

MULTIPLE-PARAMETER FUNCTIONS FOR R.K.R. DIATOMIC POTENTIAL : A SIMPLE NUMERICAL APPROACH

Mounzer Dagher

Faculty of Sciences II, Lebanese University
Beirut, Lebanon
mounzer@hotmail.com

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ABSTRACT

The problem of the representation of the diatomic potential by analytic functions is considered . Four functions $U(r)$, those of Morse , Fayyazuddin , Huffaker , and Simons-Parr-Finlan , are retained and compared to the “true” RKR potential $U^t(r)$. The relative discrepancy $\Delta U_i = (U_i - U_i^t) / U_i^t$, measuring the “local” agreement between the analytical potentials U_i and the RKR one U_i^t (at a given turning point r_i) , is defined and applied to the $X\Sigma$ - CO state. The mean value $\Delta U = \Sigma (\Delta U_i) / I$ for all the I turning points is deduced .The comparison shows that the accuracy obtained by Nakagawa for the Simons-Parr- Finlan (S-P-F) function is the best, followed in order by Huffaker , Fayyazuddin and Morse functions .

A standard least-squares method is used for the determination of the coefficients of these functions and applied to the $X\Sigma$ - CO state also . The comparison of the results , for the four considered functions shows that the accuracy obtained for the (S-P-F) function is also the best whereas the order of accuracy is conserved for the other functions .

In order to test the performance of this method , it is applied in the case of the $X O_g^+$ state of Iodine where the R.K.R. potential is known until the dissociation limit . The least-squares method is used for the determination of the coefficients of the considered functions . The comparison of the results shows that the (S.P.F.) function is so far the best and reproduces with high precision the “true” R.K.R. potential .

Moreover , the comparison of the results obtained , for every function , by the least-squares technique and the other studies shows that this technique is more simple , more efficient and more accurate.

Keywords: diatomic, molecular, physics, potential energy

INTRODUCTION

Within the Born-Oppenheimer theory (Born and Oppenheimer, 1927), the study of a diatomic molecule in a given electronic state is generally based on the potential $U(r)$ characterizing the considered state of the molecule. When the state is bound, the function $U(r)$:

- (i) has a constant limit when the internuclear distance r increases indefinitely,
- (ii) presents a minimum at the equilibrium r_e , and
- (iii) increases indefinitely when r decreases towards zero.

This behavior is roughly illustrated by the representative curve of the Morse function (Morse, 1929)

$$U(r) = D[1 - \exp(-a(r - r_e))]^2$$

where D is the constant limit (*i.e.*, the dissociation energy), a is a parameter.

Till the seventies, one could distinguish three ways to determine $U(r)$. The first is the empirical way looking to represent $U(r)$ by an analytical function depending on some parameters like that of Morse (1929), Dunham (1932), Pöschl-Teller (1933), Hulbert-Hirshfelder (1941), Frost-Musulin (1954), and others cited in the excellent review by Steele *et al.* (1962). The second is a semi-classical procedure based on the works of Rydberg (1933), Klein (1932), and Rees (1947) and well-known by the abbreviation R.K.R.. The third is a quantum-mechanical procedure elaborated by Kosman and Hinze (1977) and Vidal and Scheingraber (1977) and called the Inverted Perturbation Approach (I.P.A.). The two last methods give the potential, out of the spectroscopic data, by a numerical table giving the coordinates r_i and $U(r_i)$ of the turning points of $U(r)$ (points defined by $U(r) = E_v$, where E_v is the energy for the vibrational level v). For the other values of r between two consecutive turning points, $U(r)$ is given by convenient interpolation; in the two regions where $U(r)$ exceeds all the observed E_v , $U(r)$ is given by convenient extrapolations (Le Roy, 1974). It is commonly agreed that the R.K.R. potential (U^{RKR}) and the I.P.A. one (U^{IPA}) are usually in excellent agreement with the spectroscopic data, *i.e.*, they allow generally to obtain expectation values of E_v and B_v (rotational constants) in agreement with their corresponding values within experience uncertainties. U^{RKR} is thus called (as well as U^{IPA}) the “true” potential U^t .

Although this problem is solved, molecular physicists still look, from time to time, to empirical functions for their merits when matrix elements are needed and particularly in complex collision problem. A review paper by Varshni (1957), presented a comparative study of several functions by comparing them to the true U^t .

Recently Hua (1990) on one hand, Fayyazuddin (1995) on the other, presented works similar to that of Varshni, and proposed two “new” functions. The latter extended his work by proposing a five-parameter function (Fayyazuddin *et al.*, 1996).

The aim of this work is to make a contribution considering some functions unconsidered in the former works and to make the test of comparing these functions to the

“true” potential , along with the new Fayyazuddin function . Moreover we suggest the use of a simple procedure allowing to represent the potential by an analytical functions as accurate as the true one .

THE SELECTED FUNCTIONS

In order to present our new approach to represent an R.K.R. potential by an analytical function , we start by testing that of Fayyazuddin (Fayyazuddin *et al.*, 1996) along with other commonly used functions . Among these we restrict our choice to three other functions only, in order to avoid lengthy comparisons, and for other reasons explained in next section .

The retained functions are those of :

(a)- Morse (1929) :

$$U^M(r) = D[1 - \exp(-ax)]^2 ; \quad x = r - r_e \quad (1)$$

where D and a are adjustable parameters .

(b)- Fayyazuddin (Fayyazuddin *et al.* , 1996):

$$U^F(r) = (k/x - a - bx - cx^2) \exp(-tx) ; \quad x = r / r_e \quad (2)$$

where a , b , c , k and t are adjustable parameters .

(c)- Simons - Parr - Finlan (1973) :

$$U^S(r) = \sum_{n=1}^N b_n y^{n+1} ; \quad y = (r - r_e) / r \quad (3)$$

where b_n are adjustable parameters given by Nakagawa *et al.* (1992) .

(d)- Huffaker (1976) :

$$U^H(r) = D[y^2 + \sum_{n=1}^N b_n y^{n+3}] ; \quad y = 1 - \exp(r - r_e) \quad (4)$$

where D , a , b_n are adjustable parameters .

Note that N represents the number of the coefficients to determine .

The test of these analytical functions is done by considering , for a given electronic state of a given molecule , the true potential $U^t(r)$. To compare one analytical function $U(r)$ to $U^t(r)$, we consider the values $U_i = U(r_i)$ and $U_i^t = U^t(r_i)$ at some points r_i ; for practical reasons, it is convenient to take r_i as the abscissas of the turning points of the R.K.R. potential U^t , since U^t is defined by the coordinates of these points . Then the relative discrepancy ΔU_i

$= (U_i - U_i^t) / U_i^t$ measures the “local” agreement of the two potentials ; the mean value $\Delta U = \Sigma (\Delta U_i) / I$ for all the I turning points , measures their “global” agreement .

To illustrate this test one considers the $X\Sigma$ - CO state and for U^t , the R.K.R. potential determined by Mantz *et al.* (1975) . Table 1 gives for some turning points r_i the “true” value $U^t(r_i)$ along with those U_i^M , U_i^F , U_i^H , U_i^S , for selected analytical functions defined by equations (1) to (4) .

By looking to the “quality index” ΔU defined above , one deduces that U^F gives better results than U^M , but the two other considered functions give results far better than U^F ; these are in order of increasing quality : U^H then U^S . However it is worthy to note that the number of parameters is not the same for all these functions : it is of 2 for Morse , 5 for Fayyazidine , 9 for Huffaker , 11 for Simons - Parr - Finlan .

NUMERICAL APPROACH

For all the selected functions (equations (1-4)) , the parameters are generally determined by using quantum mechanical treatments relating the potential function parameters to the spectroscopic data .

In the present work , we skip this approach to a simple one . Since we aim to have the potential in an analytical form , as accurate as the R.K.R. potential , we limit ourselves to the representation of the R.K.R. potential by an analytical function . We proceed as follows .

Let’s take the S.P.F. function (equation (3)) as example . To fit this function to the given U^t potential , we take r_e at the minimum of U^t . The problem is then reduced to determine the coefficients b_n by imposing the condition :

$$\Sigma_{i=1}^N b_n y_i^{n+1} = U_i^t \quad ; \quad y_i = (r_i - r_e) / r_i \quad (5)$$

Since the number N of b_n is hopefully much less than that I of equations (5) , the least-squares method is well-indicated to determine b_n out of equations (5) .

This simple treatment was applied to the two functions U^S (equation (3)) and U^H (equation (4)) for the same state $X\Sigma$ - CO used above . Results are displayed in Table 2 as in Table 1 , *i.e.* , the value U_i of the analytical potential is compared to that of the R.K.R. potential U_i^t at some turning points r_i . The four functions are in the same order of quality as previously mentioned.

On this procedure the following remarks are in order:

(i)- The number N of the coefficients b_n is not imposed a priori but deduced from the observation of the variation with N of the “ global quality index “ (G.Q.I.) ΔU . We make N to vary ($N = 1, 2, \dots$) ; we notice that ΔU decreases when N increases , and reaches a stability. For the present numerical application the stability is reached for $N \sim 9$, and this for the two functions U^S and U^H (see coefficients in Table 3) .

(ii)- The use of a linear least-squares technique is obvious since equation (5) is linear in b_n . This is directly applicable for the S.P.F. function U^S (equation (3)) . For the Huffaker function U^H (equation (4)) , the condition $U_i = U_i^t$ (leading to equation (5) for U^S) becomes :

$$\sum_{i=1}^N b_n y_i^{n+1} = U_i^t / D - y_i^2 \quad (6)$$

Here too the linear least-squares technique allows a direct determination of the coefficients b_n .

DISCUSSION

The diatomic potential problem being solved with satisfactory precision by the semi-classical R.K.R. method , the present work aims to meet the trend , still alive , to represent the “numerical” R.K.R. potential by an analytical function . This trend is illustrated by the works of Dagher *et al.* (1996) .

While the other works like those of Nakagawa and Akiyama (1992), Huffaker (1976), Ogilvie (1992) and others looked to the “ direct determination of analytical diatomic potential energy functions from spectroscopic data “ , the present work looks to show that a simple numerical approach may be, not only an alternative, but also an improvement. We will designate by D.A.P. (Direct analytical potential) the functions found by the former works, and by N.A.P. (Numerical analytical potential) the functions found by using the least - squares technique to fit the function to the true potential U^t , as it was described in the previous section.

The comparison of the two approaches is presented in Table 4, where we display the “ global quality index “ ΔU for the three potentials U^F , U^S and U^H first as D.A.P. in the first line, then as N.A.P. in the second .

The study of this table shows that the use of our N.A.P. presents for every function a net improvement on the D.A.P. . Moreover , we can formulate , for the present application the following remarks :

- (i)- In the D.A.P. category , the order of quality gives to U^S the first place , followed in order by, U^H , U^F , U^M (Table 1) .
- (ii)- In the N.A.P. category , the order of quality is conserved (Table 2) .
- (iii)- In both cases the Fayyazuddin function U^F is not competitive .

Further numerical applications , to other molecules and other electronic states , show that the diatomic “true” (R.K.R.) potential can be adequately represented by functions like U^S . As an illustration , we consider the R.K.R. potential determined by Martin *et al.* (1986) describing the $X O_g^+$ of I_2 state below the dissociation limit . In spite of the great number of levels (109) and the consequently large number of turning points (218), the (S.P.F.) function , obtained by least-squares technique , succeeds in reproducing with high precision the “true” R.K.R. potential with $N=19$ coefficients . In Table 5, for some turning points r_i , the values of U_i^M , U_i^F , U_i^H and U_i^S are compared to the “true” value $U^t(r_i)$. Comparison of the result shows that the (S.P.F.) function is so far the best . It is noticed that

the number N of parameters varies between 10 and 20 , according to the shape of the potential curve.

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TABLE 1

Relative Discrepancy $\Delta U_i = (U_i - U_i^t) / U_i^t$ for Morse , Fayyazuddine , Huffaker and Simons-Parr-Finlan Potential Functions Found by the Former Studies

r_i	U_i^t	ΔU_i^M	ΔU_i^F	ΔU_i^H	ΔU_i^S
0.8879406	51329.191	0.28 D-2	0.13 D-2	0.36 D-3	0.20 D-5
0.9019224	43807.987	0.67 D-3	0.13 D-2	0.72 D-4	0.11 D-4
0.9191673	35667.961	0.11 D-2	0.12 D-2	0.52 D-5	0.11 D-4
0.9412093	26898.898	0.21 D-2	0.11 D-2	0.23 D-5	0.28 D-5
0.9712997	17490.312	0.25 D-2	0.86 D-3	0.74 D-6	0.53 D-6
1.0193935	7432.2158	0.16 D-2	0.48 D-3	0.12 D-6	0.23 D-6
1.2196123	3225.0478	0.84 D-3	0.31 D-4	0.23 D-6	0.16 D-6
1.3424424	13545.546	0.53 D-2	0.66 D-4	0.57 D-6	0.52 D-6
1.4376980	23212.783	0.87 D-2	0.11 D-3	0.16 D-5	0.23 D-5
1.5261659	32236.412	0.11 D-1	0.29 D-3	0.93 D-5	0.45 D-5
1.6130729	40626.790	0.12 D-1	0.24 D-3	0.40 D-4	0.87 D-5
1.7010130	48394.357	0.11 D-1	0.24 D-3	0.12 D-3	0.40 D-5
1.7368966	51329.191	0.40 D-1	0.60 D-3	0.18 D-3	0.24 D-5
$\overline{\Delta U}$		0.25 D-2	0.57 D-3	0.37 D-4	0.64 D-5

TABLE 2

Relative Discrepancy $\Delta U_i = (U_i - U_i^t) / U_i^t$ for Morse , Fayyazuddin , Huffaker and Simons-Parr-Finlan Potential Functions Found by Using the Least-Squares Technique

r_i	U_i^t	ΔU_i^M	ΔU_i^F	ΔU_i^H	ΔU_i^S
0.8879406	51329.191	0.85 D-2	0.85 D-3	0.17 D-5	0.13 D-6
0.9019224	43807.987	0.56 D-2	0.48 D-3	0.11 D-5	0.34 D-6
0.9191673	35667.961	0.31 D-2	0.11 D-3	0.16 D-5	0.23 D-7
0.9412093	26898.898	0.98 D-3	0.20 D-3	0.49 D-7	0.15 D-6
0.9712997	17490.312	0.43 D-3	0.47 D-3	0.78 D-6	0.57 D-7
1.0193935	7432.2158	0.78 D-3	0.69 D-3	0.52 D-7	0.15 D-6
1.2196123	3225.0478	0.80 D-3	0.11 D-3	0.19 D-6	0.20 D-6
1.3424424	13545.546	0.34 D-2	0.40 D-3	0.32 D-6	0.14 D-6
1.4376980	23212.783	0.50 D-2	0.18 D-3	0.93 D-6	0.30 D-6
1.5261659	32236.412	0.54 D-2	0.13 D-3	0.21 D-6	0.41 D-6
1.6130729	40626.790	0.44 D-2	0.25 D-3	0.28 D-5	0.34 D-6
1.7010130	48394.357	0.19 D-2	0.66 D-4	0.15 D-5	0.68 D-6
1.7368966	51329.191	0.19 D-2	0.36 D-3	0.12 D-5	0.73 D-6
$\overline{\Delta U}$		0.14 D-2	0.33 D-3	0.17 D-5	0.27 D-6

TABLE 3

Coefficients b_i of Huffaker and Simons-Parr-Finlan Potential Functions Found by Using the Least Squares Technique

i	b_i^H	b_i^S
1	0.036136	0.609454 D+6
2	0.017715	-0.424858 D+6
3	0.013801	-0.356783 D+6
4	0.013043	-0.816618 D+5
5	0.007452	0.172423 D+6
6	0.006593	0.479440 D+6
7	0.015106	0.330429 D+6
8	0.010374	-0.969965 D+6
9	0.000249	-0.126397 D+7

TABLE 4

“ Global Quality Index “ $\Delta U = \sum_{i=1} (\Delta U_i) / I$ for the Three Potential Functions U^F , U^H and U^S Calculated Respectively by D.A.P. and N.A.P. Approaches

	$\overline{\Delta U^F}$	$\overline{\Delta U^H}$	$\overline{\Delta U^S}$
D.A.P.	0.57 D-3	0.37 D-4	0.64 D-5
N.A.P.	0.33 D-3	0.17 D-5	0.27 D-6

TABLE 5

**Relative Discrepancy $\Delta U_i = (U_i - U_i^t) / U_i^t$ for Morse , Fayyazuddin , Huffaker and Simons-Parr-Finlan Potential Functions Found by Using the Least-Squares Technique:
Case of the XO_g^+ State of the Molecule I_2**

r_i	U_i^t	ΔU_i^M	ΔU_i^F	ΔU_i^H	ΔU_i^S
2.268666219	12543.9343	0.32 D-0	0.28 D-1	0.53 D-3	0.71 D-4
2.271869603	12281.2288	0.32 D-0	0.26 D-1	0.64 D-3	0.98 D-4
2.377396669	5584.27701	0.24 D-0	0.57 D-1	0.35 D-2	0.72 D-5
2.488806384	1778.67645	0.17 D-0	0.17 D-0	0.24 D-2	0.86 D-4
2.618390674	107.09814	0.99 D-1	0.24 D-1	0.97 D-4	0.83 D-4
3.070785707	3941.38303	0.68 D-1	0.83 D-1	0.45 D-2	0.57 D-4
3.342738717	7418.98449	0.10 D-0	0.12 D-1	0.33 D-2	0.26 D-4
3.675317699	10159.7208	0.93 D-1	0.26 D-1	0.20 D-2	0.63 D-5
4.266942961	11883.6450	0.39 D-2	0.13 D-2	0.64 D-2	0.51 D-4
6.083011377	12496.8578	0.12 D-2	0.75 D-3	0.15 D-2	0.28 D-4
9.077500000	12543.9343	0.25 D-3	0.28 D-4	0.29 D-2	0.48 D-5
ΔU		0.16 D-0	0.67 D-1	0.29 D-2	0.42 D-4

