

## POTENTIAL ENERGY CURVES OF DIATOMIC MOLECULES FROM THE HILL DETERMINANT METHOD

D.A. ESTRÍN, F.M. FERNÁNDEZ and E.A. CASTRO

*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),  
División Química Teórica, Sucursal 4, Casilla de Correo 16, 1900 La Plata,  
Argentina*

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### Abstract

The Hill determinant method is shown to be suitable for constructing potential energy curves of diatomic molecules. Both the Dunham and the perturbed Morse oscillator potentials are used to fit spectroscopic data. Results are shown for ionic and covalent molecules.

### 1. Introduction

The Hill determinant method (HDM) proves to be a simple way of obtaining highly accurate eigenvalues [1]. It was first applied to one-dimensional problems with parity-invariant potentials and central-field models [1]. Recently, Estrín et al. [2,3] have shown that more general problems can also be treated, and they discussed the calculation of rotation–vibration eigenvalues of diatomic molecules. To this end, they considered different potential energy curves obtained from fitting spectroscopic data.

The inverse problem, i.e. the construction of potential energy curves from spectra, is by far more interesting and several procedures have been proposed to solve it. The Rydberg–Klein–Rees (RKR) method [4] is widely used, although it is a semi-classical approximation that only yields the classical turning points corresponding to the eigenenergies.

The potential energy curve proposed by Dunham [5],

$$V(r) = a_0 x^2 (1 + a_1 x + a_2 x^2 + \dots), \quad x = (r - r_e)/r_e, \quad (1)$$

where  $r$  and  $r_e$  are the internuclear distances at a general point and at equilibrium, respectively, proves to be accurate enough around  $x = 0$ . However, owing to the pole at  $r = 0$ , the series (1) has a finite convergence radius which limits its applicability.

Several methods for improving the convergence properties of the Dunham series have been developed. Among them, we mention the Padé approximants [6] and series of the form:

$$V(r) = V_0 f(x) \{1 + V_1 f(x) + V_2 f(x)^2 + \dots\}, \quad (2)$$

where  $f(x)$  is a properly chosen function [7–9]. Some of these approaches are accurate enough provided they are applied to either ionic [6] or covalent [9] molecules.

A systematic procedure for obtaining quite accurate potential energy curves from the Dunham coefficients  $a_j$  has recently been presented by Artega et al. [10]. This is based on a nonlinear transformation of the variable  $x$  that takes into account the large- $r$  behavior of the actual  $V(r)$ . This method yields a sequence of polynomials that appear to converge smoothly to  $V(r)$ . The convergence rate is larger in the case of ionic molecules than in the case of covalent molecules.

A different approach, called the perturbed Morse oscillator (PMO) approach, has been developed by Huffaker [11]. It consists of writing  $V(r)$  as

$$V(r) = D(q^2 + \sum_{i=4}^{\infty} b_i q^i), \quad (3)$$

where  $q = 1 - \exp\{a(r_e - r)\}$ , and  $D$ ,  $a$ , and  $r_e$  are the parameters of the Morse oscillator [11]. The coefficients  $b_j$  are determined by fitting the spectrum [11].

In order to obtain the coefficients  $a_j$ , Dunham [5] fitted the spectrum with the following polynomial function of the vibrational ( $v$ ) and rotational ( $J$ ) quantum numbers:

$$E_{v,J} = \sum_j \sum_k Y_{jk} (v + 1/2)^j J(J + 1)^k. \quad (4)$$

The coefficients  $a_i$  and  $Y_{jk}$  are related through the WKB quantization formula [5]. Recently, Ogilvie and Koo [12] have put forward an iterative procedure for obtaining the  $a_i$ 's from the  $Y_{jk}$ 's, and Niay et al. [13] have calculated the former coefficients without previous determination of the latter. In both cases, a semiclassical approximation was used.

The main disadvantage of the WKB method is that it may not be accurate enough for the lowest energy levels.\* Totally quantum-mechanical methods are also available. For instance, the inverse perturbation approach (IPA) developed by Kosman and Hinze [14] has been successfully applied by Vidal [15] and Hamilton et al. [16]. It consists of systematically correcting an appropriate trial potential by means of properly chosen functions and experimental energy levels.

In this paper, the HDM is shown to be suitable for constructing potential energy curves of diatomic molecules from limited experimental data. A generalized version of the HDM is briefly summarized in section 2, and the calculation of the first coefficients  $a_j$  is discussed in section 3. They are used to build [2/2] Padé approximants [6] and the

\*Note added in proof: The expression obtained by Dunham by means of the WKB method agrees exactly with the perturbation theory result (Kilpatrick, J. Chem. Phys. 30(1959)801). For this reason, the former applies even for the ground vibration-rotational state.

sequence of polynomials of ref. [10] for twenty alkali halides whose dissociation energies are estimated. The first coefficients  $b_i$  of the PMO (3) are obtained in section 4 for the CO molecule.

## 2. The generalized HDM

The present method applies when the Schrödinger equation can be reduced to a Sturm–Liouville problem

$$\{P(q) d^2/dq^2 + Q(q) d/dq + R(E, q)\} \Psi(q) = 0, \quad (5)$$

where  $R(E, q)$  depends parametrically on the energy  $E$  and  $\Psi(q)$  satisfies given boundary conditions at  $q = a$  and  $q = b$ . We first find a function  $\Psi_0$  so that  $F = \Psi/\Psi_0$  can be adequately expressed as a Taylor series around  $q = 0$ . The new function  $F(q)$  is a solution of

$$\{P d^2/dq^2 + (2P\Psi'_0 + Q) d/dq + (P\Psi''_0/\Psi_0 + Q\Psi'_0/\Psi_0 + R)\} F = 0, \quad (6)$$

where  $\Psi'_0 = d\Psi_0/dq$ , etc. Therefore, if

$$P = \sum_{j=0}^{\infty} p_j q^j, \quad 2P\Psi'_0/\Psi_0 + Q = \sum_{j=0}^{\infty} q_j q^j, \\ P\Psi''_0/\Psi_0 + Q\Psi'_0/\Psi_0 + R = \sum_{j=0}^{\infty} r_j q^j, \quad (7)$$

the coefficients of the expansion

$$F = \sum_{j=0}^{\infty} f_j q^j \quad (8)$$

satisfy the difference equation

$$\sum_{j=0}^n \{(j+1)(j+2)p_{n-j} f_{j+2} + (j+1)q_{n-j} f_{j+1} + r_{n-j} f_j\} = 0, \quad (9)$$

where  $n = 0, 1, \dots$ .

It is clear that every coefficient  $f_j$  can be written

$$f_j = A_j f_0 + B_j f_1, \quad j = 0, 1, \dots, \quad (10)$$

where  $A_j$  and  $B_j$  are two solutions of eq. (9) with the boundary conditions  $A_0 = B_1 = 1$  and  $A_1 = B_0 = 0$ . The coefficients  $A_j$  and  $B_j$ ,  $j > 1$ , depend on the energy, and it is assumed that the roots of the simultaneous equations  $f_{N+1} = f_{N+2} = 0$  tend to the actual eigen-values as  $N$  increases. These equations become

$$A_{N+1}(E)B_{N+2}(E) - A_{N+2}(E)B_{N+1}(E) = 0. \quad (11)$$

Although no rigorous proof of the above-mentioned assumption has yet been given, the HDM has proved to be highly accurate [1–3]. Its most appealing feature is its simplicity. In fact, it reduces to obtaining the coefficients  $A_j$  and  $B_j$  through the recurrence relation (9) and then calculating the roots of eq. (11) for increasing  $N$  values. The convergence of the procedure is immediately checked. Since only two vectors have to be stored, the HDM is suitable for microcomputer calculations.

For highly excited states, eq. (11) may become numerically unstable. In that case, the user must obtain the eigenvalues from the roots of the secular determinant associated with the difference equation (9).

### 3. The Dunham series

We now consider the application of the HDM to the vibration–rotation motion of diatomic molecules. The radial part of the time-independent Schrödinger equation can be written (units are chosen so that  $\hbar = \mu = 1$ )

$$(r^2 d^2/dr^2 + 2r^2\{E - V(r)\} - J(J + 1))\Psi(r) = 0, \quad (12)$$

where  $\Psi(0) = \Psi(r \rightarrow \infty) = 0$  and  $J = 0, 1, \dots$  is the angular momentum quantum number.

In order to express  $V(r)$  as a Dunham series (1), we choose  $q = r - r_e$  and  $\Psi_0 = \exp(-\beta q^2/2)$ , where  $\beta^2 = d^2V/dr^2(r = r_e)$ . The difference equation follows immediately from the fact that  $P(q) = (q + r_e)^2$ ,  $Q(q) = 0$ , and  $R(q) = 2P(q)\{E - V(r(q))\} - J(J + 1)$ . If  $n$  vibrational eigenvalues for a given  $J$  value are available from the spectrum, then there will be  $n$  equations like eq. (11) which enable one to determine  $m \leq n$  Dunham coefficients  $a_j$  by means of (say) the Newton–Raphson method. A least-squares method may be used when  $m < n$ .

On using the first four vibrational eigenvalues for  $J = 0$  obtained from the spectroscopic constants tabulated in ref. [17], we have calculated the coefficients  $a_j$ ,  $j \leq 3$ , for twenty alkali halides (table 1). Present results are in acceptable agreement with previous ones [6], and other energy levels obtained from them proved to reproduce the experimental information accurately (proved by using the HDM).

In order to see the effect of the input data on the results, we have repeated the calculation with the energy levels obtained from the spectroscopic constants reported by Brumer and Karplus [18]. Large differences are found for some molecules. For instance, in the case of LiCl we have  $a_0 = 146455.5 \text{ cm}^{-1}$ ,  $a_1 = -2.52155$ ,  $a_2 = 3.67604$ , and  $a_3 = -3.22597$  (cf. table 1). However, we choose the energy levels of Varshni and Shukla [17] to compare present results with those of refs. [6] and [10].

The main disadvantage of the HDM is that it is unsuitable for handling highly excited vibrational energy levels or too shallow potentials. This is due to the fact that the harmonic-oscillator ground state  $\Psi_0$  is not adequate when  $V(r)$  differs too much from

Table 1

Dunham coefficients  $a_j$  for several alkali halides obtained from the first four vibrational energy levels for  $J = 0$  calculated by means of the spectroscopic constants given in ref. [17]

	$a_0$ (cm <sup>-1</sup> )	$a_1$	$a_2$	$a_3$
LiF	154044.5	-2.42405	3.37762	-2.75536
LiCl	145403.5	-2.43607	3.43451	-2.93152
LiBr	142938.8	-2.64053	4.03220	-3.71183
LiI	140021.1	-2.76310	4.41604	-4.25903
NaF	164397.5	-2.78741	4.49968	-4.41416
NaCl	152421.1	-2.83571	4.67002	-4.77422
NaBr	147261.7	-2.76844	4.45771	-4.50248
NaI	142572.1	-2.85973	4.75767	-4.97653
KF	164358.7	-2.92609	4.96523	-5.16522
KCl	152427.3	-3.01363	5.28002	-5.78045
KBr	147848.3	-3.05408	5.42819	-6.08718
KI	142892.3	-3.06120	5.39482	-5.61299
RbF	165347.6	-2.92164	4.95723	-5.20957
RbCl	155335.9	-3.12456	5.68001	-6.49600
RbBr	151048.1	-3.12064	5.67236	-6.57158
RbI	146074.0	-3.19378	5.94321	-7.08005
CsF	168542.0	-2.96521	5.11846	-5.51021
CsCl	159154.9	-3.20323	5.97144	-7.02461
CsBr	154907.6	-3.15968	5.81699	-6.85607
CsI	150307.7	-3.27964	6.26854	-7.79946

$\frac{1}{2}\beta^2(r - r_e)^2$ . However, in most cases of practical interest the HDM proves to be a valuable quantum-mechanical alternative or complementary technique.

To further check the quality of the coefficients in table 1, we build the whole curve  $V(r)$  ( $r \geq r_e$ ) by means of the [2/2] Padé approximants [6] and the polynomial sequence of order 2 and 3 of ref. [10]. The dissociation energies ( $D$ ) obtained from these approaches are compared with the experimental ones ( $D_{\text{exp}}$ ) in table 2. The agreement is remarkable in most cases.

When using the coefficients  $a_j$  of table 1, the Padé approximants [6] prove to be more accurate than the polynomial sequences [10], as shown in table 3. On the other hand, the latter are found to yield better results if the coefficients reported by Jordan et al. [6] are considered.

In some cases, particularly those with large errors, the accuracy of the calculated dissociation energy can be dramatically improved by using the more accurate spectroscopic constants reported by Brumer and Karplus [18] (see LiCl in table 2).

Table 2

Percent deviation for the dissociation energy  $d = 100(1 - D/D_{\text{exp}})$  obtained from (a) second- and (b) third-order polynomial sequences [10] and (c) [2/2] Padé approximants [6]. Results in parentheses for LiCl were obtained from the energy levels given in ref. [18].

	$d^a$	$d^b$	$d^c$
LiF	-3.4	7.4	3.8
LiCl	-15.2 (-8.2)	-3.1 (3.1)	-7.7 (-1.1)
LiBr	-0.7	9.9	5.9
LiI	-2.0	8.7	4.7
NaF	-0.4	10.1	6.1
NaCl	-3.7	7.2	2.8
NaBr	-9.4	2.3	-2.5
NaI	-7.8	3.6	0.3
KF	-0.9	9.7	5.5
KCl	-3.6	7.3	2.8
KBr	-3.0	8.9	4.4
KI	-3.7	7.2	3.4
RbF	-5.2	5.8	1.4
RbCl	-0.7	9.9	5.4
RbBr	-2.8	8.1	3.4
RbI	-0.4	10.3	5.6
CsF	-6.1	4.9	0.3
CsCl	-1.3	9.4	4.9
CsBr	-3.7	7.4	2.6
CsI	-1.8	9.1	4.3

Table 3

Average percent absolute deviation (Av) for the dissociation energy when using the coefficients  $a_j$  of (1) table 1 and (2) ref. [6]. (a), (b), and (c) have the same meaning as in table 2

	a	b	c
(1)	3.8	7.5	3.9
(2)	2.1	6.0	5.9

#### 4. The PMO

The Schrödinger equation for the potential (3) in terms of the variable  $q$  is a particular case of eq. (5), with  $P(q) = a^2(1 - q)^2$ ,  $Q(q) = -a^2(1 - q)$ ,  $R(E, q) = E - V(r(q)) - J(J + 1)/r(q)^2$ . If we choose  $\Psi_0 = y^{b/2} e^{-y/2}$ , where  $y = 2d(1 - q)$ ,  $d = (2D)^{1/2}/a$ , and  $b^2 = -8E/a^2$ , then we have (cf. eq. (9)):

$$\begin{aligned} & (j+1)(j+2)f_{j+2} - (j+1)(b-2d+2j+1)f_{j+1} \\ & + \{j(j-1) + j(b-4d+1) + 2d^2 + d(b+1)\}f_j \\ & - \{2d^2 - 2d(j-1) - d(b+1)\}f_{j-1} - d^2 \sum_{i=0}^j r_i f_{j-i} = 0. \end{aligned} \quad (13)$$

The coefficients  $r_k$  are easily obtained from eq. (3) and the expansion of  $1/r(q)^2$  in a power series of  $q$  [3].

The CO molecule is chosen to illustrate the method because there are enough available experimental data to check the results. On using the experimental vibration-rotation energy levels  $E_{v,J}$  given in ref. [19], we have tried the following strategies:

(a) The Morse parameters

$$D = 88887.12 \text{ cm}^{-1}, \quad ar_e = 2.618415 \quad (14a)$$

are chosen so that the two first Morse eigenvalues agree with the actual energy levels [19] and then

$$b_4 = -8.097 \times 10^{-3}, \quad b_5 = -0.35634, \quad b_6 = 0.44799, \quad b_7 = 0.01735 \quad (14b)$$

are obtained from eq. (11) with  $N = 26$  (convergence up to the last figure) and  $E = E_{v,0}$ ,  $1 < v < 6$ .

(b) We first calculate the Dunham coefficients  $a_0 = 609518.22 \text{ cm}^{-1}$  and  $a_1 = -2.694300$  as discussed in the previous section by means of  $E_{v,0}$ ,  $v \leq 3$  [19], from which

$$D = 83964.32 \text{ cm}^{-1}, \quad ar_e = 2.69430 \quad (15a)$$

are derived. Then,

$$b_4 = 0.0345136, \quad b_5 = 0.133682, \quad b_6 = 0.10083, \quad b_7 = 0.06261 \quad (15b)$$

are computed through eq. (11) with  $N = 26$  and  $E = E_{v,0}$ ,  $1 < v < 6$ .

(c)  $D$  and  $ar_e$  are calculated as in (b) and

$$b_4 = 0.0284018, \quad b_5 = 0.0748523, \quad b_6 = 0.056665, \quad b_7 = -0.53513 \quad (16)$$

from eq. (11) with  $N = 26$  and  $E = E_{v,0}$ ,  $0 < v < 4$ . Although somewhat different, all these potentials yield the energy levels used in the calculation of the  $b_j$ 's exactly up to the last figure. Other eigenvalues are given with reasonable accuracy as shown in table 4, where present results are compared with experimental data. In order to check eigen-values with  $J \neq 0$ , we have applied the HDM to the PMO with the coefficients  $b_j$  given by Huffaker [11].

Table 4

Vibration-rotation eigenvalues (in  $\text{cm}^{-1}$ ) of the CO molecule obtained by means of the PMO parameters given in eqs. (14) (A); (15) (B); and (16) (C). Present results are compared with (a) experimental data, and (b) a calculation carried out with the PMO of ref. [11]

$v$	$J$	(A)	(B)	(C)	(a)	(b)
0	0	1081.6565	1081.7721	–	1081.7778	–
0	2	1093.1936	1093.3075	1093.3129	–	1093.3126
1	0	3225.0281	3225.0489	–	3225.0502	–
4	0	–	–	9496.127	9496.2497	–

We conclude that it is more convenient to derive the Morse parameters  $D$  and  $a r_e$  from the Dunham series than from equating the Morse eigenvalues with the experimental energy levels.

## 5. Conclusions

An alternative method for constructing diatomic potential energy curves has been presented. Since it is completely based on quantum-mechanical principles, it is preferable when the available experimental data are restricted to the small quantum numbers. For the same reason, the HDM is expected to yield reliable coefficients of the Dunham series (1). In addition to this, the algorithm is so simple that the calculation can be carried out on a microcomputer.

The main disadvantage of the present procedure is that it cannot handle in a simple way highly excited vibrational energy levels, and is useless when the potential function is too shallow. However, in most cases the HDM may be suitable either for constructing the curve or for checking the potential obtained through other techniques [2,3].



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