to, say, 40 %) already guarantees an error limit smaller than 0·002 Å in the extension of the *repulsive* limb up to the dissociation limit. If this degree of accuracy is considered as sufficient, this one-parameter GRPC approximation may be employed for the extension of the repulsive limb. For the extension of the attractive limb, the most suitable set of GRPC parameters should be found.

In the following, we discuss only the calculations performed for the attractive limb of the ground state potentials of the alkali diatomic molecules for which all experimental data are very accurately known.

Apart from the exponential parameter α, the parameter ξ appears to be important, modifying the zero of r in the exponent (equation (19)). The parameter ε which modifies the 'reduced force constant' also appears to be important, in particular in cases where the value of the force constant, k_e, is not quite reliable, which may often be the case for *ab initio* potentials (the variation of ε is equivalent to the variation of the parameter k_e in ρ_{ij}, (equation (20)).

The set of these three parameters indeed gave the best overall results for the extension of the attractive limb of the ground state potentials of the alkali diatomic molecules in the tests performed for the eight molecules listed above. For the 56 test cases, the error limit in this three-parameter GRPC extension of the attractive limb from 45 % of D_e up to the dissociation limit was smaller than 10 cm^{-1} with only a few exceptions (see below). For the combinations of the set of molecules heavier or equal to Na$_2$, it was in fact essentially smaller (less than 1 cm^{-1}) in many cases. (So for the combinations of K$_2$ with Na$_2$, NaK, Rb$_2$, RbCs, and Cs$_2$, already the *one-sided* variations of the GRPC parameters led to an error limit of 1–3 cm^{-1}, figures 3 and 4 of [28].) Larger errors appeared only in calculations including the lightest molecules Li$_2$ and LiNa, in particular in combination with the heaviest molecules. So the limit of error in the extension of the potential of K$_2$, calculated from the potentials of Li$_2$ and LiNa, was only less than 6 and 5 cm^{-1}, respectively. The largest errors appear around 90 % of D_e or higher (largest bend of the RPC).

The numerical implementation is given at the end of [28], where it was stipulated that no damping was necessary and equal weight was given to all points of the potentials, and the calculated values of the parameters were statistically well-defined. In spite of the high correlation of the parameters (which might be partly responsible for the good extrapolation), the convergence was very good. There are only three exceptions, i.e. the extension of the potentials of Cs$_2$, RbCs, and Rb$_2$ with the use of the potential of Li$_2$.

In the calculation of the extension of the potentials of the three heavy molecules using the RKR potential of Li$_2$, damping had to be used and the calculation of the constant ρ_{ij} did not converge. The reason could be to some extent due to the relatively large difference between the RPCs of the two molecules (figure 10) and the small value of ρ_{ij}(Li$_2$) = 1·17285. In such a case, the fitting procedure must be considered as an
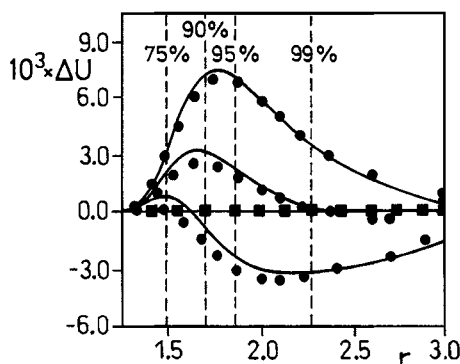
Figure 32. Attractive limb. Differences in energy from the IPA ground state potential of Rb_2 or Cs_2 (zero line) of the GRPC extensions from 45% of D_e up to the dissociation limit of these IPA potentials using the IPA ground state potential of Li_2. For each molecule, the values of its r_e and D_e are taken as the units of internuclear distance and energy, respectively. VAR = variation of α, ε, and ζ, AV = average (see text). (———) from top to bottom: Cs_2 (VAR-Cs_2), Cs_2 (AV), Cs_2 (VAR-Li_2). (●) from top to bottom: Rb_2 (VAR-Rb_2), Rb_2 (AV), Rb_2 (VAR-Li_2). (■) average extension of the IPA ground state potential of Cs_2 from 30% of D_e up to the dissociation limit using the IPA ground state potential of K_2. The vertical lines denote the percentage of D_e (Cs_2).

asymptotic method, i.e. the calculation is stopped when the value of ρ_{ij} begins to rise above a certain limit (say, $\rho_{ij} = 10$). This means that the resulting values of the varied parameters are not so uniquely determined as in the converging case, with respect to the special procedure used, however, one easily finds that the dependence of the result on the chosen upper limit of ρ_{ij} is practically insignificant, i.e. the results are reproducible and are very good (figure 32). For such a procedure, the more interactive program [28] is more suitable than the fully automatic program [56]. As these calculations are more problematic than for other cases, we show in figure 32 the results for Rb_2 and Cs_2 and give the values of the parameters in table 1. It is interesting to note, in figure 32, that the relatively large limit of error (about $10.7\ cm^{-1}$ for Cs_2 at about 90% of D_e) is not caused by the errors in the procedure where the parameters are varied in the GRPC of Li_2 (limit of error about $12\ cm^{-1}$), but by the errors arising when the parameters in the GRPC of Cs_2 are varied (limit of error about $22\ cm^{-1}$). However, in contrast to the other cases (see figure 5 of [25]), the maximum error in the extension obtained from the GRPC of Li_2 is shifted to very large values of r so that the errors in the two extensions compensate to a much lesser extent (in fact, the extension obtained from the GRPC of Li_2 would give a much better approximation to the IPA potential than the average extension up to 90% of D_e).

As the D_e value of Li_2 is much larger ($8516.8\ cm^{-1}$), the absolute error in the corresponding extension of the RKR potential of Li_2 using this procedure was somewhat larger (about $20\ cm^{-1}$ in these three 'pathological' cases). On the other hand, the limit of error in the (average) extension of the IPA potential of LiNa calculated from the IPA potential of Cs_2 was less than $2\ cm^{-1}$ (D_e (LiNa) = $7105.3\ cm^{-1}$).

The following important point should be emphasized as it can sometimes lead to a misunderstanding for the reader: the GRPC parameters in the fitting procedures described above have *no direct physical meaning*, they are simply formal (geometrical) fitting parameters. A certain change in the numerical procedure may imply a slight change in the value of the varied GRPC parameters which has, however, no significant

Table 1. Values of the GRPC parameters for the GRPC extension of the IPA ground state potential of Cs_2 from 45 % of D_e up to the dissociation limit using the RKR ground state potential of Li_2 (VAR = variation of the GRPC parameters).

Molecule 1	Molecule 2	α	ε	ξ
Li_2(VAR)	Rb_2	0·164 4418	1·007 952	−3·915 931
Li_2	Rb_2(VAR)	3·022 408	1·006 394	2·176 295
Li_2(VAR)	RbCs	0·187 0198	1·006 766	−3·246 340
Li_2	RbCs(VAR)	3·326 359	1·014 523	2·437 972
Li_2(VAR)	Cs_2	0·192 4324	1·010 004	−2·950 598
Li_2	Cs_2(VAR)	3·579 692	1·017 236	2·662 362

effect on the result, i.e. on the extension of the potential (an effect which is practically invisible even with the very fine scale of the difference curves shown in the figures). It is clear that, in an optimization procedure, one never attains the absolute minimum in the parameter space. With a small change in the fitting procedure (e.g. the order of the polynomials, etc.) only a slight but consistent change may occur in the values of all varied parameters in such a way as if one moves in a small circle around a minimum. The orthogonal polynomials used throughout in the piecewise polynomial interpolation of the potentials [88, 28, 56] yield, of course, essentially better results than normal polynomials.

The second possibility for the extension of a potential is the use of *ab initio* potentials. All calculations of this type performed so far have been based on the one-sided variation of the GRPC parameters in the RKR (IPA) potential (an accurate interpolation of the few points of the *ab initio* potential would be problematic). Such calculations have been shown [42, 28] for the ground state of LiNa, Na_2, NaK, and K_2 (for heavier molecules, the *ab initio* calculations are not considered reliable for this procedure, they should be made with the GRPC application already in view). All extensions were again made from 45 % of D_e up to the dissociation limit. For Li_2, the extension using the *ab initio* potential of [39(a)] and the simple inversion of the RPC formula (§4.8.2) already leads to practical coincidence with the RKR potential. For the *ab initio* potential of LiNa of [39(b)], the use of the one-parameter (α) GRPC approximation led to negligble errors in the extension of the IPA potential for $\alpha = 1\cdot01$ (see figure 4 of [42]).

As has been mentioned in §3.2, the errors in the *ab initio* value of D_e (cm^{-1}) of Li_2, LiNa, Na_2, and K_2 [39(a)–(d)] were 50, 49, 77, and 56, respectively, but the deviation of the *ab initio* RPC from the RKR (IPA)/RPC increased with increasing number of electrons. Therefore, for the heavier molecules Na_2 and K_2, more parameters had to be used. Figure 33 shows the deviation of the GRPC extensions from the RKR (IPA) potentials, where apart from the *ab initio* potential of Na_2 [39(c)], less accurate and less suitable *ab initio* potentials were also used for Na_2 and NaK. The use of two parameters, α and ε, leads to an error limit less than 4 cm^{-1} for the *ab initio* potential of Na_2 from [39(c)] (appearing above 95 % of D_e) but to a slightly larger limit of error for the *ab initio* potential of K_2 from [39(d)]. However, the use of the third parameter, ξ, essentially improves the result for K_2, reducing this limit of error to a value significantly less than 1 cm^{-1}. The error in the value of D_e (cm^{-1}) was much larger for the *ab initio* potentials of Na_2 and NaK [89(a), (b)] (300 and 215, respectively) and the corresponding errors in the extensions are also larger but are still acceptable. For Na_2, the limit of error is about 11 cm^{-1}, using the parameters α and ε. The use of a further
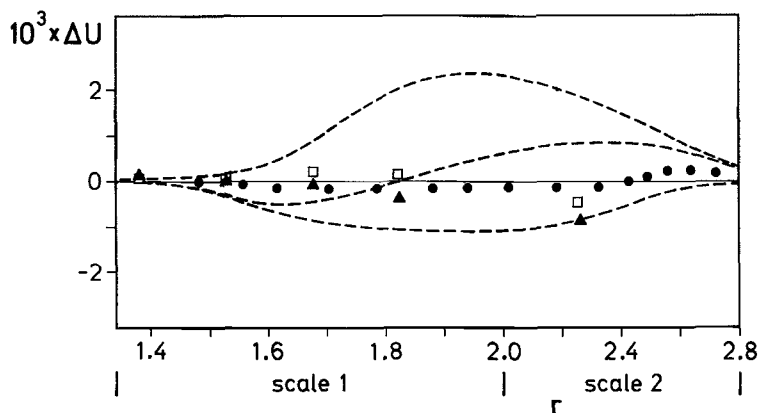
Figure 33.   Ground state (from [28]). *Ab initio* GRPC extensions of the attractive limb from 45% of D_e (i.e. using *ab initio* potentials). Differences in energy from the RKR potential curve of Na_2, NaK, or K_2 are shown. The zero line represents the RKR potential curve of Na_2, NaK, or K_2, respectively, and for each molecule its experimental values of r_e and D_e are taken as units of r and U, respectively. (-----) from top to bottom: Na_2 [89(a)], Na_2 [39(c)], K_2 [39(d)], variation of α and ε. ($\bullet$) K_2 [39(d)], variation of α, ε, and ξ. ($\square$) NaK [89(b)], variation of α, ε, and r_e. ($\blacktriangle$) NaK [89(b)], variation of α, ε, ξ, and r_e. All curves have a common minimum. Two different scales are used for the two intervals of r to make the figure more readable (i.e. not too compressed for small values of r).

parameter could not bring about any improvement. For NaK, the use of three parameters, α, ε, and r_e led to an error limit less than 3 cm^{-1}. It seems that, in general, the use of the parameter r_e might be more efficient in these calculations than the use of the parameter ξ. The use of the parameter ε is, of course, important because of a possible small uncertainty in the *ab initio* value of k_e (see above, and also [28]).

It is apparent that the application of the GRPC method could give a new significance to the calculation of the *ab initio* potentials (under the condition that the rules of §3.2 be respected), since the accuracy of the *ab initio* potentials may be significantly improved by the GRPC method. Perturbations often appear in higher excited states and a full deperturbation may sometimes be a difficult task. Deviations of the corresponding RPC in the RPC scheme then result (see §4.4). The *ab initio* potentials are, of course, free from this perturbation effect so that they could, in fact, be more suitable for the application of the GRPC method than the corresponding RKR (IPA) potentials if the conditions of §3.2 are respected. This would not pose serious problems for light molecules: however, it is still not possible for the present *ab initio* calculations of the potentials of heavy molecules. (Also as has been mentioned in §3.2, such *ab initio* potentials are not published and could not be obtained from the authors.)

The application of the GRPC method is not limited to the use of the potentials of affiliated molecules or an *ab initio* potential of the same molecule and state; potentials of other non-affiliated molecules or *ab initio* potentials of other molecules may also in principle be used. One should, of course, expect *a priori* that the results would then be worse. We have mentioned already in §4.8.3 the one-parameter (α) extension of the attractive limb of the potential of HCl from 30% of D_e up to the dissociation limit using an *ab initio* potential of HF, where the limit of error was only $5 \times 10^{-4} D_e$ (HCl). In figure 34, we show the one-sided three-parameter (α, ε, ξ) GRPC extension of the
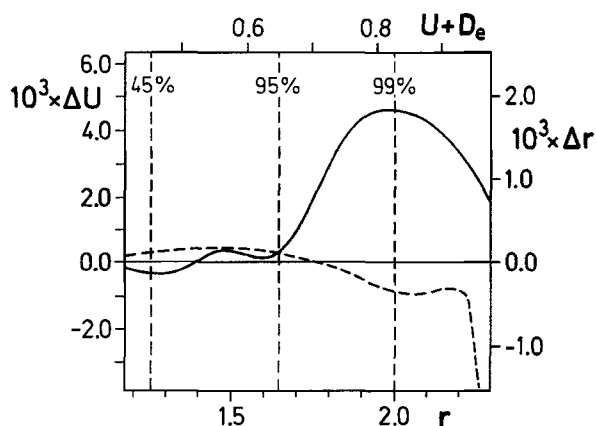
Figure 34. Attractive limb. Differences from the RKR ground state potential of Cl_2 of the GRPC extension of this potential from 45 % of D_e up to the dissociation limit using the ground state potential of H_2 and varying the parameters α, ε, and ξ in the GRPC of Cl_2. The values of $r_e(Cl_2)$ and $D_e(Cl_2)$ are taken as units for the internuclear distance and the energy, respectively. The vertical lines denote the percentage of $D_e(Cl_2)$. The left hand and lower scale for differences in energy U, the right hand and upper scale for differences in r. Solid line: differences in U. Broken line: differences in r. $\alpha(Cl_2) = 2\cdot3309049$, $\varepsilon(Cl_2) = 1\cdot0030099$, $\xi(Cl_2) = 0\cdot5272726$.

attractive limb of the ground state potential of Cl_2 (from 45 % of D_e) using the ground state potential of H_2. (The variation of the exponential parameters cannot be used for H_2 where the value of $\rho_{ij} = 0\cdot018$ is too small.) One may verify, in figure 34, that the error is of the order of $10^{-4} D_e$ up to 95 % of D_e (error limit less than $6\cdot5$ cm^{-1}) but then abruptly rises to a maximum at about 99 % of D_e (error limit of about 108 cm^{-1}). The asymptotic confluence with the RKR potential is, of course, guaranteed by definition of the GRPC method. So one could use such a procedure if the critical region above, say, 93 % of D_e is omitted. A satisfactory extension from 45 % of D_e up to 90 % of D_e can still be obtained.

In figures 2–5, we have shown the change of the GRPC with changing values of the different GRPC parameters. An inspection of figures 2 and 3 shows that the effect of these parameters decreases rapidly above 80 % of D_e and is quite small above 95 % of D_e. For this reason, the variation of the parameter D_e was tested and figure 1 of [42] shows that a change of 4 cm^{-1} in the value of D_e (Na_2) could make the errors negligible in the one-parameter GRPC approximation ($\alpha = 1\cdot016$). However, a change in the value of D_e leads in principle to incorrect behaviour of the potential in the far asymptotic tail. Perhaps a suitable choice of the correction functions, in particular of the correction function in the definition of the reduced energy (14), could improve the results for high energy values. At any rate, the asymptotic confluence of all RPCs is guaranteed by definition so that the GRPC method could be employed for accurate approximation of the far tail of the potential above 99·9 % of D_e, in particular using RKR (IPA) potentials of (affiliated) molecules with similar atomic numbers or an *ab initio* potential (see figures 10, 32–36).

4.9. *Calculation of the spectrum by the GRPC method*

One of the tasks of the GRPC method is the *prediction* of the spectrum of a diatomic system above the energy limit of the measured spectrum. If such a calculation
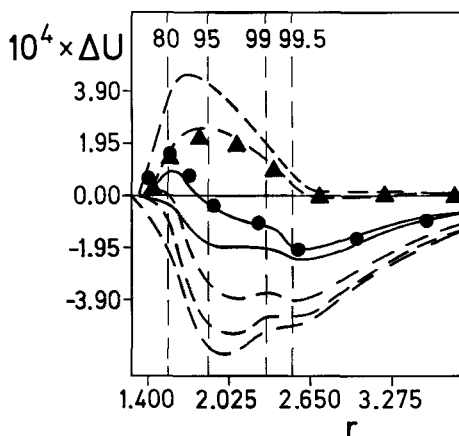
Figure 35. Attractive limb (from [56]). Differences in energy from the IPA potential of Cs_2 (zero line) of the GRPC extensions from 30%, 50%, and 70% of D_e, respectively, calculated from the IPA potential of K_2 by variation (VAR) of the GRPC parameters α, ε, and ξ in the GRPC of K_2 or Cs_2, respectively, and their average (AV). (——) from top to bottom: 70%, AV; 50%, AV; (●) 30%, AV. (-----) from top to bottom: 30%, VAR-Cs_2; 70%, VAR-Cs_2; 70%, VAR-K_2; 30%, VAR-K_2; 50%, VAR-K_2, (▲) 50%, VAR-Cs_2. The values of $r_e(Cs_2)$ and $D_e(Cs_2)$ are used as units of the internuclear distance and the energy, respectively. The numbers on the vertical broken lines denote percentage of D_e.

is to be meaningful, high accuracy in the GRPC extension of the RKR (IPA) potential of the respective diatomic system was to be achieved. A concrete problem was the prediction of the spectrum of the ground state of KRb that has been measured only up to $v = 45$. The experimental value of D_e (KRb) is not known and was estimated using the GRPC method to be 4220 $cm^{-1} \pm 10$ cm^{-1} (§4.6). (Hence the spectrum of KRb has been measured only up to about 68% of the estimated value of D_e). The highest value $v = 45$ was not considered because of possible errors which may often occur for the last levels.

The method had, of course, to be tested first on the known potentials of other alkali diatomic molecules [56]. Figure 35 shows the three-parameter $(\alpha, \varepsilon, \xi)$ GRPC extensions of the IPA ground state potential of Cs_2 [83(a)] from 30%, 50%, and 70% of D_e, respectively, using the IPA ground state potential of K_2 [44(i)] together with the corresponding extensions calculated by the variation of the GRPC parameters in the GRPCs of the two molecules. (The LeRoy–Bernstein extrapolations of these potentials have been included. The values of the constants C_n etc. given by the experimenters were used and very slightly adapted to smooth off any discontinuities in the potentials.) The extension from 70% of D_e was interesting in view of the prediction for KRb, and the calculation of the other two extensions makes possible a comparison of the functioning of the method for an extension from different energy levels. Figure 36 shows the extensions from 70% of D_e up to the dissociation limit of the IPA potential of Rb_2 [80] using the ground state IPA potentials (with the LeRoy–Bernstein extrapolation) of K_2 [44(i)] and Cs_2 [83(a)].

In figure 35, the error limits for the extension from 30% and 70% are about 0.7 cm^{-1}. Curiously enough, the error limit for the extension from 50% of D_e (and around 50%) is slightly higher (0.88 cm^{-1}) and the errors are also slightly larger in the region between 90% and 99% of D_e. The maximum error appears, in all cases, above
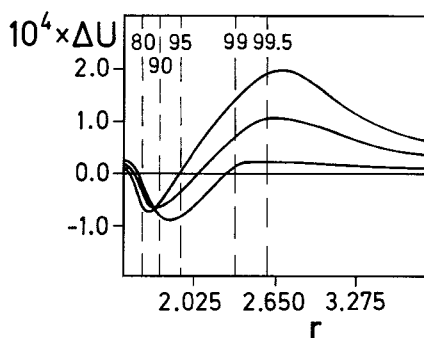
Figure 36.   Attractive limb (from [56]). Differences in energy from the IPA potential of Rb_2 (zero line) of the average GRPC extensions from 70% of D_e calculated from the IPA potentials of K_2, and Cs_2, respectively, and their average. (———) from top to bottom (for large r): Cs_2, average, K_2. The values of $r_e(Rb_2)$ and D_e (Rb_2) are used as units of internuclear distance and energy, respectively. The vertical broken lines denote the percentage of D_e (Rb_2).

99·5% of D_e. (One may also verify that the errors in the one-sided extensions partly compensate.)

In figure 36 only the average extensions are shown, together with their average. The limits of error in the extensions using the potential of K_2 and Cs_2, and in their average, are $0·36$ cm^{-1}, $0·80$ cm^{-1} and $0·58$ cm^{-1}, respectively. It may be verified (table 3 of [56]) that this three-parameter GRPC extension is in fact almost a two-parameter (α, ξ) GRPC extension, since the parameter ε changes its nominal value ($\varepsilon = 1$) only slightly.

Extensions of the attractive limb using current empirical functions like the Morse [6] or the Hulburt–Hirschfelder [27] function are, of course, ridiculously inaccurate (figure 3 of [56]).

However, it appears that the accuracy obtained in the one-parameter (α) GRPC extension of the repulsive limb, even with an error limit of $0·001$ Å (§4.8.3), is not sufficient. It implies too large an error in energy, which is, of course, decisive for the 'energetic' calculation of the spectrum (see figures 5 and 6 of [56]). Other methods currently used by the spectroscopists for the extension of the repulsive limb have been shown to be impossibly inaccurate (figure 4 of [56]).

The use of other GRPC parameters does not seem to lead to a satisfactory improvement. Therefore, a correction function in ρ (19) of the type

$$F_{corr}(r, \varphi_i) = \varphi_0 + \varphi_1 r^{\varphi_2} + \varphi_3 r^2 \qquad (21)$$

was used, although the last term has proved to have little significance. Two GRPC parameters, α and ε, were employed. φ_0, φ_1, φ_2, and φ_3 are additional fitting parameters. In contrast to the three-parameter $(\alpha, \xi, \varepsilon)$ case, the correlation of the parameters here is not large, however, the fitting procedure does not converge and the procedure must again be considered as an asymptotic method, interrupting the calculation when a sufficiently small standard deviation is achieved. (Again the interactive program enabling a supervision on the monitor is more suitable here.)

In spite of these problems, extremely good and reproducible results have been obtained and speak for themselves. The difference between the results of the two calculations using the variation of the parameters in the GRPCs of the two molecules

is, as a rule, negligible. The limit of the difference from the IPA potential was, for example for Cs_2, less than 5×10^{-4} Å (less than 3.6 cm^{-1}) for the extensions from 50% and 70% of D_e, and slightly larger for the extension from 30% of D_e (not considering the wiggles in the IPA potential, see figures 5 and 6 of [56]). This difference appeared only in the highest portion of the extension. For Rb_2, this difference was even smaller.

The remaining problem was the existence of the wiggles in the highest portion of the repulsive limb of RKR (IPA) potentials which could make the extension of the potential and the calculation of the spectrum for high energy levels inaccurate. In our case, these wiggles were most significant in the IPA potential of Cs_2 and already appeared above 85% of D_e (which may be easily visualized by comparison with an analytic function, see figures 5 and 6 of [56]). For Rb_2, the wiggles are small and appear only in the highest portion; for K_2, the wiggles are essentially smaller than for Cs_2 but must be eliminated. This problem was solved by extrapolating the repulsive limb above 85% of D_e for K_2 and Cs_2 and above 97% of D_e for Rb_2 using the LeRoy [90] or the Morse [6] function. The IPA method is an iterative procedure comparing the potential with the energy values so that the wiggles were certainly included in the calculation of the points of the IPA potential of Cs_2 [83(a)] where no extrapolation of the repulsive limb is indicated. This should be taken into account in judging the errors in the highest energy levels of the spectrum of Cs_2 calculated by the GRPC method (table 7 of [56]).

The results were very good. The spectrum was calculated by a Numerov–Cooley type method [18], and the numerical implementation is given in [56]. The method was tested on a Schrödinger equation with a Morse potential for Li_2 (Li_2 has the least density of points hence represents the more difficult case) and for all 46 existing vibrational levels the errors were less than 0.0003 cm^{-1}. (On the eigenvalues of the Morse potential see Appendix 3 of [56]).

The results for the vibrational energy levels are shown in tables 7–10 of [56]. For the extensions of the potential of Cs_2 from 30%, 50%, and 70% of D_e, the limit of error in the vibrational energy levels G_v(cm^{-1}) was 0.4422, 0.6577, and 0.3807, respectively, appearing only for the highest vibrational level ($v = 137$), i.e. for 99.44% of D_e. The error of 0.1 cm^{-1} appeared at 92.5%, 75%, and 95% of D_e for the extension from 30%, 50%, and 70% of D_e, respectively. The worst result for the extension from 50% of D_e is a consequence of the worst approximation of the potential mentioned above (figure 35). The reason is not quite clear and may have computational reasons.

The limit of error in the differences between adjacent vibrational energy levels ΔG_v(cm^{-1}) was 0.0404, 0.0263, and 0.0402 for the extension from 30%, 50%, and 70% of D_e, respectively, and the error of 0.01 cm^{-1} appeared at 94.6% of D_e for the extensions from 30% and 70% of D_e, and for 88% of D_e for the extension from 50% of D_e. (Errors greater than 0.01 cm^{-1} appeared above $G_v = 88\%$ of D_e with a maximum of 0.056 at 96% of D_e for the application of this procedure to the nominal IPA potential of Cs_2 itself and the limit of error for ΔG_v was here 0.0036 cm^{-1} at 97% of D_e.)

For the extension of the IPA potential of Rb_2 from 70% of D_e, using the IPA potential of K_2, the limit of error in G_v was 0.1925 cm^{-1} at 96.2% of D_e, decreasing to 0.0255 cm^{-1} for 99.59% of D_e. Errors greater than 0.1 cm^{-1} appeared above 93% of D_e. The limit of error in ΔG_v was 0.0371 cm^{-1} for 98.94% of D_e, and errors greater than 0.01 cm^{-1} appeared above 88% of D_e.

For the extension of the IPA potential of Rb_2 from 70% of D_e, using the IPA potential of Cs_2, the limit of error in G_v was 0.5210 cm^{-1} at 99.59% of D_e, and an error

greater than $0\cdot1$ cm^{-1} appeared above 98 % of D_e. The limit of error in ΔG_v was $0\cdot0559$ at $99\cdot59$ % of D_e, and errors greater than $0\cdot01$ cm^{-1} appeared above 97 % of D_e. For the average, the limit of error in G_v was $0\cdot2768$ cm^{-1} at $99\cdot59$ % of D_e and an error of $0\cdot111$ cm^{-1} appeared at $96\cdot21$ % of D_e. The limit of error in ΔG_v was $0\cdot0429$ at $98\cdot94$ % of D_e.

As the rotational term (in the Schrödinger equation) is an exact function of r, analogous error limits would be obtained in the calculation of the rotational spectrum from the effective potentials, as has also been confirmed by direct calculations.

To my knowledge, there exists no other method that could yield a comparable accuracy in the calculation of the spectrum. For the extensions from energy values less than 30 %, this accuracy could not be obtained, since for Cs_2, the extensions from 25 % and 20 % of D_e had limits of error of $1\cdot85$ cm^{-1} and $3\cdot28$ cm^{-1}, respectively.

The results of these tests make clear that the use of the GRPC method could guarantee a sufficient accuracy in the prediction of the unmeasured spectrum of the ground state of KRb if the accurate value of D_e (KRb) were known. However, the experimental value of D_e (KRb) is not known and had to be estimated with the use of the GRPC method as 4220 ± 10 cm^{-1} (§4.6). Therefore, the prediction of the spectrum above $v = 44$ was made for the following values of D_e (cm^{-1}): 4210, 4220, 4225, 4230. The IPA potential of K_2 [44(i)] was used for the extension (the maximum difference from the extension using the IPA potential of Rb_2 [80] was only $0\cdot24$ cm^{-1}, slightly larger than the difference from the extension using the IPA potential of Cs_2 [83(a)], see figure 7 of [56]). The predicted values of the vibrational energy levels and the differences ΔG_v are contained in tables 13 and 14 of [56]. The values above $v = 66$ (90 % of the estimated D_e) are given for the sake of interpolation between the data for the various values of D_e. The rotational (and vibrational) energy levels are given in tables 15 and 16 of [56] as shorthand information in the form of Dunham-type coefficients [5] calculated for $J = 0$–50 only for the vibrational quantum numbers $v = 46$–66 because of the uncertain value of D_e, to avoid unnecessary errors. Maximum error in the energy levels calculated with these Dunham-type coefficients was of the order of 10^{-3} cm^{-1}. As for the vibrational energy levels, these values could be interpolated if the exact value of D_e (KRb) could be determined, say, from the predissociation of some excited state. We hope that this information—together with the potentials—could also be helpful for the experimenters.

A remark seems worthwhile with respect to [56]. The intention was to give the values of all parameters so that all the results should be easily verifiable. Unfortunately, the print of the programs was not set up for so many digits as would have been necessary for an exact reproduction of the results, since such a high degree of accuracy had not originally been expected. I became aware of this fact after having concluded the calculations. Printing more digits would have meant repeating the whole computational procedures, for which I no longer had the time because of my retirement. I think that the values of the parameters given in [56] will suffice to reproduce the figures (i.e. the errors in the potentials), however, they will not be sufficient for the accurate reproduction of the spectrum. Nevertheless, all the potentials (even the test potentials) may be obtained on request by e-mail from the editor of [56]. They are given to seven and nine figures for r and U, respectively, which may suffice to reproduce the spectrum at least up to the order of 10^{-2} cm^{-1} correctly. I am sorry for this inadvertence, it would have been no problem to have the results printed to more figures if this problem had been realized earlier.

In concluding, the following remarks seem necessary: the test calculations of the

spectrum evidently show the extreme accuracy of the GRPC extensions for the heavier alkali diatomic molecules. It is to be noted that the relative errors are always very small (i.e. in units of D_e) but the absolute errors (in cm^{-1}) may be, of course, larger for molecules with a very high value of D_e (see the example of Cl_2 in §4.8.4). The very small order of the errors was also due to the fact that the errors in the two extensions, calculated by varying the GRPC parameters in the GRPC of the two molecules at a time, were of opposite sign and compensated for in the calculation of the average extension (the RPC is moved in the RPC scheme in the opposite direction in the two calculations). For further hints, see [56].

5. Criticism of the RPC method

In the following a few words should be said on the possible critical remarks with respect to the (G)RPC method.

5.1. *Theoretical background*

As has been explained in the Introduction (§1.1) the idea of the RPC has its origin in a clearly stated mathematical problem of quantum mechanics. However, it is not possible to derive the RPC formulas ((5)–(7) or (13)–(20)) by contemporary mathematical methods. This is regrettable, however, it is not a fundamental objection against the use of the method. Mendeleev's Periodic Table was at first only an empirical scheme, the theoretical background of which was not understood. Only much later was this scheme understood and supported by theoretical arguments in the framework of the (in fact very rough) 'one-electron' approximation of quantum mechanics using the Fermi principle. It is also true that many computational methods are currently used that in principle have a theoretical basis but are not fully justified by correct mathematical arguments. For example, for the Hylleraas method [91] and its application to molecules by James and Coolidge [92], the convergence could not be proved [93] (the old 'proof' [92(*c*)] contains an unpermitted interchange of two limiting procedures). In general, the convergence of the wave function in the Ritz variational method is problematic [94] and has been proved only for special cases. Nevertheless, the Hylleraas and the James–Coolidge method give excellent results [17] and the variational methods are currently used. Similar remarks are also relevant with respect to the perturbation calculations.

It is undeniable that the RPC scheme reflects the laws of the physical structure of the diatomic system (which also permits the detection of errors). It also yields approximation methods much more accurate than other known methods, and it may give a new significance to the *ab initio* calculations of the potentials. Hence its use is justified pragmatically, which finally is the important criterion in the practice.

5.2. *The RPC scheme*

In the RPC scheme, the differences between the RPCs of different diatomic systems are large in the attractive limb, which has been the basis of critical remarks about the RPC method [24]. This criticism was, of course, based on a mistake: the RPC scheme was not conceived for an approximation of the potential or for the construction of a universal potential function (the GRPC approximations are only applications, i.e. a by-product). It was conceived as a scheme for the demonstration of certain *laws* governing the potentials of diatomic systems (§1). In this sense, the larger distances of the attractive limbs may serve for a better distinction of the different RPCs and do not

represent any deficiency (see §3). The very accurate GRPC approximation method is then based exactly on these laws and regularities in the RPC scheme which only make its definition possible.

There is, however, another feature of the RPC scheme which might be considered as a deficiency. For some heavy molecules and weakly bound systems as well as for some higher excited states, the value of p_{ij} is larger than the value of r_e [3]. As a consequence, the value of p is negative for very large values of r and the RPC is no longer defined in this region (e.g. the RPC of the ground state of I_2 can be constructed only up to about 98% of D_e). This fact does not present any problem for the comparison of the RPCs and verification of the laws mentioned above (§3). It is, of course, unwanted in the applications of the RPC method, e.g. for the extension of the potentials. The problem may be solved, for a group of affiliated molecules like the halogens, by moving all RPCs 'upwards' in the attractive limb using a suitable value of some GRPC parameter. For instance, for the value $\alpha = 1·27$, the ground state RPCs of all halogen molecules are already well-defined ($p_{ij} < r_e$). (The ordering is preserved but a slight crossing of the close-lying RPCs of ICl and F_2 then appears which might correspond to the anomalous case of F_2 and also be partly caused by the relatively large uncertainty in the value of D_e (F_2).)

Notwithstanding, this fact seems to show that the definition of the RPC is still not the ideal correct definition and a perfection of this definition may be possible. We shall briefly discuss this question in §6.

5.3. *Criticism of the applications of the RPC method*

As has been shown in §4.8, the RPC method has many useful applications and the GRPC method yields extremely accurate results for the extension of the potentials. Of course, for the application of the (G)RPC method, accurate values of the molecular constants r_e, k_e, and D_e are required as is, of course, the case for any methods using empirical functions or any other definition of a reduced potential. The detection of errors in the potentials or in the analysis of the spectrum using the sensitive repulsive limb is an exception, since the repulsive limb is insensitive to relatively large errors in the value of D_e. (Of course, the accurate value of D_e is not known if the RPC method is used for its estimation.)

An accurate value of D_e is required especially for the use of the GRPC method for the extension of the RKR (IPA) potentials and the calculation of the spectrum. However, even if only the lower portion of a potential is known, an accurate experimental value of D_e may often be obtained from the dissociation energy of a higher excited state, from predissociation or by other methods (see the equations and examples on p. 1325 of [28]).

As for the possible small uncertainties in the *ab initio* value of k_e, this deficiency may be compensated for in the GRPC fit of the parameter ε, the variation of which is equivalent to the variation of k_e (see §2.2). Of course, as has been stipulated in §3.2, the *ab initio* calculations should satisfy certain conditions if they are to be successfully employed in the GRPC method.

The use of the three parameters α, ξ, and ε in general gives good results in the applications of the GRPC method. However, as emphasized in §4.8.4, in general the most suitable set of GRPC parameters (and correction functions) has to be found for any group of affiliated molecules and any *ab initio* method, which is the price to be paid for high accuracy. A further study of this problem will be necessary when more experimental data are available.

6. Perspectives of further development of the RPC method

Further development of the RPC method will only be possible when more experimental material and more suitable *ab initio* calculations are available so that the obligatory tests can be made. There are two essential points that will be briefly discussed below.

6.1. *The GRPC method*

In the GRPC method based on the definition of equations (14) and (19), the use of the correction functions in connection with different GRPC parameters should be tested. As mentioned in §4.8.4, the correction function in equation (14) (definition of u) could possibly bring about some improvement in the extensions of the attractive limb of the potentials.

6.2. *The RPC scheme*

The RPC scheme undeniably has a deeper physical meaning (§3) and provides a useful orientation in the jungle of diatomic systems. However, it appears that the definition of equations (5) and (6) is still not the ideal correct physical definition of the RPC. This is indicated by certain deficiencies mentioned in §5.2. It is my opinion that a correct physical definition of the RPC should contain an *explicit* dependence on the atomic numbers Z_1, Z_2, and the number of electrons, N, in the attractive limb (this dependence being negligible in the repulsive limb, which makes the redefinition of the attractive limb alone possible, see the end of §2.2). The parameter α as a function $\alpha(Z_1, Z_2, N)$ would intuitively seem most suitable for this purpose. One may easily verify that, with $\alpha = 1\cdot27$, $\rho_{ij} < r_e$ follows for all cases so far tested with the exception of the weakly bound and van der Waals systems (§3.4). $\alpha = 1\cdot5$ suffices for all systems except the b- and d-excited states of XeO and $\alpha = 1\cdot8$ suffices for all systems so far studied.

With increasing values of α, the RPCs become more 'compressed' in the attractive limb (§2.2; for $\alpha = \infty$, one obtains the definition of [22]). However, the use of a unique value of α for the definition of ρ could disturb the regularities mentioned in §3. So for $\alpha = 1\cdot27$, figure 10 (alkali diatomic molecules) remains essentially unchanged (no crossings or violation of the ordering rule), however, small irregularities appear in the repulsive limb and, for example, the ordering of the ground state potentials of LiH and KH is slightly violated in the attractive limb. For $\alpha = 1\cdot5$, the non-crossing and the ordering rules are violated in the lower portion of the RPCs in figure 10 and for $\alpha = 1\cdot8$, a strong crossing in figure 10 would result.

Hence a correction of the RPC scheme using a fixed value of α is not possible and a function $\alpha = \alpha(Z_1, Z_2, N)$ should perhaps be used. As no theoretical prescription exists, such a function should again be found intuitively, which seems impossible without a sufficient supply of experimental material or reliable *ab initio* potentials satisfying the conditions of §3.2. Such research would require team work on a large scale which, unfortunately, was not feasible for the author. Nevertheless, it may prove worthwhile. I am sure that my own work was just a start in the right direction and that this way might be followed by some interested scientists toward interesting goals.

Appendix

Corrections of some errors in the publications on the RPC method

Ref.	Page	Line etc.	Correction
25	403	equation (2)	In the denominator, replace r by r_e
25	415	reference 4(a)	should read: Collection Czech. Chem. Commun.
25	411	figure 11	The horizontal scale should be denoted by $U + D_e$
	406	figure 5	as above
41	3295		In equation (A2), the denominator should be corrected according to equation (6) of this paper
41	3292	figure 10	In line 4 from top of the legend replace K_2 Ref. 14(f) by K_2 Ref. 14(g)
41	3292	figure 10	In line 5 from top of legend replace Rb_2 Ref. 14(h) by Rb_2 Ref. 14(f)
30(a)	4574	figure 15	In line 2 from top of the legend, replace Ref. 20(c) by Ref. 19(c)
42	38	15, 16 from bottom	replace: calculate extension of *ab initio* potentials by: calculate with the use of *ab initio* potentials extensions of
33(c)	145	20, 21 from top	replace: equal or less than 14 680 cm^{-1} by: for values equal or less than 14 180 cm^{-1}
30(a)	4562	36, 13 from bottom	replace: (i) and (ii) by (A) and (B)

References

[1] JENČ, F., 1962, PhD thesis, Czechoslovak Academy of Sciences, Prague.

[2] (*a*) JENČ, F., and PLIVA, J., 1963, *Czech. Chem. Commun.*, **28**, 1449; (*b*) JENČ, F., *ibid.*, 2064; (*c*) ibid., 2052.

[3] JENČ, F., 1983, *Adv. At. Mol. Phys.*, **19**, 265.

[4] (*a*) KYU SOO JHUNG, IN HO KIM, KI BOK HAHN, and KI-HWAN OH, 1989, *Phys. Rev.* A, **40**, 7409; (*b*) KYU SOO JHUNG, IN HO KIM, KI-HWAN OH, and KI BOK HAHN, 1990, *ibid.*, **42**, 6497; (*c*) KYU SOO JHUNG, IN HO KIM and KI-HWAN OH, 1991, *ibid.*, **44**, 5611.

[5] HERZBERG, G., 1964, *Molecular Spectra and Molecular Structure*, Vol. 1 (Princeton: van Nostrand).

[6] MORSE, PH. M., 1929, *Phys. Rev.*, **34**, 57.

[7] (*a*) VARSHNI, Y. P., 1957, *Rev. mod. Phys.*, **29**, 664; (*b*) STEELE, D., LIPPINCOTT, E. R., and VANDERSLICE, J. T., 1962, *ibid.*, **34**, 239.

[8] ZAVITSAS, A. A. 1991, *J. Am. chem. Soc.*, **113**, 4755.

[9] KOLOS, W., 1970, *Adv. quant. Chem.* 5, 99.

[10] (*a*) BORN, M., and OPPENHEIMER, R., 1927, *Ann. Phys.*, **84**, 457; (*b*) BORN, M., 1951, *Nachr. Akad. Wiss. Göttingen* 1.

[11] (*a*) COMBES, J. M., DUCLOS, P., and SEILER, R., 1980, *Rigorous Atomic and Molecular Physics*, edited by G. Velo and A. S. Wightman (New York: Plenum Press), pp. 185–212. (*b*) RÖCHELT, J., 1983, *Int. J. quant. Chem.*, **24**, 627.

[12] LEVEBRE-BRION, H., and FIELD, R. W., 1986, *Perturbations in the Spectra of Diatomic Molecules* (Orlando: Academic Press).

[13] PLESNER, A. I., 1965, *Spektralnaja Teorija Linejnych Operatorov* (Mosow: Nauka), in Russian. English translation: *Spectral Theory of Linear Operators*, Vol. 1 and 2, 1969 (New York: Ungar).

[14] For a comprehensible exposition and references see: VANDERSLICE, J. T., MASON, E. A., MAISCH, W. G., and LIPPINCOTT, R. E., 1959, *J. mol. Spectrosc.*, 3, 17.

[15] For an adequate treatment and references see FRÖMAN, N., and FRÖMAN, P. O., 1965, *JWKB Approximation* (Amsterdam: North Holland).

[16] SPINDLER, R. J., JR., 1969, *J. quant. Spectrosc. Radiat. Transfer*, **9**, 597.

[17] KOLOS, W., SZALEVICZ, K., and MONKHORST, H. J., 1986, *J. chem. Phys.*, **84**, 3278.

[18] (a) NUMEROV, B., 1933, *Publ. Observ. Central Astrophys. Russ.*, **2**, 188; (b) COOLEY, J. W., 1961, *Math. Comput.*, **15**, 363.

[19] (a) KOSMAN, W. M., and HINZE, J., 1975, *J. mol. Spectrosc.*, **56**, 93; (b) VIDAL, C. R., 1986, *Comm. at. mol. Phys.*, **17**, 173.

[20] (a) MCWEENY, R., 1992, *Methods of Molecular Quantum Mechanics*, 2nd Edn (New York: Academic Press); (b) LEVINE, I. N., 1991, *Quantum Chemistry*, 4th Edn (New York: Prentice Hall); (c) CHRISTOFFERSEN, R. E., 1989, *Basic Principles and Techniques of Molecular Quantum Mechanics* (Berlin: Springer).

[21] PUPPI, A., 1946, *Nuovo Cimento*, **3**, 338.

[22] FROST, A., and MUSULIN, J., 1954, *J. Am. chem. Soc.*, **76**, 2045.

[23] FERRANTE, J., SMITH, J. R., and ROSE, J. H., 1983, *Chem. Phys. Lett.*, **50**, 1385.

[24] TELLINGHUISEN, S., HENDERSON, S. D., AUSTIN, D., LAWLEY, K. P., and DONOVAN, R. J., 1989, *Phys. Rev. A.*, **39**, 925.

[25] JENČ, F., 1990, *Phys. Rev. A*, **42**, 403.

[26] JENČ, F., 1994, *J. mol. Spectrosc.*, **167**, 477.

[27] HULBURT, H. M., and HIRSCHFELDER, J. O., 1941, *J. chem. Phys.*, **9**, 61. (for correction of an error see [7(b)].)

[28] JENČ, F., BRANDT, B. A., ŠPIRKO, V., and BLUDSKÝ, O., 1993, *Phys. Rev. A*, **48**, 1319.

[29] (a) LEROY, R. J., and BERNSTEIN, M. E., 1970, *Chem. Phys. Lett.*, **5**, 42; (b) LEROY, R. J., 1973, *Molecular Spectroscopy, Periodical Report*, Vol. 1, p. 113 (London: Chemical Society, Burlington House).

[30] (a) JENČ, F., and BRANDT, B. A., 1989, *Phys. Rev. A*, **39**, 4561; (b) 1987, *ibid.*, **35**, 3784.

[31] (a) COXON, J. A., and WICKRAMAARATCHI, M. A., 1981, *J. mol. Spectrosc.*, **87**, 85; (b) DOUGLAS, A. E., and HOY, A. R., 1975, *Can. J. Phys.*, **53**, 1965; (c) MCFEETERS, B. D., PERRAM, R. P., CRANNAGE, R. P., and DORKO, E. A., 1989, *Chem. Phys.*, **139**, 347; (d) COXON, J. A., 1971, *J. quant. Spectrosc. Radiat. Transfer*, **11**, 443; (e) BRAND, J. C. D., and HOY, A. R., 1985, *J. mol. Spectrosc.*, **114**, 197; (f) WEINSTOCK, E. M., and PRESTON, A., 1978, *J. mol. Spectrosc.*, **70**, 188; (g) MARTIN, F., BACIS, R., CHURASSY, S., and VERGES, J., 1986, *J. mol. Spectrosc.*, **116**, 71; (h) COLBOURN, E. A., DAGENAIS, M., DOUGLAS, A. E., and RAYMONDA, J. W., 1976, *Can. J. Phys.*, **54**, 1343; (i) KRUPENIE, P. H., 1972, *J. phys. Chem. Ref. Data*, **1**, 423; (j) SINGH, A. N., and RAI, D. K., 1965, *J. chem. Phys.*, **43**, 2151; (k) PROSSER, S. J., BARROW, R. F., EFFANTIN, C., D'INCAN, J., and VERGES, J., 1982, *J. Phys. B*, **15**, 4151; (l) VERGES, J., EFFANTIN, C., BABAKY, O., D'INCAN, J., PROSSER, S. J., and BARROW, R. F., 1982, *Physica Scripta*, **25**, 338; (m) BLOMBERG, M. R. A., and SIEGBAHN, P. E. M., 1981, *Chem. Phys. Lett.*, **81**, 4.

[32] JENČ, F., and BRANDT, B. A., 1987, *J. Chem. Soc. Faraday Trans. I*, **83**, 2857.

[33] (a) JENČ, F., and BRANDT, B. A., 1985, *J. chem. Phys.*, **83**, 5488; (b) 1986, *ibid.*, **85**, 3702; (c) 1991, *Spectrochimica Acta*, **47A**, 141.

[34] (a) JENČ, F., and BRANDT, B. A., 1985, *Spectrochimica Acta*, **41A**, 1211; (b) 1985, *Chem. Phys.*, **99**, 285.

[35] DEUTSCH, H., SCHREIER, P., and MARK, T. D., 1986, *Int. J. Mass Spectrom. Ion Proc.*, **74**, 81.

[36] JENČ, F., and BRANDT, B. A., 1987, *Theor. Chim. Acta*, **72**, 411.

[37] (a) DUNHAM, J. L., 1929, *Phys. Rev.*, **34**, 438; (b) 1932, *ibid.*, **41**, 721.

[38] JENČ, F., and BRANDT, B. A., 1994, *J. mol. Spectrosc.*, **165**, 590.

[39] (a) SCHMIDT-MINK, I., MÜLLER, W., and MEYER, W., 1985, *Chem. Phys.*, **92**, 263; (b) 1984, *Chem. Phys. Lett.*, **112**, 120; (c) SCHMIDT-MINK, I., 1987, Ph.D. thesis, University of Kaiserslautern, Germany; (d) YAN, L., and MEYER, W., 1996, *J. chem. Phys.* (in press).

[40] BALASUMBRAMANIAN, K., 1988, *J. chem. Phys.*, **89**, 6310, and other papers using this method.

[41] JENČ, F., and BRANDT, B. A., 1989, *J. chem. Phys.*, **91**, 3287.

[42] JENČ, F., and BRANDT, B. A., 1992, *J. mol. Spectrosc.*, **152**, 38.

[43] (a) COLIN, R., DREEZE, V., and STEINHAUER, M., 1983, *Can. J. Phys.*, **61**, 641; (b) LARSSON, M., 1984, *J. chem. Phys.*, **81**, 6409; (c) COOPER, D. L., 1984, *ibid.*, **80**, 1961.

[44] (a) READ, S. M., VANDERSLICE, J. T., and JENC, F., 1962, *J. chem. Phys.*, **37**, 205; (b) CHAN, Y. C., HARDING, D. R., STWALLEY, W. C., and VIDAL, C. R., 1986, *ibid.*, **85**, 2436; (c) MAKI, A. G., and OLSON, W. B., 1989, *ibid.*, **90**, 6887; (d) HUSSEIN, K. C., EFFANTIN, J., D'INCAN, J., VERGES, J., and BARROW, R. F., 1986, *Chem. Phys. Lett.*, **124**, 105; (e) CREPIN,

C., Verges, J., and Amiot, C., 1984, *ibid.*, **112**, 10; (*f*) Coxon, J. A., and Ogilvie, J. F., 1982, *J. Chem. Soc. Faraday Trans.* 2, **78**, 1345; (*g*) Barakat, B., Back, R., Carrot, F., Churassy, S., Crozet, S., Martin, R., and Verges, J., 1986, *Chem. Phys.*, **102**, 212; (*h*) Babaky, O., and Hussein, K., 1989, *Can. J. Phys.*, **67**, 912; (*i*) Amiot, C., 1991, *J. mol. Spectrosc.*, **145**, 370; (*j*) Simmons, J. D., Maki, A. G., and Hougen, J. T., 1979, *ibid.*, **74**, 70; (*k*) Stwalley, W. C., Zemke, W. T., and Sze Cheng Yang, 1991, *J. phys. Chem. Ref. Data*, **20**, 153.

[45] Huber, H. P., and Herzberg, G., 1979, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*, Vol. 4 (New York: van Nostrand).

[46] Peek, J. M., 1965, *J. chem. Phys.*, **45**, 3004.

[47] (*a*) Daborn, G. T., and Handy, N. C., 1983, *Mol. Phys.*, **49**, 1277; (*b*) Meyer, W., and Rosmus, P., 1975, *J. chem. Phys.*, **63**, 2356; (*c*) Lie, G. C., Hinze, J., and Liu, B., 1973, *ibid.*, **59**, 1872 (extended CI).

[48] (*a*) Klein, R., Rosmus, P., and Werner, H. J., 1982, *J. chem. Phys.*, **77**, 3559; (*b*) Saxon, R. P., Kirby, K., and Liu, B., 1980, *ibid.*, **73**, 1873.

[49] (*a*) Liu, B., and McLean, A. D., 1989, *J. chem. Phys.*, **91**, 2348; (*b*) Maas, J. G., Van Asselt, N. P. F. B., Nowak, P. J. C. M., Los, J., Peyerimhoff, S. D., and Buenker, R. J., 1976, *Chem. Phys.*, **17**, 217 (table 5); (*c*) Michels, H. H., 1986, *Chem. Phys. Lett.*, **126**, 537; (*d*) Tang, K. T., and Toennies, H. H., 1991, *Chem. Phys.*, **156**, 413; (*e*) Kolos, W., and Peek, J. M., 1976, *ibid.*, **12**, 381, and Kolos, W., 1976, *Int. quant. Chem.*, **10**, 217; (*f*) Peterson, G. A., Shirley, W. A., 1989, *Chem. Phys. Lett.*, **160**, 494 (table 2, exp.); (*g*) Fischer, J., Bondybey, V. E., Rosmus, P., and Werner, H. J., 1991, *Chem. Phys.*, **151**, 295.

[50] Theodorakopoulos, G., Petsalakis, I. D., Nicolaides, C. A., and Buenker, R. J., 1987, *J. Phys.* B, **20**, 2339.

[51] (*a*) Berriche, H., and Gadea, F. X., 1995, *Chem. Phys.*, **191**, 119; (*b*) Olson, R. E., Saxon, R. P., and Liu, B., 1980, *J. Phys.* B, **13**, 297; (*c*) Ilyabeav, E., and Kaldor, U., 1993, *J. chem. Phys.*, **98**, 7126.

[52] (*a*) Karo, A. M., Gardner, M. A., and Hiskes, J. R., 1978, *J. chem. Phys.*, **68**, 1942; (*b*) Krauss, M., and Stevens, W. J., 1981, *ibid.*, **74**, 570; (*c*) Michels, H. H., Hobbs, R. H., and Wright, L. A., 1985, *Chem. Phys. Lett.*, **118**, 67.

[53] (*a*) Iwata, S., and Sato, N., 1985, *J. chem. Phys.*, **82**, 2346; (*b*) Hillier, I. H., Guest, M. F., Dirg, A., Karlau, J., and Weise, J., 1979, *ibid.*, **70**, 864; (*c*) Gatland, I. R., Thackston, M. G., Pope, W. M., Eisele, F. L., Ellis, H. W., and McDaniel, E. W., 1978, *ibid.*, **68**, 2775.

[54] Jenč, F., and Brandt, B. A., 1985, *J. Quant. Spectrosc. Radiat. Transfer*, **33**, 597.

[55] Nai-Ho-Cheung and Cool, T. A., 1979, *J. Quant. Spectrosc. Radiat. Transfer*, **21**, 397.

[56] Bludský, O., Juřek, M., Špirko, V., Brandt, B. A., and Jenč, F., 1995, *J. mol. Spectrosc.*, **169**, 555.

[57] (*a*) Jenč, F., 1969, *J. chem. Phys.*, **50**, 2766; (*b*) 1989, *J. mol. Spectrosc.*, **138**, 13.

[58] Douglas, A. E., Moller, C. K., and Stoicheff, B. P., 1963, *Can. J. Phys.*, **41**, 1174.

[59] Rao, Y. V., and Venkateswarlu, P., 1962, *J. mol. Spectrosc.*, **9**, 173.

[60] (*a*) Rao, T. V. R., and Lakshman, S. V. J., 1970, *Ind. J. Pure Appl. Phys.*, **8**, 775; (*b*) Aslund, G. M., Barrow, R. F., and Richards, R. F., 1965, *Ark. Fys.*, **30**, 171.

[61] Jenč, F., 1967, *J. chem. Phys.*, **47**, 4910.

[62] Douglas, A. E., and Hoy, A. R., 1975, *Can. J. Phys.*, **53**, 1965.

[63] Effantin, J., Topouzkhanian, A., Figuet, J., d'Incan, J., Barrow, E. F., and Verges, J., 1982, *J. Phys.* B, **15**, 3829.

[64] Jenč, F., and Brandt, B. A., 1985, *J. Phys.* B, **18**, 2241.

[65] Kato, H., and Kobayashi, H., 1983, *J. chem. Phys.*, **79**, 123.

[66] (*a*) Engelke, G., Ennen, G., and Meiweis, K. H., 1982, *J. chem. Phys.*, **66**, 391; (*b*) Hessel, M. M., 1971, *Phys. Rev. Lett.*, **26**, 215.

[67] (*a*) Kaminsky, M. E., 1977, *J. Chem. Phys.*, **73**, 3520; (*b*) *ibid.*, **66**, 4951.

[68] Gustavson, T., Amiot, C., and Verges, J., 1988, *Mol. Phys.*, **64**, 279.

[69] Fellows, C. E., 1991, *J. chem. Phys.*, **94**, 5855.

[70] Shawla, G., 1985, PhD. thesis, MIT, Cambridge, USA.

[71] Tiemann, E., 1995, private communication.

[72] Fellows, C. E., Verges, J., and Amiot, C., 1990, *J. chem. Phys.*, **93**, 6281.

[73] WELLS, B. H., SMITH, E. B., and ZARE, B., 1983, *Chem. Phys. Lett.*, **89**, 244.

[74] LI, S., RICE, F., and FIELD, R. W., 1985, *J. chem. Phys.*, **82**, 1178.

[75] FRIEDMAN-HILL, E. J., and FIELD, R. W., 1992, *J. chem. Phys.*, **96**, 2444.

[76] (*a*) ENGELKE, F., HAGE, H., and SPRICK, U., 1984, *Chem. Phys.*, **88**, 443; (*b*) HAGE, H., 1985, PhD thesis, University of Bielefeld, Germany.

[77] (*a*) KASAHARA, SH., BABA, M., and KATO, H., 1991, *J. chem. Phys.*, **94**, 7713; (*b*) YOU-CHANG WANG, KAJITANI, M., KASAHARA, SH., BABA, M., ISHIKAWA, K., and KATO, H., 1991, *ibid.*, **95**, 6229.

[78] JENČ, F., 1964, *Collection Czech. Chem. Commun.*, **29**, 1745.

[79] (*a*) JENČ, F., 1964, *Collection Czech. Chem. Commun.*, **29**, 2579; (*b*) 1966, *J. mol. Spectrosc.*, **19**, 63; (*c*) VIDAL, C. R., and STWALLEY, W. C., 1982, *J. chem. Phys.*, **77**, 883; (*d*) PATRIDGE, H., LANGHOFF, ST. R., STWALLEY, W. C., and ZEMKE, W. T., 1981, *J. chem. Phys.*, **75**, 2299; (*e*) PATRIDGE, H., and LANGHOFF, ST. R., 1981, *ibid.*, **74**, 2361; (*f*) MULLIKEN, R. S., 1936, *Phys. Rev.*, **50**, 1028; (*g*) ADELMAN, S. A., and HERSCHBACH, D. R., 1977, *Mol. Phys.*, **33**, 793.

[80] AMIOT, C., 1990. *J. chem. Phys.*, **93**, 8591.

[81] (*a*) JENČ, F., 1991, *J. mol. Spectrosc.*, **147**, 274; (*b*) JENČ, F., and BRANDT, B. A., 1992, *ibid.*, **154**, 226.

[82] (*a*) ROSS, A., EFFANTIN, C., CROZET, P., and BOURSEY, E., 1990, *J. Phys.* B, **23**, L247; (*b*) ROSS, A. J., 1991, Private communication (the whole potential).

[83] (*a*) WEICKENMEIER, W., DIEMER, U., WAHL, M., RAAB, M., DEMTRÖDER, W., and MÜLLER, W., 1985, *J. chem. Phys.*, **82**, 5354; (*b*) DIEMER, U., WEICKENMEIER, H., WAHL, M., and DEMTRÖDER, W., 1984, *Chem. Phys. Lett.*, **104**, 489.

[84] JENČ, F., 1990, *J. mol. Spectrosc.*, **143**, 396.

[85] TELLINGHUISEN, J., and MOELLER, M. B., 1980, *Chem. Phys.*, **50**, 301.

[86] JENČ, F., and BRANDT, B. A., 1992, *J. mol. Spectrosc.*, **155**, 436.

[87] WANG, Y. CH., KAJITANI, M., KASAHARA, SH., BABA, M., ISHIKAWA, K., and KATO, H., 1991, *J. chem. Phys.*, **95**, 6229.

[88] RALSTON, A., and RABINOWITZ, PH., 1978, *A First Course in Numerical Analysis* (Tokyo: McGraw-Hill Kogakusha Ltd.).

[89] (*a*) KONOWALOW, D. D., ROSENKRANTZ, M. E., and OLSON, M. L., 1980, *J. chem. Phys.*, **72**, 2612; (*b*) STEVENS, W. J., KONOWALOW, D. D., and RATCLIFF, L. B., 1984, *J. chem. Phys.*, **80**, 1215.

[90] LEROY, R. J., 1992, *Chemical Physical Research Report CP-425* (University of Waterloo: Waterloo, Canada).

[91] (*a*) HYLLERAAS, E. A., 1928, *Z.f.Phys.*, **48**, 469; (*b*) 1929, *ibid.*, **54**, 347; (*c*) 1930, *ibid.*, **65**, 209.

[92] (*a*) JAMES, H. M., and COOLIDGE, A. S., 1933, *J. chem. Phys.*, **1**, 825; (*b*) JAMES, H., 1934, *ibid.*, **2**, 794; (*c*) COOLIDGE, A. S., and JAMES, H. M., 1937, *Phys. Rev.*, **51**, 855; (*d*) *ibid.*, **51**, 860.

[93] KATO, T., 1951, *Trans. Amer. Math. Soc.*, **70**, 212.

[94] MILNE, D., 1980, *Applied Functional Analysis: An Introductory Treatment* (London: Pitman).