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The rational fraction representation of diatomic potentials

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The representation of diatomic potential energy curves by rational fractions using low order polynomials in numerator and denominator is investigated. The rational fraction method, which is illustrated by examples, is shown to fail in providing a robust representation of diatomic potentials for wide application.

Key words: Potential energy curves — Rational fractions

Several studies show that rational fractions can give a good representation of diatomic potentials [1–7]. For example, in recent work Beckel (and co-workers) [3–7] made a least-squares fit to *ab initio* data on the potential curves of the ground and some excited states of H_2^+ and the ground-state of H_2 using the function

$$V(R)=\frac{p_0+p_1R+\cdots p_LR^L}{1+q_1R+\cdots q_NR^N}\equiv\left[\frac{L}{N}\right]. \tag{1}$$

They obtained very accurate representations of these potentials but only by using high order polynomials in numerator and denominator; $L=4$, $N=10$.

Our interest in such functions lies in the possibility that the coefficients p and q can be chosen so as to reproduce the long-range part of the potential, normally expressed as a power series in R^{-1}, as well as the region around the minimum. Beckel and co-workers [3] have thought along similar lines, for example, by taking for the H_2 ground state $N=L+6$ and $(p_L/q_N)=-C_6=-6.499027a_0^{-6}$, which reproduces the leading term $(-C_6R^{-6})$ in the dispersion energy. However,

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what is not clear from previous work is whether a function such as (1) will be widely useful as a representation of diatomic potentials. To be so it must be possible to obtain the coefficients p and q from spectroscopic data rather than from *ab initio* calculations, and, in view of the differing amount of data for different systems, the function needs to be robust to changes in the length of the polynomials L and N. The evidence on this is not encouraging. For example, Sonnleitner and Beckel [6] showed that the potential of the $2p\sigma_u$ state of H_2^+ could be fitted well by $[L/N]=[3/5]$, $[4/8]$ and $[6/10]$ functions but they found no satisfactory independent $[5/9]$ function. For the H_2 ground-state [3] no satisfactory even-L functions could be obtained.

Our strategy will be to start by imposing minimum requirements on the function and to add further conditions which lead progressively to a more accurate function. However, we first note that (1) does not have a pole at $R=0$ as required for the nuclear repulsion and for that reason we have made our most extensive studies with the function $R^{-1}[L/N]$. This function was also considered by Beckel and co-workers [4] for the ground-state of H_2 but was not examined in any depth. For the systems we studied, the additional factor R^{-1} gave a more satisfactory function.

The asymptotic limit can be imposed by writing the function in the form

$$V(R)=\frac{p_L}{q_N R^{N-L+1}}\left(1+\frac{p_{L-1}}{P_L R}+\cdots\frac{p_0}{p_L R^L}\right)\left(1+\frac{q_{N-1}}{q_N R}+\cdots\frac{1}{q_N R^N}\right)^{-1} \tag{2}$$

and making a Taylor expansion in $(1/R)$. Thus, if the potential approaches infinity with a leading term $-C_k R^{-k}$, then $k=N-L+1$ and $C_k=-(p_L/q_N)$. If the higher terms in the $(1/R)$ expansion are known then these provide further restrictions on the coefficients. For example, for neutral atoms in ^1S or ^2S states the asymptotic expansion contains only even powers of $(1/R)$ hence the polynomials L and N are best written with only odd or even powers of R, one being odd the other even [1] (except for the leading term in the denominator which is even of order zero). In particular we have the result

$$C_{k+2}=\frac{p_L q_{N-2}}{q_N^2}-\frac{p_{L-2}}{q_N} \tag{3}$$

$$C_{k+4}=\frac{p_L q_{N-4}}{q_N^2}+\frac{p_{L-2} q_{N-2}}{q_N^2}-\frac{p_{L-4}}{q_N}-\frac{p_L q_{N-2}^2}{q_N^3}. \tag{4}$$

A minimal requirement for most potentials is that there is a single minimum at $R=R_e$ of depth D_e; This may be either a van der Waals or valence minimum. To ensure that this is minimum and not some other stationary point we can

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[1] A more general procedure would be to consider even and odd terms in both polynomials, and impose the additional requirement that the odd terms of the asymptotic expansion should vanish. Such an approach has however been found to give results even poorer than those reported here, mainly due to singularities arising for values of R between R_0 and R_e; thus, it will not be discussed any further

require that the potential becomes zero at some point $R = R_0$, $R_0 < R_e$. R_0 marks the onset of the net repulsive part of the potential.

The simplest function with four parameters that satisfies this requirement has the form

$$V(R) = \frac{p_0 + p_2 R^2}{R[1 + q_A R^A + q_{k+1} R^{k+1}]}, \qquad A < k+1. \tag{5}$$

The two-term numerator ensures that there is only one zero in $V(R)$ for positive R. The coefficients of this function must satisfy the following equations

$$C_k = -(p_2/q_{k+1}) \tag{6}$$

$$R_0^2 = -(p_0/p_2) \tag{7}$$

$$D_e = -\frac{(p_0 + p_2 R_e^2)}{R_e(1 + q_A R_e^A + q_{k+1} R_e^{k+1})} \tag{8}$$

$$2p_2 = -D_e[R_e^{-1} + (A+1) q_A R_e^{A-1} + (k+2) q_{k+1} R_e^k]. \tag{9}$$

For any choice of A and k equations (6)–(9) can be linearized in the four coefficients and hence solved. This has been done for the three examples $Ne_2(X\,{}^1\Sigma_g^+)$, $Ar_2(X\,{}^1\Sigma_g^+)$ and the first triplet excited state of Li_2 $(a\,{}^3\Sigma_u^+)$ which is also a van der Waals state. Taking $k = 6$ and $A = 1$ we obtain results shown in Table 1 and Figs. 1, 2 and 3. It is seen that the potential (5) gives a too narrow bowl for the van der Waals well, and displays a plateau at a positive energy similar in absolute value to that of the well depth.

We now impose the more stringent requirement that the potential agrees with the first three terms of the asymptotic expansion in $(1/R)$, plus the constraint that there is a minimum at R_e and a zero at R_0. To do this we take the function

$$V(R) = \frac{p_0 + p_2 R^2}{R(1 + qR + q_3 R^3 + q_5 R^5 + q_7 R^7)} \tag{10}$$

and again examine the systems $Ne_2(X\,{}^1\Sigma_g^+)$, $Ar_2(X\,{}^1\Sigma_g^+)$, and Li_2 $(a\,{}^3\Sigma_u^+)$.

The potentials for Ne_2 and Ar_2 are quite satisfactory up to a repulsive energy of about twice the depth of the well but above that they deviate substantially from the best empirical potential because there are zeros in the denominator of (10) for positive values of R. The Ne_2 potential has a singularity at $R = 0.75a_0$ and that of Ar_2 at $3.5a_0$.

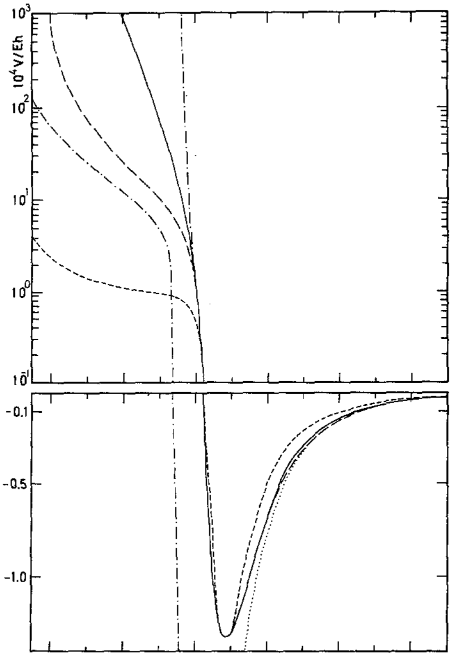
For Li_2 the potential is quite unsatisfactory as the singularity occurs close to R_0 at $R \cong 6.2a_0$, being negative from this point inwards (this part of the potential curve falls outside the scale of Fig. 3 and hence is not shown).

The problem of singularities was noticed by Beckel and co-workers [4] and any potential with such a singularity was dropped without further consideration. As a result their polynomials were of high order and the coefficients can only be obtained by a least-squares fitting to *ab initio* data.

Table 1. Parameters obtained for the rational fraction potentials, in a.u.

System	Potential	L	A	p_0	p_A	p_L	q_A	q_{L+1}	q_{L+3}	q_{L+5}
Ne($X\,^1\Sigma_g^+$)^a	(5)	2	1	1.970 (−4)		−7.246 (−6)	−2.020 (−1)			1.055 (−6)
	(10)	2	1	−3.865 (−2)		1.422 (−3)	−1.482 (0)	−5.442 (−2)	7.915 (−3)	−2.070 (−4)
	(11)	4	2	7.200 (−3)	−6.268 (−4)	1.332 (−5)		−1.984 (−3)	1.127 (−4)	−1.938 (−6)
Ag$_2$($X\,^1\Sigma_g^+$)^a	(5)	2	1	7.141 (−4)		−1.779 (−5)	−1.668 (−1)			2.648 (−7)
	(10)	2	1	−1.489 (−2)		3.711 (−4)	−2.683 (−1)	−4.050 (−3)	3.432 (−4)	−5.522 (−6)
	(11)	4	2	1.792 (−2)	−1.045 (−3)	1.492 (−5)		−5.756 (−4)	2.045 (−5)	−2.220 (−7)
Li$_2$($a\,^3\Sigma_u^+$)^a	(5)	2	1	3.804 (−2)		−9.003 (−4)	−6.474 (−2)			6.477 (−7)
	(10)	2	1	−5.402 (−3)		1.278 (−4)	−1.662 (−1)	−9.365 (−5)	9.444 (−6)	−9.198 (−8)
	(11)	4	2	4.045 (−2)	−1.426 (−3)	1.108 (−5)		−7.884 (−5)	1.507 (−6)	−7.971 (−9)

[a] The input values for σ, ε and R_m were taken from [8], [9] and [10], for Ne$_2$, Ar$_2$ and Li$_2$, respectively. The values of C_6, C_8 and C_{10} were in all cases taken from [11]



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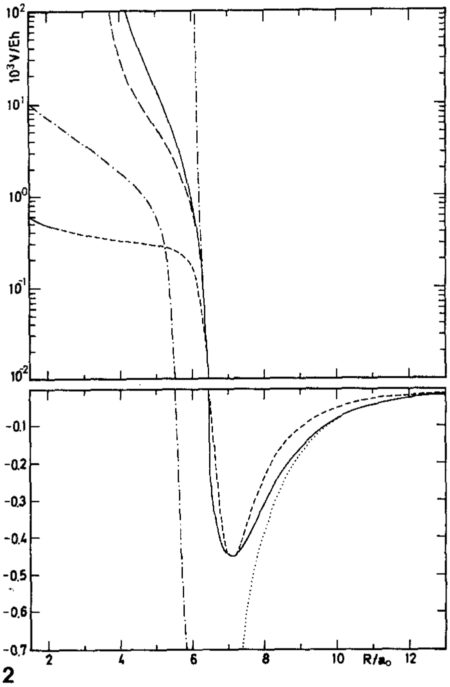

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Fig. 1. A comparison of the rational fraction potentials of the present work [---- (5), - - - (10), —·—·— (11)] with an accurate empirical curve [8] (——) for $Ne_2(X\ ^1\Sigma_g^+)$. Also shown is the asymptotic dispersion energy curve (· · · ·) terminated at the R^{-10} term

Fig. 2. A comparison of the rational fraction potentials of the present work with an accurate semiempirical curve [12] for $Ar_2(X\ ^1\Sigma_g^+)$. Legend as in Fig. 1

The only other simple function that can reproduce our input data is

$$V(R)=\frac{p_0+p_2R^2+p_4R^4}{R(1+q_5R^5+q_7R^7+q_9R^9)}. \tag{11}$$

However, we again found singularities and for both Ne_2 and Ar_2 they were close to R_0 ($4.5a_0$ for Ne_2 and $6.0a_0$ for Ar_2) so that the potentials were less satisfactory than the function (10). For Li_2 the discontinuity occurs beyond the van der Waals minimum and hence is totally unsatisfactory.

A more accurate test of the potential in the attractive region can be obtained by comparing the calculated with the observed vibrational frequencies. This is done in Table 2 for Ne_2 and Ar_2 using the potentials (10) and (11). Function (10) is clearly almost as accurate as the best empirical potentials in the attractive well.

In conclusion we have found that if a rational fraction is parametrized to the asymptotic expansion, to the depth and position of the potential minimum, to the position R_0 of the zero, then this can be a very accurate representation of the potential in the attractive region. However, singularities will usually occur at

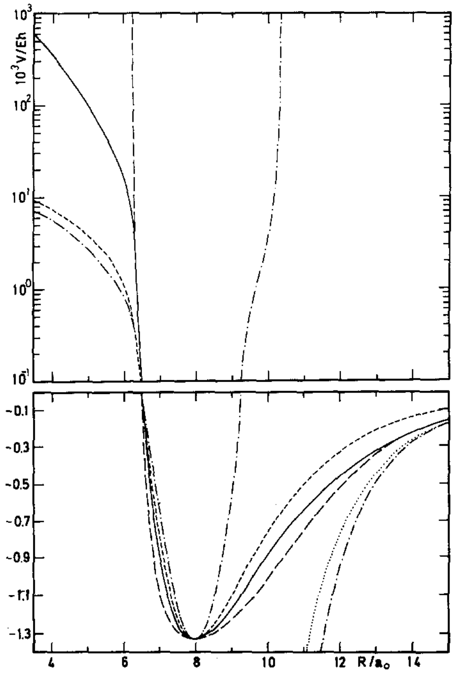

Fig. 3. A comparison of the rational fraction potentials of the present work with an accurate theoretical curve [13] for $Li_2(a\,^3\Sigma_u^+)$. Legend as in Fig. 1

Table 2. A comparison of the spectroscopic constant $G(v)$ from the various potentials for Ne_2 and Ar_2 with experiment. All values, in cm^{-1}, are relative to the ground-state constant $G(0)$

System	Potential	$G(1)$	$G(2)$	$G(3)$	$G(4)$	$G(5)$
$Ne_2(X\,^1\Sigma_g^+)$	(10)	13.72	16.75	—	—	—
	(11)	13.68	16.61	—	—	—
	exp [14]	13.7±0.75	n.o.[a]	—	—	—
$Ar_2(X\,^1\Sigma_g^+)$	(10)	26.42	47.02	62.24	72.71	79.21
	(11)	25.93	46.62	62.12	72.87	79.57
	exp [9]	25.74±0.1	46.15±0.2	61.76±0.2	72.66±0.2	79.44±0.25

[a] Not observed

some values of R between 0 and R_0, and, as our example of Li_2 has shown, these may even occur for $R > R_e$.

Because of these singularities we believe that rational fractions cannot be described as a robust representation of a diatomic potential for wide application.

There are other representations based on the same input data which have generality and accuracy, and these provide alternative functions for practical use (see [13, 15–17] for examples).

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