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Generalized reduced-potential curve method and its applications

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The generalized reduced-potential curve (GRPC) is defined and analyzed. A special form of the GRPC formula is defined with respect to the reduced-potential curve (RPC) employed previously (parametrized formula). It is shown that the definition of the reduced potential used by Ferrante *et al.* [Phys. Rev. Lett. **50**, 1385 (1983)] and Tellinghuisen *et al.* [Phys. Rev. A **39**, 925 (1989)] is equivalent to the old definition of Frost and Musulin (FM) [J. Am. Chem. Soc. **76**, 2045 (1954)] that is obtained from the GRPC as a limit case. It is further shown that the FM reduced potential cannot be used for a systematic comparative study of the potentials of diatomic molecules (which, however, may be successfully made in the RPC scheme), nor can the FM formula be employed to obtain accurate approximations of the potentials. On the other hand, it is demonstrated by a series of examples that very accurate approximation methods for the extensions of the potentials may be defined with the use of the GRPC formula in the framework of the RPC scheme. A parametrized RPC formula appears to be a good GRPC formula: For the inner wing, the one-parameter approximation already leads to a degree of accuracy that seems satisfactory also to a spectroscopist (limit of error in the internuclear distance less than 0.001 Å). One-parameter approximations of potentials published previously are evaluated and shown to have reached a satisfactory degree of accuracy also in the outer wing (limit of error in energy less than 3 cm^{-1}). The GRPC method is also employed to obtain an essentially more accurate approximation from theoretical *ab initio* calculated potentials. The potentials obtained with the aid of the GRPC method may then be used for the calculation of the spectra.

I. INTRODUCTION

In a recent paper, Tellinghuisen *et al.*[1] published a formula of reduced internuclear potential of diatomic molecules comparing their method with my reduced-potential curve (RPC) method;[2-4] they also formulated some criticisms of the latter. This makes a few remarks on my RCP method and the use of its generalizations worthwhile. It will be shown in Sec. II that the formula proposed by Tellinghuisen *et al.* [Eq. (4) of Ref. 1] and hence also the formula proposed by Ferrante *et al.* [Eqs. (3) and (4) of Ref. 5(a); for a discussion of Ref. 5(a), cf. also Ref. 5(b)] are fully equivalent to the old Frost-Musulin formula[6] which the authors, however, evidently did not realize. It will further be shown in Sec. IV that the use of the generalized RPC (GRPC) formula within the RCP scheme leads to very accurate approximation procedures for the calculation (extension) of interatomic potentials of diatomic molecules. In fact, in case of a small difference in the atomic numbers of two molecules *A* and *B*, a simple inversion of the RPC formula in general yields better results than the inversion of the Frost-Musulin formula (suggested in Ref. 1) in a calculation of the potential of *A* from the reduced potential of *B*.

It will be demonstrated in Sec. III that the Frost-Musulin formula cannot be used for any systematic comparative study of the interatomic potentials of diatomic molecules and that so far only the RPC method can be employed for this purpose.

II. GENERALIZED REDUCED POTENTIAL CURVES

The reduced interatomic potential is defined in terms of dimensionless "reduced" interatomic distance ρ and "reduced" potential energy u.[2] Postulating also a universal "reduced" force constant κ, ρ and u may be defined in introducing a parameter ρ_{ij}, characterizing a particular combination of the atoms i and j. (For ions, a third index n should in fact be used, denoting the number of electrons.) Here we shall discuss a class of reduced potentials where the parameter ρ_{ij} is introduced only into the formula of ρ:

$$u \equiv \frac{U}{D_e} , \tag{1}$$

$$\rho \equiv \frac{r - F(r,\rho_{ij},\xi_k)}{r - F(r,\rho_{ij},\xi_k)} . \tag{2}$$

Here r_e is the equilibrium internuclear distance, D_e is the depth of the minimum of the potential curve, and ξ_k denotes parameters in a functional form F which may be used to make the definition of the function F more flexible. It follows that

$$F(r_e,\rho_{ij},\xi_k) = r_e - \left[\frac{\kappa D_e}{k_e} \right]^{1/2} , \tag{3}$$

where $k_e \equiv (d^2U/dr^2)_{r=r_e}$ is the force constant. ρ_{ij} is calculated from the implicit Eq. (3).

In the original definition of the RPC (Refs. 2 and 3) the function F had the form

$$F(r,\rho_{ij},\xi_k)=\left[1-\exp\left[\frac{-r}{\rho_{ij}}\right]\right]\rho_{ij}\ . \tag{4}$$

From (2) then follows the "doubly reduced" formula for ρ,

$$\rho=\frac{x-1+\exp(-x)}{x_e-1+\exp(-x)}\ , \tag{5}$$

with

$$x\equiv\frac{r}{\rho_{ij}},\quad x_e=\frac{r_e}{\rho_{ij}}\ . \tag{6}$$

Therefore ρ_{ij} has here in the RPC the meaning of the *unit of length* used for the internuclear distance of a molecule if inserted into the formula of ρ.

The simplest generalization of my RPC definition may then be written as its parametrized form, e.g.,

$$\rho=\frac{r-[f(r)]^{\eta}\left\{\beta-\gamma\exp\left[-\alpha\left[\frac{r-\xi}{\rho_{ij}}\right]^{\sigma}+\tau\right]\right\}^{\delta}\rho_{ij}}{r_e-[f(r)]^{\eta}\left\{\beta-\gamma\exp\left[-\alpha\left[\frac{r-\xi}{\rho_{ij}}\right]^{\sigma}+\tau\right]\right\}^{\delta}\rho_{ij}}\ , \tag{7}$$

$$\rho_{ij}=\frac{r_e-\left[\frac{\epsilon\kappa D_e}{k_e}\right]^{1/2}}{[f(r_e)]^{\eta}\left\{\beta-\gamma\exp\left[-\alpha\left[\frac{r_e-\xi}{\rho_{ij}}\right]^{\sigma}+\tau\right]\right\}^{\delta}}\ , \tag{8}$$

$$\kappa=3.96\ .$$

$f(r)$ might be used as a suitable correction function. The parameters (Greek letters) on the right-hand side of Eqs. (7) and (8) could, in principle, be functions of Z_1, Z_2, and n. In the original definition of the RPC [Eq. (5)], I put $\eta=\tau=0$, all other parameters were put equal to 1. The value $\kappa=3.96$ followed from setting $\rho_{ij}=0$ for H_2^+ (cf. Ref. 2). (A slightly different value would correspond to the new data which, however, is here not of much interest, since it refers only to the heuristic approach.) The parameter ϵ enables a change of the "reduced force constant."

Other formulations of the reduced distance are, of course, possible, e.g., taking r or r/r_e or $(r-r_e)/r_e$ instead of r/ρ_{ij} in the exponential factor of Eq. (5) or (7), which would lead to a simpler explicit equation for ρ_{ij}. Also other functional forms of F could be tried out for the approximation procedures discussed in Sec. IV. However, one finds that the definition of the RPC corresponding to Eq. (5), though still not being ideal, is in fact quite a good definition, since very good approximations are obtained in using just one parameter in Eq. (7) (cf. Sec. IV). In this context, it is interesting to note that, in Eq. (2), different forms of the function F (in particular different values of the parameters) may be used for the left and right limb, respectively, while the reduced potential and its first derivative are continuous in the minimum and the same value of the second derivative κ in $\rho=1$ holds for both limbs.

The formula of Frost and Musulin[6] follows from Eq. (7) for $\eta=\tau=0$, $\beta=1$, and $\alpha\rightarrow\infty$ (i.e., for sufficiently large α),

$$\rho=\frac{r-\rho_{ij}}{r_e-\rho_{ij}},\quad \rho_{ij}=r_e-\left[\frac{\epsilon\kappa D_e}{k_e}\right]^{1/2}\ . \tag{9}$$

In fact, Frost and Musulin used the value $\kappa=4.0$ (i.e., $\epsilon=1.0101$).

From (9), it follows for $\epsilon\kappa=4.0$

$$\rho=\left[\frac{k_e}{4D_e}\right]^{1/2}(r-r_e)+1\ , \tag{10}$$

which may be compared with the definition of Tellinghuisen *et al.*,[1]

$$\rho=\left[\frac{k_e}{2D_e}\right]^{1/2}(r-r_e)\ , \tag{11}$$

and with the definition of Ferrante *et al.*,[5(a)]

$$\rho=\left[\frac{k_e}{D_e}\right]^{1/2}(r-r_e)\ , \tag{12}$$

which shows that all three definitions differ only in taking a different scale for ρ (which may be done in drawing any figure, anyway); in Eq. (10), the minimum is shifted from 0 to 1. As Eqs. (9)–(12) differ only in the arbitrarily chosen value of the universal "reduced" force constant, it is evident that in Frost and Musulin's approach a change in the value of the "reduced" force constant κ, is, in fact, irrelevant, leading only to a change in the scale of ρ.[7,8] On the other hand, it is important in my definition in Eqs. (5) and (7).

A change of one of the parameters α, β, γ, and δ has a similar, though somewhat different effect: an increase in the value of α or β turns the RPC to the left, whereas an increase in the value of γ or δ turns the RPC to the right. The RPC becomes broader for a lower value of ϵ. Hence increasing value of α turns the right limb of the RPC to the left, thus leading to a "compression" of the RPC scheme, i.e., the differences between the various RPC's become smaller for large values of α. That is also the case of formulas (9)–(12).

Setting $\rho_{ij}=0$ for all molecules in Eq. (5), (7), or (9), one has, for a molecule, $(d^2u/d\rho^2)_{\rho=1}=r_e^2k_e/D_e$ and the reduced potentials of the molecules will not agree in the neighborhood of the minimum, so that the simple definition $\rho=r/r_e$ cannot be very interesting.

In the following, the reduced potential defined by formulas (1) and (5) will be denoted by RPC, formulas (1) and (9) will be called the "Frost-Musulin reduced potential" (FMRP), and formulas (1) and (7) will be called the "generalized RPC" (GRPC).

III. COMPARISON OF THE FMRP AND RPC METHODS

The aim of my work was to see whether the dependence of the internuclear potential of a diatomic system on the fundamental physical parameters Z_1, Z_2, and n (atomic numbers and the number of electrons) leads to some simple regularities (laws) in the RPC scheme. This dependence clearly exists,[2] however, it does *not* by any means follow that it may show up in some simple geometric regularity in the graphical scheme of the potential curves. A positive result rather is an agreeable surprise and the problem is by far not trivial. This may be well illustrated by a comparison of the FMRP and the RPC scheme.[9] The reduced potentials are calculated from the RKR (Rydberg-Klein-Rees) potentials.[10]

The study of a large number of molecules and states[2,11,12] has revealed interesting regularities existing in the RPC scheme[13] which thus appears to be an appropriate framework for a systematic comparative study of interatomic potentials of diatomics.

On the other hand, in the FMRP scheme, *no* systematic comparative study of the potentials is possible since, apart from the crossing of the various FMPR curves, there is no systematic ordering, there are no rules.

Figure 1 shows the right limbs of the FMRP curves (here the value $\kappa = 3.96$ was used) of a selection of different molecules and should be compared with Fig. 2, containing the right limbs of the RPC's of the same molecules. The experimental data and the potentials were taken from Refs. 14(a)–14(d), 14(e) and 14(f), and 14(g)–14(k) for Li_2, HF, HCl, CO; NO; and F_2, Cl_2, Br_2, I_2, and Bi_2, respectively (cf. also Ref. 15).

In Fig. 2, the noncrossing and ordering RPC rules[13] are fulfilled (the same holds for the left limb). One also notes that the RPC's of different molecular groups do not intersect.[16–20] In case of small difference in the atomic numbers of two molecules, their RPC's lie close together (e.g., HF-HCl and CO-NO).

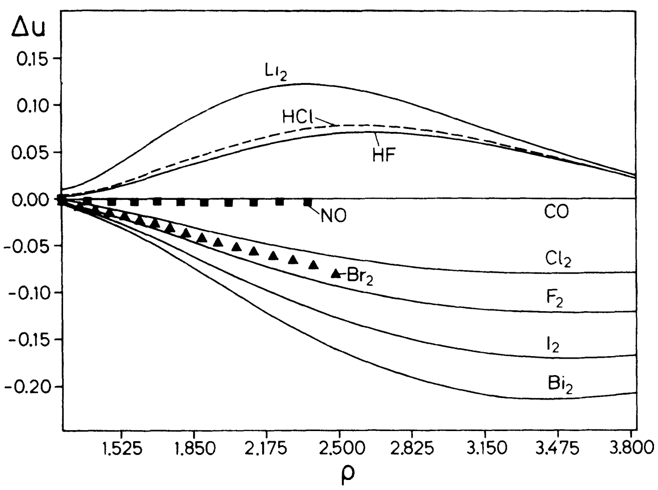

FIG. 2. Right limb. Differences in u of the ground-state RPC's from the ground-state RPC of CO (zero line). ——, from top to bottom, Li_2, HF, Cl_2, F_2, I_2, Bi_2; — — —, HCl; ■, NO; ▲, Br_2.

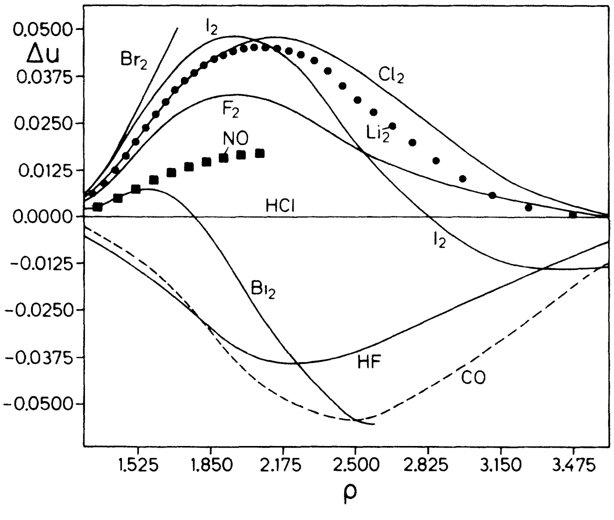

FIG. 1. Right limb. Differences in u of the ground-state FMRP curves from the ground-state FMRP curve of HCl (zero line). ——, from top to bottom (for small ρ), Br_2, I_2, Cl_2, F_2, Bi_2, HF; — — —, CO; ●, Li_2; ■, NO.

On the other hand, in Fig. 1, one has intersecting curves without any system or ordering. For instance, the gap between the FMRP curves of HF and HCl is very large, the FMRP of CO almost coincides with that of Bi_2 and is very distant from the FMRP of NO, the FMRP of I_2 approximates that of Li_2 and there is a crossing of the FMRP's of the halogen molecules. With respect to the examples of Ref. 1, one should note here the large differences between the FMRP's of Br_2 and of the other halogen molecules. For the FMRP scheme, there is *no* correlation between the left and the right limb with respect to the location of the curve in the FMRP scheme. Such a correlation clearly exists in the RPC scheme.[13]

Let us note that Fig. 2 also demonstrates an important anomaly of the F_2 molecule: here the ordering rule is violated (in both limbs) and the RPC of F_2 lies between the RPC's of Br_2 and I_2.[21–23] A similar anomaly is observed also for the HF molecule (cf. also Fig. 2), i.e., the fluorine compounds seem to behave in an anomalous way. As has also been shown for the excited states,[11(h)] the RPC method offers a very pictorial visualization of such anomalies.

The regular dependence of the RPC on the atomic numbers may also be seen in groups of heteronuclear molecules containing the same atom. We demonstrate it on the example of nonmetal nitrides and oxides in Figs. 3 and 4, respectively. The data were taken from Refs. 24 and 15 (cf. comments in Ref. 25). No such regularities exist in the FMRP scheme. So evidently it is not trivial to find a suitable definition of the reduced potential leading to a scheme where certain simple laws hold.

In Fig. 16 of Ref. 12(b), the asymptotic confluence of the nonintersecting RPC's of alkali-metal diatomic molecules was shown, which has now been confirmed by the recent new data on RbCs (Ref. 26) and Rb_2 (Ref. 27). On the other hand, in the FMRP scheme the reduced poten-

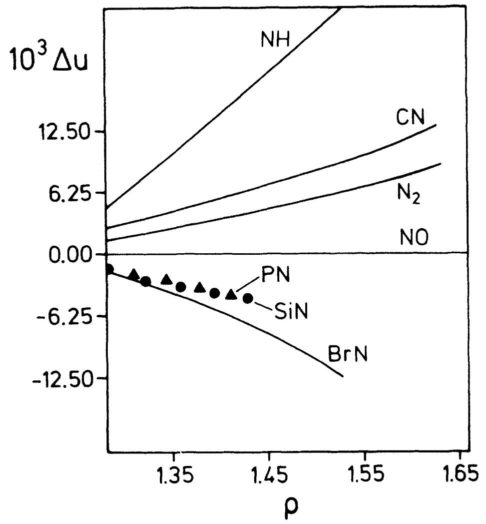

FIG. 3. Right limb. Differences in u of the ground-state RPC's from the ground-state RPC of NO (zero line). ——, from top to bottom, NH, CN, N_2, BrN; ▲, PN; ●, SiN. The dependence on the atomic number is much less pronounced for large atomic numbers (cf. Ref. 2, p. 275).

tials of these molecules form a complicated system of intersecting curves. The difference in ρ between the FMRP curves of these molecules in the left limb are ten times larger than the differences between the RPC's. Although, in this special case, the FMRP curves lie closer together than the RPC's in the right limb, the differences still amount to $25\times10^{-3}D_e$ (about 100 cm^{-1}), i.e., are still too large to permit a high degree of accuracy in the approximation, satisfactory also for a spectroscopist. Such a high degree of approximation (limit of error about 3 cm^{-1}) may be achieved only using the GRPC formula in the framework of the RPC scheme (cf. Sec. IV, extension of the potential).

In the left limb, the FMRP curves do not cross and lie relatively close together, however, the RPC's of molecules with a small difference in the atomic numbers lie again essentially closer together than the corresponding FMRP curves, as the comparison, e.g., of the pairs RbCs-Cs_2, HF-HCl, or CO-NO shows. This fact implies that, e.g., *direct inversion* of the RPC formula for the RPC of NO using the molecular constants of CO, gives a much better approximation of the potential of CO than the analogous FMRP calculation, as may be seen in Fig. 5, where we also show the approximation of the potential of CO calculated from the RPC of NO by the GRPC method described in Sec. IV. It is clear that the latter yields *essentially* better results.

For affiliated molecules with a *small* difference in the atomic numbers, in particular, molecules differing only in one atomic number, direct inversion of the RPC formula (in the sense explained above) gives much better approximation than the inversion of the FM formula also in the right limb. (Due to the RPC rules, this should in general hold also for nonaffiliated molecules.[13]) We illustrate it on the example of the pair HF-HCl in Fig. 6, where we again also show the excellent approximation obtained with the use of the GRPC method to be discussed in Sec. IV. (The same holds, e.g., for CO, NO, etc., cf. Figs. 1 and 2.)

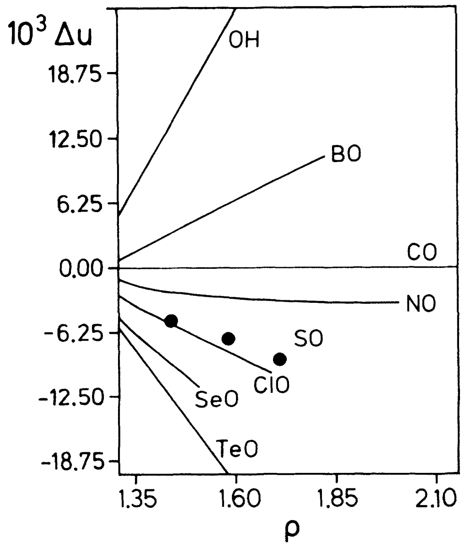

FIG. 4. Right limb. Differences in u of the ground-state RPC's from the ground-state RPC of CO (zero line). ——, from top to bottom, OH, BO, NO, ClO, SeO, TeO; ●, SO (cf. commentary to Fig. 3).

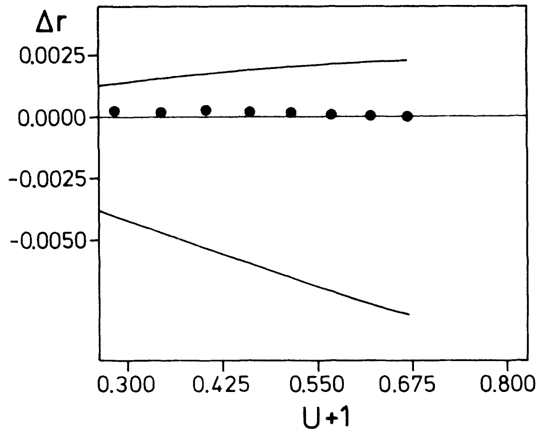

FIG. 5. Left limb. Differences in r of the ground-state potential curves of CO (calculated by different methods) from the ground-state RKR potential curve of CO [zero line, corrected for $(u+1)>0.65$, cf. Ref. 32]. ——, from top to bottom, potential calculated by inversion of the RPC formula from the ground-state RKR RPC of NO; potential calculated analogously from the FMRP of NO. ●, potential calculated by the GRPC method from the potential of NO [α(CO$=$1.065, extension from 30% of D_e]. The values of $r_e(\mathrm{CO})=1.1283$ Å and $D_e(\mathrm{CO})=91\,100$ cm^{-1} are taken as units of internuclear distance and energy, respectively. All curves have a common minimum.

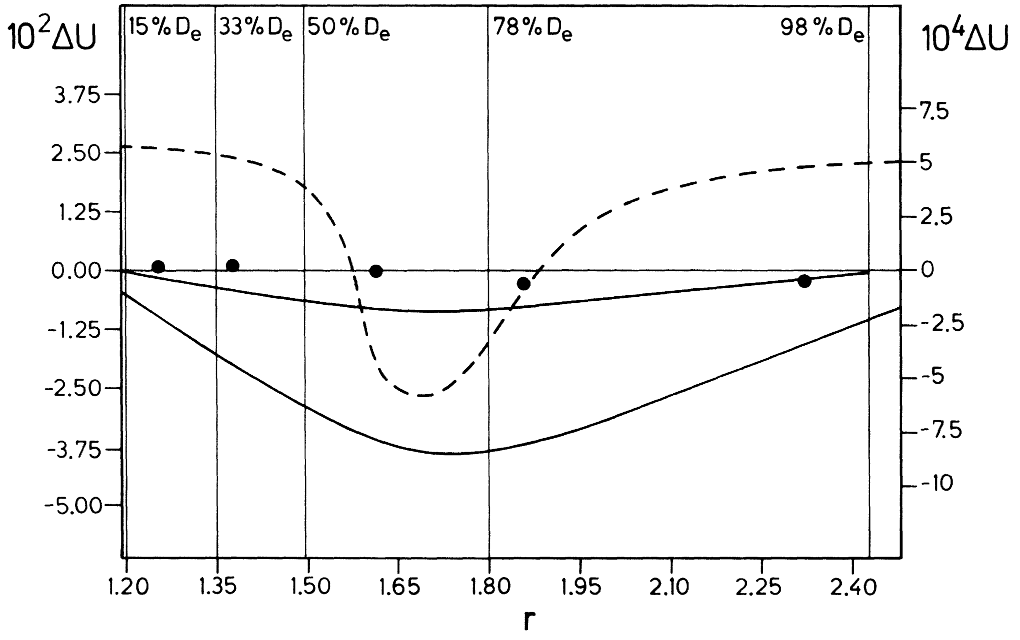

FIG. 6. Right limb. Differences in energy of the ground-state potential curves of HCl (calculated by different methods) from the ground-state RKR potential curve of HCl (zero line). ——, from top to bottom, potential of HCl calculated by inversion of the RPC formula from the ground-state RKR potential of HF; potential of HCl calculated analogously by inversion of the FMRP formula. — — —, extension of the RKR potential of HCl (supposed to be known only up to 30% of D_e) calculated by the GRPC method [$\alpha(\text{HF})=1.35$] from the ground-state RKR potential of HF. ●, potential of HCl calculated by the GRPC method from the (inaccurate) theoretical potential of HF of Ref. 36 ($\alpha_{\text{theor}}=1.1$), cf. text. The values of $r_e(\text{HCl})=1.274\,55$ Å and $D_e(\text{HCl})=37\,243$ cm^{-1} are taken as units of internuclear distance and energy, respectively. The right-hand scale belongs to the dotted line (GRPC method). The left-hand scale belongs to all other cases. All curves have a common minimum.

IV. APPLICATIONS OF THE GRPC METHOD

A. One-parameter approximations

The calculation of the potential of a molecule A from the potential of a molecule B by inversion of the reduced potential formula–in the RPC *as well as* in the FMRP scheme–is meaningful *only* if sufficiently accurate values of the molecular constants r_e, k_e (ω_e), and D_e are known for both molecules. That means in practice that at least the low portion of the spectrum of molecule A has been measured and the values of r_e and k_e determined. The value of D_e can often be obtained from the predissociation of an excited state (for the ground state as well as for an excited state) or from other than spectroscopic data [cf. Ref. 14(c)]. In general, a sufficiently high portion of the spectrum must be known if accurate values of r_e and k_e should be obtained. Errors in these constants may cause large errors in the estimate of the potential from the RPC as well as from the FMRP scheme. Therefore in practice, any approximate methods for the determination of the interatomic potential of a molecule A from the reduced potential of another molecule B are more or less accurate *extensions* of the already known lower portion of the potential of A. In the FMRP scheme, only direct inversion of the FM formula (9) may be used;[1] as has been shown in Sec. III, this method is in general rather inaccurate.

In the framework of the RPC scheme, other possibilities exist. In Sec. II, together with the RPC formula (5), we also gave its generalized (parametrized) version (7). One may now use the GRPC formula (7) to obtain approximate coincidence of two curves in the RPC scheme which then makes the calculation of the potential of a molecule A from the potential of a molecule B possible through inversion of the reduced potential formula. It appears that formula (5) is a relatively well-behaved formula, since the use of only *one* parameter in the GRPC formula (7) is, in many cases, sufficient to obtain a very accurate approximation satisfying also a spectroscopist. It should be emphasized that the primary reason for the success of these approximation methods is, of course, the regularities of the RPC scheme,[13] in particular the "quasiparallelity" of the RPC's in both limbs, illustrated by Fig. 2 for the right limb.

It appears that the parameter α is most suited for this approximation procedure; nevertheless, similar calculations may be made also using the other parameters. We shall demonstrate here the use of the parameter α on a few examples.

The method of calculation is the following: let us assume that the potential of a molecule A is known, say, only up to 30–40 % of D_e and the potential of a molecule B is known up to the dissociation limit, and the constants r_e, D_e, and k_e (ω_e and Y_{10}) are known for both molecules. Then, say, for the molecule A, the parameter α is varied until the GRPC of A approximately coincides with the RPC of B in the range of the internuclear distance where both potentials are known. Then the potential of A is calculated from the RPC of B inverting the GRPC formula with the use of the molecular constants of A. The variation of α must be made separately for the left and right limb of the potential, respectively. Conversely, the variation of α may, of course, be also made for B or also for both molecules at the same time.

If a very accurate approximation should be obtained, a certain amount of experience may be of great help, as in any approximation calculations. There are, indeed, certain rules (confirmed on a large series of examples) that facilitate this task substantially.

1. Estimation of the right limb of the potential

Let us first examine the more difficult right limb. In using the GRPC method as explained above, one does, of course, not obtain exact coincidence of the two reduced potential curves. However, there are certain geometric rules which are characteristic for the RPC scheme and which may substantially help in obtaining a good approximation.

Let us consider the RPC's of two affiliated molecules A and B (i.e., chemically related molecules, like alkali-metal diatomic molecules, alkali-metal hydrides, etc.). Let the lower lying RPC A be lifted in the right limb using a suitable value of $\alpha(A) > 1$ (cf. Sec. II) so that it now lies only slightly above the RPC B in the low portion of the right limb. Then it will run almost parallel with the RPC B, then it will cross it and run slightly below it, turning then up again and running almost parallel slightly above it. (Alternatively, the RPC B may be shifted below the RPC A in the lower portion of the right limb by taking $\alpha(B) < 1$.) The differences are small. This rule seems to hold quite generally, with the exception of the anomalous alkali-metal hydride molecules.[16] The differences of the calculated potential from the true potential then have a similar dependence on r. This behavior of the potentials is demonstrated[9] in Fig. 6 (*right-hand scale*) where the potentials of HF and HCl were both known quite accurately up to the dissociation limit. Assuming that the potential of HCl is known only up to 30% of D_e, the upper portion of the potential of HCl was calculated from the potential of HF using the value $\alpha(\mathrm{HF}) = 1.35$ [due to the anomaly of fluorine compounds, the RPC of HF lies below the RPC of HCl, cf. Sec. III and Ref. 11(g)]. As may be seen in Fig. 6, the error in energy is smaller than $5\times10^{-4}D_e$, which means here smaller than about 18 cm^{-1}. A similar degree of approximation is obtained for the one-parameter approximation with $\beta = 1.275$; variation of γ gives a somewhat worse result.

The (simple) working technique is as follows: one takes such a value of α that the crossing still does not take place in the known range of the potential which should be extended and the difference between the two RPC's is sufficiently small. An *a priori* rough estimate of the limit of error is obtained in testing also other different values of α for which the crossing already occurs for lower values of energy. In this way, one gets an idea about the geometry of the GRPC used for the approximation (cf. discussion of the left limb below and Figs. 9 and 10; cf. also Fig. 8).

Though the approximation for the potential of HCl shown in Fig. 6 is very good in terms of the reduced energy, it still does not quite reach the desired degree of accuracy, because the dissociation energy of the HCl molecule is large (37 243 cm^{-1}), i.e., though the relative error is here very small, the absolute error in cm^{-1} does not satisfy the strict requirements of spectroscopic accuracy. However, the absolute error can be made much smaller for molecules which have a low value of D_e. (Possibly also for many excited states, cf. below.)

Nevertheless, as examples of theoretical calculations with a much larger relative error show (cf., e.g., Ref. 28 with an error in D_e of about $6\times10^{-3}D_e$), one possibly may obtain with our limit of error, $5\times10^{-4}D_e$, a very good approximation for the spectroscopic *difference* quantities ΔG. (The same degree of approximation is obtained, e.g., for the pair CO, NO; cf. remark at the end of Sec. III.)

In Ref. 12(b), the potential of RbCs that was then known only up to 72% of D_e, was effectively predicted with the use of this GRPC method up to the dissociation limit. The recommended value of D_e was 3833 cm^{-1}; the calculation was alternatively made also for two other alternative values of D_e (± 10 cm^{-1}), since the value of D_e was not guaranteed. Recently, the spectrum of the ground state of RbCs has been measured and the potential of RbCs has been determined by experimentalists almost up to the dissociation limit which was fixed as 3845 ± 1 cm^{-1}.[26] However, the authors felt that the limits of error might be larger and that the value 3845 cm^{-1} represents the upper limit of D_e. This is also confirmed by the RPC method since, with the value $D_e = 3845$ cm^{-1}, the RPC of RbCs would already slightly cross[20] the RPC of Cs_2 thus violating the noncrossing RPC rule.[13] Hence the value used in Table XXII of Ref. 12(b), i.e., $D_e(\mathrm{RbCs}) = 3843$ cm^{-1}, seems more probable. In Fig. 7 we give an evaluation of our prediction of Table XXII from Ref. 12(b). The potential of RbCs was calculated using the known potential of Cs_2 and the value $\alpha(\mathrm{Cs}_2) = 1.027$. It results that the limit of error is smaller than $7\times10^{-4}D_e$, i.e., smaller than 3 cm^{-1}. Thus here a very high degree of accuracy has been achieved, which is not possible in the FMRP scheme (cf. Sec. III). This case was a favorable one, since the RPC's of RbCs and Cs_2 are not very distant (cf. Ref. 12) and a very good coincidence of the RPC of RbCs and the GRPC of Cs_2 was obtained for $u+1 < 0.72D_e$, the differences appearing only for some points and not surpassing about $(1-2)\times10^{-4}$. Hence one would have obtained the same degree of approximation if the potential of RbCs should have been known only up to, say, 40%, since the same value of α would have been chosen. It is, of course, clear that the limits of this method depend directly on the limits of the RKR method.

In Ref. 12(b), this estimation of the right limb of the potential was illustrated in Fig. 15 on the example of the ground-state potential of NaK which was calculated from

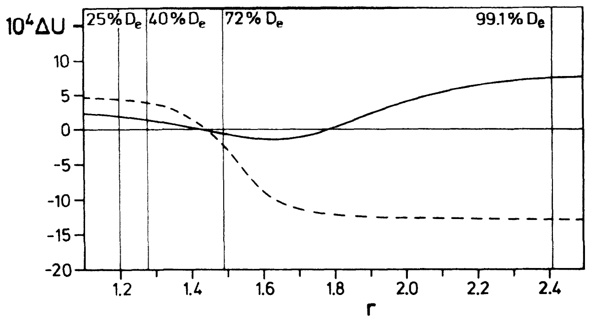

FIG. 7. Right limb. Evaluation of the estimation of the upper portion of the ground-state potential of RbCs (from 72% to 100% of D_e) calculated in Ref. 12(b) from the ground-state IPA potential of Cs_2 by the GRPC method. Differences in energy from the RKR potential of RbCs (zero line). ——, potential calculated with the value $D_e(\mathrm{RbCs})=3843$ cm^{-1} $[\alpha(\mathrm{Cs}_2)=1.027]$, cf. Table XXII of Ref. 12(b). — — —, potential calculated with the value $D_e(\mathrm{RbCs})=3833$ cm^{-1} $[\alpha(\mathrm{Cs}_2)=1.029]$, cf. Table XVIII of Ref. 12(b). The value of $r_e(\mathrm{RbCs})=4.4271$ Å and $D_e(\mathrm{RbCs})=3843$ cm^{-1} were taken as units for internuclear distance and energy, respectively. All curves have a common minimum.

the RKR potentials of Na_2 $[\alpha(\mathrm{NaK})=1.085]$ and $K_2[\alpha(K_2)=1.085]$. The limit of error was also less than 3 cm^{-1} in both cases.

In Table XVIII of Ref. 12(b), this calculation was performed using the incorrect value D_e (RbCs)$=3833$ cm^{-1}, recommended by the experimenters, and the value $\alpha(\mathrm{Cs}_2)=1.029$. As may be seen in Fig. 7, the limit of error for this estimate is still only about 12.5×10^{-4}, i.e., about 4.5 cm^{-1}.

The extension of the right limb of the ground-state potential of Rb_2 (which was then known only up to about 80%) was calculated in Ref. 12(b) from the potential of K_2, applying the GRPC formula to Rb_2 for the value $D_e(\mathrm{Rb}_2)=3950$ cm^{-1} recommended by experimenters[15] as the most probable value [Table XVII of Ref. 12(b), $\alpha(\mathrm{Rb}_2)=1.0435$] as well as for the lower limit 3939 cm^{-1} [Table XIX of Ref. 12(b), α $(\mathrm{Rb}_2)=1.038$] and a somewhat higher value $D_e(\mathrm{Rb}_2)=3960$ cm^{-1} [Table XX of Ref. 12(b), $\alpha(\mathrm{Rb}_2)=1.0485$]. However, new measurements have shown[27] that the error in $D_e(\mathrm{Rb}_2)$ was essentially larger, the correct value being[29] $D_e(\mathrm{Rb}_2)=3993.5$ cm^{-1}. Therefore, the estimates for the right limb of Rb_2 are relatively inaccurate, which is, however, due to the error in the D_e value, not to a deficiency of the method. Table XX of Ref. 12(b) for $D_e=3960$ cm^{-1} gives the best estimate. The error near the dissociation limit is of the order of the error in D_e (about 25 cm^{-1}) diminishing rapidly with decreasing internuclear distance. This error in D_e does not affect the estimate of the left limb [cf. Ref. 14 in Ref. 12(b)].

As for the estimates of the potential of LiNa by the method (B) of Ref. 12(b) (calculating the potential from the theoretical potential of Ref. 28 with the use of experimental values of the molecular constants), the experimental value of D_e (LiNa) seems now to be still larger than the value 7093 cm^{-1} recommended in Ref. 28, namely, about 7100 cm^{-1}.[30] Hence Table XII of Ref. 12(b) should yield the best estimate of the right limb of the LiNa potential with an error corresponding to the difference in D_e (about 5–10 cm^{-1}) in the neighborhood of the dissociation limit, diminishing with decreasing internuclear distance. Unfortunately, further experimental results on the ground state of LiNa still are not available.

The estimated boundaries for the left limb (method A) of the ground state potential of LiNa [Tables II and III of Ref. 12(b)] may be taken for granted, since they are satisfied in reduced form[12(b)] by the very accurate theoretical potential of Ref. 28.

The accuracy of the extrapolation will evidently be the better the closer the RPC's of the two molecules lie. Since a relatively small change of both atomic numbers leads to a more important change in the RPC than a large change in only one atomic number (cf. Ref. 2), the approximation will be somewhat more difficult for a group of affiliated molecules like, e.g., the homonuclear halogen molecules where the gap between the RPC's is large in the right limb. However, even here, an essentially better approximation (extension) than that obtained by the FMRP method may be achieved. This is illustrated in Fig. 8, where the potential of Cl_2 was calculated from the potential of F_2. Let us assume that the potential of Cl_2 is known only up to about 50% of D_e. Then according to the geometric rule explained above, one will choose such a value of $\alpha(F_2)$ that the RPC of F_2 is lifted slightly above the RPC of Cl_2, then running quasiparallel with the latter. Here the value $\alpha(F_2)=1.1$ was taken and the limit of error is smaller than $5\times10^{-3}D_e$. The errors are, however, concentrated only in the highest portion for energies larger than 95% of D_e and the limit of error is only about $1\times10^{-3}D_e$ (i.e., about 20 cm^{-1}) in the region be-

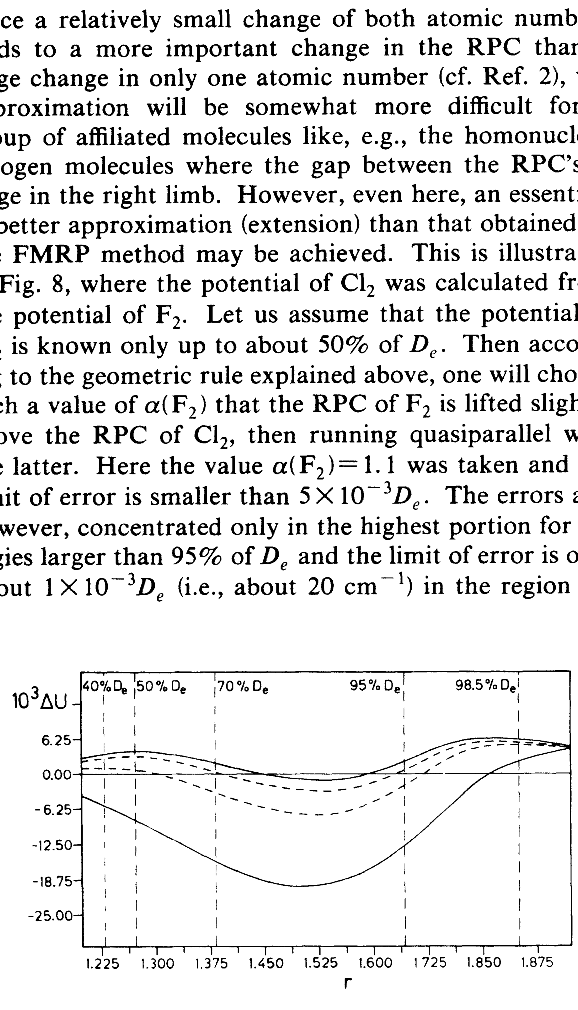

FIG. 8. Right limb. Estimation of the ground-state potential of Cl_2 from the ground-state potential of F_2 with the use of the GRPC method and comparison with the FMRP method. Differences in U from the RKR potential of Cl_2 (zero line) of the potential curves calculated by different methods. ——, from top to bottom, GRPC extension $[\alpha(F_2)=1.1]$, assuming that the potential of Cl_2 is known about up to 50% of D_e; potential calculated by inversion of the FMRP formula. ---, from top to bottom, GRPC extension for $\alpha(F_2)=1.095$, the same for $\alpha(F_2)=1.085$, cf. text. The values of $r_e(\mathrm{Cl}_2)=1.9879$ Å and $D_e(\mathrm{Cl}_2)=19\,997$ cm^{-1} are taken as units for internuclear distance and energy, respectively. All curves have a common minimum.

tween 70% and 95% of D_e. Hence one would have only this limit of error between 70% and 95% of D_e. This is not quite the desired accuracy, because the value of $D_e(\mathrm{Cl}_2)=19\,997.28\ \mathrm{cm}^{-1}$ is relatively large; for a value of $D_e=6000\ \mathrm{cm}^{-1}$, say, the error would only be about 6 cm^{-1}. If the potential of Cl_2 were known only up to 40% of D_e, one possibly would take a slightly lower value of $\alpha(\mathrm{F}_2)$, since the RPC of F_2 for $\alpha(\mathrm{F}_2)=1.1$ is still rising in this region. The value of $\alpha(\mathrm{F}_2)=1.095$ would do it; the approximation would then be only slightly worse between 70% and 95% of D_e but somewhat better for lower and higher energies (see Fig. 8); the choice of too low a value of $\alpha(\mathrm{F}_2)=1.085$ would, of course, lead to an increase in the limit of error (about $6\times10^{-3}\ D_e$). However, the limit of error resulting from direct inversion of the FMRP formula is $2.5\times10^{-2}D_e$ (about 500 cm^{-1}), i.e., essentially larger. Nevertheless, for such molecules, the multiparameter GRPC method should be tried to achieve a better approximation in the right limb.

With respect to all these examples, one should note that, of course, the approximation of the potential by the GRPC extension would be worse if only an essentially lower portion of the potential should be known. However, in most cases, it would still be better than the approximation obtained by inverting the FM formula (as suggested in Ref. 1).

2. *Estimation of the left limb of the potential*

The approximation of the left limb does not present such problems and the one-parameter approximation seems entirely sufficient. Again, a simple geometric rule (cf. Fig. 9) facilitates the task to obtain an accurate estimate. By an increase in the value of α, the RPC is shifted to the left (cf. Sec. II). If the RPC of a molecule A which lies to the right of the RPC of a molecule B is shifted to lie very close to the right ($\Delta\rho$ still positive) of the RPC of B by taking $\alpha(A)>1$ [or, alternatively, B is shifted by taking $\alpha(B)<1$], then it runs almost quasiparallel to this RPC of B, crosses it and runs quasiparallel on the other side of the latter. The differences between the two curves may be made very small. The potential calculated by the GRPC method then shows a similar behavior with respect to the true potential.

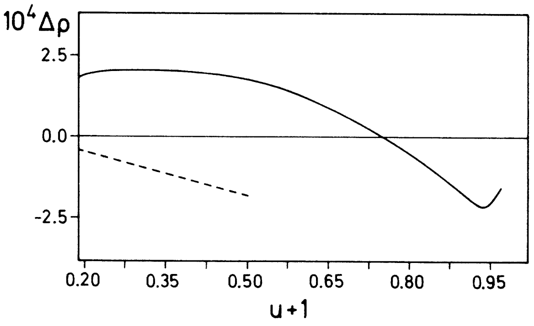

FIG. 9. Left limb. Estimation of the ground-state potential of HF from the ground-state potential of I_2 by the GRPC method. Differences in ρ from the RKR RPC of HF (zero line). ——, GRPC of I_2 [$\alpha(\mathrm{I}_2)=1.47$]; – – –, GRPC of I_2 [$\alpha(\mathrm{I}_2)=1.475$] as a test curve, cf. text.

Due to the regular behavior of all RPC's in the left limb, one needs not use the RPC of an affiliated molecule for this approximation, any not anomalous RPC will do. The approximation will presumably be better the closer the two RPC's lie. However, a very good approximation is obtained also with the use of quite distant RPC's.

This procedure is demonstrated[9] in Fig. 9, where the potential of the light molecule HF was calculated from the potential of the heavy molecule of I_2; the difference between the RPC's of these two molecules is large amounting to $\Delta\rho=0.03$ for $u=0$. (In the same way, one could calculate the potential of I_2 from the potential of HF.)

Let us assume that the potential of HF is known only up to 40% of D_e. The technique is then the following. One takes first a somewhat larger value of $\alpha(\mathrm{I}_2)$ (here 1.475, dotted line in Fig. 9) to verify that the GRPC of I_2 will, indeed, cross the RPC of HF when a smaller value of $\alpha(\mathrm{I}_2)$ is taken [since for a smaller value of $\alpha(\mathrm{I}_2)$ the descending portion in the difference curve scheme of Fig. 9 sets on later]. After this preliminary test, one chooses a suitable value of $\alpha(I_2)=1.47$ by which the GRPC of I_2 is shifted into the vicinity of the RPC of HF, so that it lies slightly to the right of the latter. As may be seen in Fig. 9, the limit of the resulting difference in ρ is about 5×10^{-4}, which means here that the limit of error in the turning points of the potential in the repulsive limb will be smaller than 0.001 Å, i.e., compares with the limit of accuracy of the RKR method. The small irregularity just below the dissociation limit is due to a corresponding slight irregularity in the potential of I_2.

To make the thing more interesting let us consider a more exotic case where the left limb of the ground-state potential of I_2 is calculated from the RKR potential of the excited d state of XeO from Ref. 31 (the gap between these two RPC's is again large, amounting to $\Delta\rho=0.035$). Let us again assume that the potential of I_2 is known only up to, say, 45–50 % of D_e. With the value $\alpha(\mathrm{XeO})=1.32$, an extremely good approximation of the potential of I_2 is evidently obtained (Fig. 10). The irregularity in the highest portion is due to slight irregularities in the potentials and is immediately recognized so that the correct upper portion of the potential may be obtained by an evident extension of the lower portion (dotted lines in Fig. 10). The limit of error in ρ attains only about 2×10^{-4}, i.e., the error in r lies again below the limit of error of the RKR method in this case.

Let us emphasize that, according to the geometric rule formulated above, it would be false to choose $\alpha(\mathrm{XeO})$ so that the GRPC of XeO would cross the RPC of I_2 already for $u+1<0.5$, since then the limit of error must of necessity be larger, as shown in Fig. 10 for $\alpha(\mathrm{XeO})=1.33$. However, even here, the limit of error seems to still be smaller than the limit of error of the RKR method. The correct trend of the extension of the potential is verified in testing also an evidently too high value $\alpha(\mathrm{XeO})=1.35$ (lowest curve in Fig. 10).

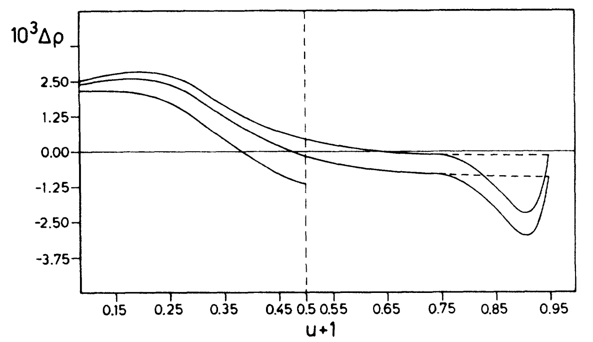

FIG. 10. Left limb. Estimation of the ground-state potential of I_2 from the potential of the $d\,{}^1\Sigma^+$ excited state of XeO. Differences in ρ from the RKR ground-state RPC of I_2. ——, from top to bottom, GRPC of XeO [α(XeO)=1.32), the same for α(XeO)=1.33 and for α(XeO)=1.35. — — —, corrections of irregularities of the RKR calculation by natural extension of the lower portion. The lowest solid line serves as a test curve, cf. text.

In Fig. 5, we have shown the extension of the potential of CO from $u+1=0.3$ [α(CO=1.065] calculated by this GRPC method from the potential of NO. The limit of error was again of the order 10^{-4} Å.

In Fig. 11, the prediction of the upper portion (above 72% of D_e) of the left limb of the potential of RbCs from Ref. 12(b) is evaluated. [See Table XIV of Ref. 12(b), where the potential of RbCs was calculated from the potential of Cs_2 using the value α(RbCs)=1.015. The RKR RPCs of RbCs and Rb_2 lie *very* slightly to the right of the IPA-RPC (Ref. 10) of Cs_2, cf. Ref. 12(b) Fig. 4.] The result is excellent, the errors are negligible (smaller than 3×10^{-4} Å). The irregularity just below the dissociation limit is caused by a slight irregularity in the Cs_2 potential which is immediately recognized so that the correct highest portion of the potential is obtained by a direct extension of the lower portion (dotted line in Fig. 11). Let us mention that such very small irregularities in the RKR potentials often appear due to slight errors in the spectroscopic constants[10] or in the RKR calculation; they may be visualized through comparison with a standard regularly behaved (e.g., analytic) curve.

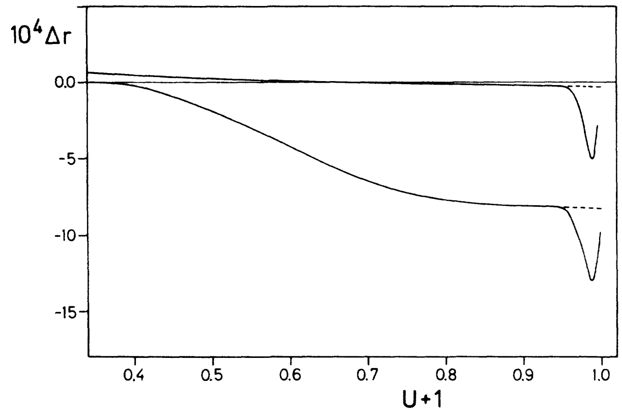

FIG. 11. Left limb. Evaluation of the estimation of the upper portion of the ground-state potential of RbCs (from 72% to 100% of D_e), calculated in Ref. 12(b) from the ground-state IPA potential of Cs_2 by the GRPC method. Differences in r from the RKR potential of RbCs (zero line). ——, from top to bottom, α(RbCs)=1.015 [cf. Table XIV of Ref. 12(b)]; α(RbCs)=1 [cf. Table XVI of Ref. 12(b)]. The values of r_e(RbCs)=4.4271 Å and $D_e(Cs_2)$=3833 cm^{-1} were taken as units for internuclear distance and energy, respectively. All curves have a common minimum.

In the low portion of the left limb, the RPC of RbCs almost coincided with the RPC of Cs_2 [Fig. 4 of Ref. 12(b)]. So if the potential of RbCs were known only up to 40% of D_e, the extension could be calculated from the potential of Cs_2 directly, as has been done in Ref. 12(b) in Table XVI. The extension of Table XVI of Ref. 12(b) is also evaluated in Fig. 11: the limit of error is somewhat larger but still smaller than $10^{-3}r_e$, i.e., about 0.003 Å. In this calculation, the geometric rule has then not been employed and the potential was calculated directly from the Cs_2 potential. The use of the geometric rule could have essentially reduced the (small) error. Fortunately, the RPC of RbCs lies very close to the RPC of Cs_2 in the left limb; the potential of RbCs presents a somewhat difficult case being unusually unsmooth.

A quite similar evaluation is obtained for the prediction of the upper portion of the left limb of the potential of Rb_2 which was also calculated in Ref. 12(b) from the IPA potential of Cs_2, using the value $\alpha(Rb_2)$=1.005 [Table XIII of Ref. 12(b)]. One obtains a similar picture as shown for the potential of RbCs calculated from the potential of Cs_2 in Fig. 11 and the limit of error is smaller than 0.001 Å.

All these examples show that the one-parameter GRPC method yields a highly accurate approximation for the left limb which is in general satisfactory even from the rigorous point of view of the spectroscopist, since the limit of error is comparable with the limit of error of the RKR methods. This fact is very satisfying, since the extrapolation of the left limb is by far not trivial as the example of Ref. 14(d) shows (cf. discussion in Ref. 32).

3. *The use of theoretical potentials*

The estimates of the potential may also be calculated from an *ab initio* theoretical RPC of the same molecule, inverting the theoretical RPC with the use of the experimental values of the molecular constants [method (*B*) of Ref. 12(b)] if an *appropriate* theoretical method was used [cf. Refs. 12(b) and 33]. A more accurate approximation may be obtained if the *ab initio* theoretical RPC is made to coincide more closely with the known portion of the RKR RPC using a suitable value of the parameters in the GRPC formula. [For this purpose, also an *ab initio* potential of another—possibly lighter—(affiliated) molecule may be used, for which the calculation might be easier, cf. below and Fig. 6.] Since, *a priori*, one may consider different types of theoretical methods, we refrain here from formulating any "geometric rules" as in the foregoing paragraphs; they may depend on the type of the theoretical calculation.

Such a procedure is necessary if one wants to use also theoretical potentials calculated with the use of the "effective core-potential" method. This method sometimes poorly represents the whole electron correlation and the polarization, which results in significant errors in the left limb.[11(h)] Figure 12 illustrates it on the example of the singlet $C(3\,^1\Sigma^+)$ state of NaK. The RKR potential was taken from Ref. 34, the theoretical potential from Ref. 35. Whereas for the triplet b state $(1\,^3\Pi)$ (potentials from the same references) the theoretical RPC almost coincides with the RKR RPC, an enormous discrepancy is found for the C state $(3\,^1\Sigma^+)$, cf. Fig. 12.

The error is so large that the variation of the parameter α for one of the RPC's does not suffice for an approximate coincidence. Instead, the parameter α must be varied for both the RKR and the theoretical RPC to obtain approximate coincidence. This is achieved in Fig. 12 by taking $\alpha^{\mathrm{RKR}}=0.72$ and $\alpha_{\mathrm{theor}}=1.8$. The theoretical potential may then be used for an extension of the RKR potential by inverting the GRPC with the use of the experimental values of the molecular constants and the corresponding values of the parameter α.

In Fig. 6, the approximation for the upper portion of the potential of HCl is shown, which was obtained by using the rather *inaccurate* theoretical potential of HF from Ref. 36 (only 88.9% of the experimental value of D_e was obtained) and the value $\alpha_{\mathrm{theor}}=1.1$ in fitting the lower portion of the RKR potential (up to 30% of D_e). The result is not so bad, the limit of error being about $2\times10^{-3}D_e$.

It has already been illustrated by Figs. 13 and 14 of Ref. 12(b) that the RPC method (B) brings an essential improvement also for accurate *ab initio* theoretical calculations. With the use of the GRPC, the method (B) of Ref. 12(b) may be still essentially improved, which might be important for the excited states, where the theoretical approximation is sometimes not quite ideal. This is illustrated here in Figs. 13 and 14 on the example of the excited A state $(1\,^1\Sigma_u^+)$ of Na_2. Here we compare the accurate theoretical results of Ref. 37 with the much less accurate theoretical calculation of Ref. 38. The study of this case will also make clear some problems involved in such calculations.

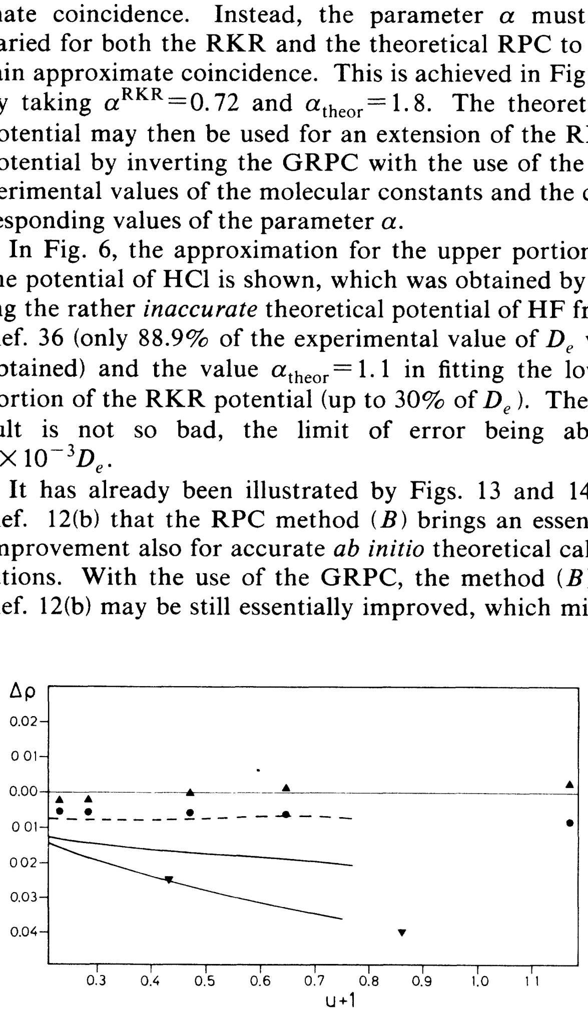

FIG. 12. Left limb. Application of the GRPC method to theoretical potentials of excited states calculated with the use of the effective-core potential method. Differences in ρ from the ground-state RPC of HF (zero line). ——, from top to bottom, RKR RPC of the $3\,^1\Sigma^+(C)$ state of NaK; RKR RPC of the $1\,^3\Pi(b)$ state of NaK. — — —, RKR GRPC $(\alpha^{\mathrm{RKR}}=0.7)$ of the C state of NaK. ▲, theoretical RPC of the C state of NaK; ▼, theoretical RPC of the b state of NaK; ●, theoretical GRPC of the C state of NaK $(\alpha_{\mathrm{theor}}=1.8)$.

One may expect that the calculation of Ref. 37 is as accurate for the first excited $1\,^1\Sigma_u^+$ state as it is for the ground $1\,^1\Sigma_g^+$ state, which may be also verified on the theoretical values of the molecular constants. So one may assume that, in reduced form, it represents the true RPC correctly and a very accurate approximation of the potential of the A state of Na_2 could be calculated from this theoretical *ab initio* potential using the (B) method of Ref. 12(b), i.e., inverting the RPC formula with the use of the experimental values of the molecular constants r_e, D_e, and k_e, similarly as calculated for the ground state of the LiNa molecule in Table XII of Ref. 12(b). However, the same procedure would lead to more significant errors if applied to the theoretical potential of Ref. 38 because of the more pronounced discrepancy between this theoretical RPC and the RKR RPC, cf. Fig. 13.

Figure 13 shows reduced energy difference curves for the RKR RPC and the theoretical RPC's in the right limb. Differences from an auxiliary curve must be evaluated, since the few points of the theoretical potential do not permit a really accurate calculation of small differences (as is necessary in view of the sensitivity of the RPC method) even if most sophisticated methods of interpolation are used.[39]

It seems that slight errors exist in the highest known portion of the RKR potential (up to 60% of D_e) of the A state of Na_2 of Ref. 40(a): the theoretical RPC of Ref. 37 gives an excellent approximation of the RKR RPC (differences of a few parts in $10^{-4}\,D_e$) with the exception of the highest portion where the difference abruptly increases to about $3\times10^{-3}D_e$, i.e., about 8 cm^{-1}. We do not believe that this bend of the highest portion of the

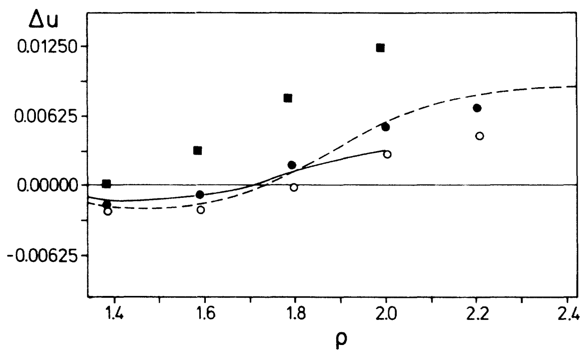

FIG. 13. Right limbs of the RPC's. Differences in u between the RKR RPC of the $1\,^1\Sigma_u^+(A)$ state of Na_2 and the theoretical RPC's of this state evaluated with respect to an auxiliary potential curve (zero line). ——, RKR RPC. — — —, theoretical RPC (Ref. 37); ■, theoretical RPC (Ref. 38); ●, theoretical GRPC for Ref. 38 $(\alpha_{\mathrm{theor}}=0.82)$; ○, theoretical GRPC for Ref. 38 $(\alpha_{\mathrm{theor}}=0.78)$.

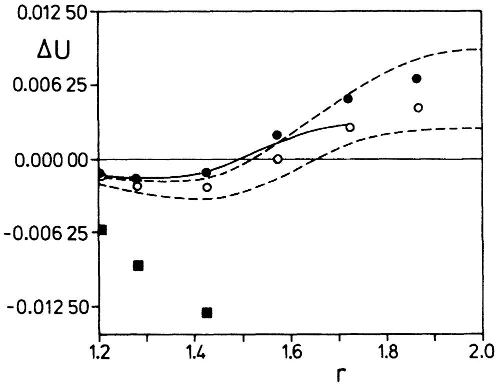

FIG. 14. Right limbs of the (not reduced) potentials corresponding to Fig. 13. Differences in U between the RKR potential of the $1\,^1\Sigma_u^+$ (A) state of Na_2 and the theoretical potentials, and the potentials calculated with the use of the GRPC method, evaluated with respect to an auxiliary potential curve (zero line). ——, RKR potential. — — —, from bottom to top: theoretical potential (Ref. 37); potential calculated with the use of the RPC method (B) [Ref. 12(b)] from the theoretical potential of Ref. 37. ■, theoretical potential of Ref. 38; ●, potential calculated from the theoretical potential of Ref. 38 with the use of the GRPC method ($\alpha_{\text{theor}}=0.82$); ○, potential calculated from the theoretical potential of Ref. 38 with the use of the GRPC method ($\alpha_{\text{theor}}=0.78$), cf. text. All curves are shifted to a common minimum. Experimental values of $r_e=3.6384$ Å and $D_e=8309$ cm^{-1} for the $A\,^1\Sigma_u^+$ state of Na_2 are taken as units for the internuclear distance and the energy, respectively.

RKR curve is due to the perturbations existing in this state.[41]

The errors in the potential of Ref. 38 are much larger, since the differences of the corresponding RPC from the RKR RPC attain values of almost $10^{-2}D_e$ (about 25 cm^{-1}) in the lower portion. However, with the use of the generalized RPC formula, one obtains also here a GRPC which nearly coincides with the RPC corresponding to Ref. 37. It may be seen on the example of Fig. 13 that the method must be applied with caution, since slight errors in the highest known portion of the RKR potential may often exist, corresponding to slight inaccuracies in the spectroscopic constants. Such errors would, however, lead to relatively large errors in the extension of the potential constructed with the use of the GRPC method if one insists on the coincidence in the highest points of the RPC. In Fig. 13, the RPC which gives a good coincidence with the lower portion of the RKR RPC (for $\alpha=0.82$) gives the good result; on the other hand, insisting upon the coincidence in the highest point of the RKR RPC ($\alpha=0.78$) would cause an error of more than 5 cm^{-1}.

Figure 14 shows the right limbs of the potentials calculated from the theoretical RPC's by inverting the RPC or GRPC formula with the use of the experimental values of the molecular constants r_e, D_e, and k_e. In addition to our potentials calculated by this method, we also show here the original theoretical potentials of Refs. 37 and 38 which, of course, asymptotically approach the incorrect theoretical value of D_e which is by 100 cm^{-1} and by 300 cm^{-1} in error in Ref. 37 and 38, respectively. The RKR potential also *erroneously* turns into this direction. Let us emphasize that our argument was based on the assumption of the correctness of the D_e value for the A state of Na_2. (This value of D_e is determined from the T_e value of Ref. 40(b) for the A state of Na_2 and from the D_e value for the ground state,[42] assuming dissociation into ^2S and ^2P atomic states). Since the RPC still is not very sensitive to errors in the D_e value in the portion of the potential where the RKR curve has been determined, a relatively large error in the D_e value should exist if the potential is correct, which seems improbable.

The result of our RPC methods is quite satisfactory: it appears that (a) even accurate theoretical potentials of the excited states may be improved by the use of the RPC method, and (b) even rather inaccurate potentials may be improved (using the generalized RPC formula) in such a way that they yield results almost equivalent to those yielded by the accurate calculation. At the same time, this example suggests the hope that the extension of the potential with the use of this method may be obtained even if only a relatively low portion of the potential is known, since the "good" potential in Fig. 13 is obtained in fitting the RKR RPC up to about $\rho=1.6$, corresponding to about 30% of D_e. The approximation will be, of course, better the higher the portion of the potential well of the RKR potential that could be determined from the spectra. We think that a portion of the RKR potential up to about $0.4D_e-0.5D_e$ should be available for not very accurate *ab initio* calculations to obtain high accuracy results also in the right limb. Essentially better results could, of course, be obtained with the use of the multiparameter GRPC method. The calculation of the left limb of the potential is essentially easier and unproblematic in view of the (normally) small differences in the left limb and its simpler geometry. (For comments on the theoretical methods in relation to this problem cf. Ref. 33.)

B. Multiparameter approximation

The foregoing examples have shown that the one-parameter approximation seems quite satisfactory in the left limb, though it certainly might be still improved by using more parameters in the GRPC formula.

In the right limb, the one-parameter approximation seems also acceptable for molecules where the gap between the different RPC's is not too large, such as hydrides or even alkali-metal diatomic molecules or, say, heteronuclear combinations of C, N, and O atoms, etc.

For groups of affiliated molecules for which the RPC's are more distant in the RPC scheme, e.g., the homonuclear halogen molecules, the one-parameter approximation certainly gives a better approximation for the extension of the potentials than any other method known, however, it still should be improved by the variation of more parameters in the GRPC formula.

The GRPC formula is adapted to the RPC scheme and sufficiently flexible to obtain a coincidence of any two RPC's in the current format of figures normally used in the literature. As an example we show in Fig. 15 one of

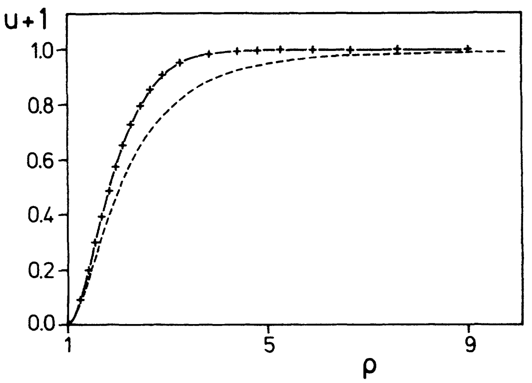

FIG. 15. Right limb (ground state). ——, RPC of H_2; — — —, RPC of Cl_2; +, GRPC of Cl_2 ($\xi=-0.6$, $\alpha=1.18$).

the possibilities—here the variation of only two parameters, ξ and α—which leads to an approximate coincidence of the RPC's of H_2 (potential from Ref. 43) and Cl_2 [with the values $\xi(Cl_2)=-0.6$ and $\alpha(Cl_2)=1.18$] where the gap between the RPC's is large. Such figures are currently shown in publications to prove coincidence. However, such results are in fact not very interesting. For instance, in Fig. 15, the limit of error in energy is still about $5\times10^{-3}D_3$, i.e., for Cl_2 about 100 cm^{-1}. One can, of course, reduce this error with the use of more parameters.

However, the question of real interest is not to improve the accuracy of the coincidence by a few cm^{-1}: the real aim is to find a method which could permit an extension of the potentials with an *error* of only a few cm^{-1} in a general case. An appropriate correction function $f(r)$ in formula (7) might here be of great help. The solution of this problem will, of course, need some time, since the method should be tried on different groups of (also heavy) molecules. However, with the exception of some alkali-metal hydrides and nonmetal hydrides, the alkali-metal diatomic molecules and the halogens, there are practically no other molecular groups where the RKR potentials were known up to the dissociation limit. For heavier molecules, the theoretical calculations still cannot be used as reliable approximations. Moreover, close coincidence of two GRPC's in the lower portion does not necessarily imply close coincidence also in the upper portion unless the formula used intrinsically corresponds to the geometry of the RPC scheme. Simple auxiliary geometric rules which hold for the one-parameter function can hardly be formulated for the multiparameter function. Therefore, a serious attempt to give a *definitive* definition of such an *accurate* GRPC approximation method can be made only when more RKR potentials are known up to the dissociation limit.

It is possible that the GRPC formula could then also be used for a more perfect definition of the reduced potential in general. The present definition of the RPC certainly is still not ideal: as has been discussed in Ref. 2, for some heavier molecules the inequality $\rho_{ij}>r_e$ appears. As a consequence, the RPC is then well defined only up to a certain limit of ρ. For instance, the RPC's of Cl_2, ICl, and I_2 are defined up to 99.9%, 99.6%, and 97% of D_e, respectively. (The RPC of F_2 is defined for all known points of the potential, i.e., for more than 99.4% of D_e.) In that case, e.g., a finer estimation of D_e from the comparison of the tails of the RPC's could not be made. This, however, is not so serious, since for a definitive group of affiliated molecules, one can make ρ_{ij} smaller than r_e by using some parameter of the GRPC. For instance, the value $\alpha=1.3$ is sufficient for this purpose in the group of halogen molecules and permits a comparison of the tails of the RPC's (cf. Ref. 2, p. 274).

Further, one would like to have a general validity of the noncrossing rule for all molecules also in the right limb. So far, a concrete case of a (small) crossing of the RPC's of two different groups of affiliated molecules has been observed for the close-lying RPC's of the group of alkali-metal hydrides and the group of alkali-metal diatomic molecules. This crossing is due to the anomaly of the alkali hydrides[16] and, therefore, probably cannot be removed by any redefinition of the RPC. It is nevertheless possible that other crossings of the RPC's of different groups of affiliated molecules might appear.

However, as explained above, also the problem of perfecting the definition of the reduced potential may be seriously attempted only when still more RKR potentials are known up to the dissociation limit. Hence we shall postpone the final discussion of the multiparameter approximation to a later publication.

V. CONCLUSIONS

We have shown that the definition of the reduced potential of diatomic molecules given by Ferrante *et al.*[5(a)] or Tellinghuisen *et al.*[1] is equivalent to the old definition of Frost and Musulin[6] and cannot be used for a systematic comparative study of diatomic molecules. We have further shown that it cannot be used to obtain reliable and satisfactory approximations of the potentials either.

On the other hand, the RPC formula[2] leads to systematic regularities in the RPC scheme. The GRPC formula then yields approximation methods for the extension of the potentials *within this RPC scheme*, which appear to be much better than any other methods known.

At any rate, the results show that the starting *conception*[2,3] was correct: The fundamental aim should be a search for the *laws* (regularities) of the whole RPC scheme; good approximation methods should then appear as a consequence. In fact good approximation methods can always be constructed (quantitative results obtained) only in the framework of the regularities of a definite global scheme (qualitative characterization of the problem). As the comparison with the FMRP method (Sec. III) shows, it is important to insist on this type of approach. It is certainly regrettable that the rules of the RPC scheme[13] cannot be deduced from the principles but they do exist.

However, many practioners interested only in practical applications (numerical results), are just looking, e.g., for a universal coincidence of the potential curves, which does not seem to exist. I am emphasizing this point, since it has led to some misunderstandings about the RPC method in the past.

The potentials obtained with the help of the GRPC method may then be used for the calculation of the spectra in a numerical solution of the corresponding Schrödinger equation with the use of standard methods.[44]

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[17] Compare Refs. 18 and 19. In Ref. 18, two sets of spectroscopic constants were used for the lower and upper portion of the potential of CsH and the corresponding RKR potential shows anomalous irregularities [cf. also Refs. 11(e) and 11(f)]. In Ref. 19(b), a set of spectroscopic constants quite different from that of Ref. 19(a) was used when the highest vibrational levels of NaH were included; whereas the value of Y_{10} of Ref. 19(a) represents correctly the force constant, the new value of Ref. 19(b) does not. With the value of D_e(NaH) of Ref. 19(b), the RPC of NaH could give a confluence with the RPC's of LiH and KH, however, the highest portion shows the same irregular behavior as demonstrated for CsH in Refs. 11(e) and 11(f). Through a small change in the energy values of the low portion of the potential of NaH corresponding to the new constants (Refs. 19(b)], a slightly incorrect behavior of the lower portion of the RPC of NaH also results (Ref. 20).

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