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On the Convergence of Effective Hamiltonian Expansions

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The superiority of the convergence behavior of effective rotational Hamiltonians expressed in terms of Padé approximants over more conventional power series Hamiltonians is well known. For diatomics it is suggested that the failure of the conventional expansions is due to singularities in the complex J plane. This theory is supported by numerical calculations on rotationally excited H_2 with both real and imaginary J. These calculations show that the Padé expansions represent the data 30 times better than a power series and locate a singularity at $J \sim 25$ for negative $J(J+1)$. The rotational structure of quasilinear molecules is found to have a more serious singularity corresponding to that of the Borel Hamiltonian. The implications of these findings for effective Hamiltonian expansions are discussed.

1. INTRODUCTION

Effective Hamiltonians are very widely used as a means of representing molecular rovibrational spectroscopic data. For rotational levels, these effective Hamiltonians are conventionally expressed as power series expansions in terms of the quantum numbers $J(J+1)$ and K^2 (*1*). For light molecules and molecules with large amplitude vibrational motion such power series are often poorly convergent. In some cases, such as water (*2, 3*), the power series is known to actually diverge.

As a solution to this problem, other effective Hamiltonian expansions have been suggested. Suggestions, based on the study of quartic perturbed harmonic oscillators (*4, 5*), include the use of Padé and Borel approximants (*3*). These have been found to give greatly improved representations of the spectroscopic data of water (*3, 6*), H_2D^+ (*7, 8*), and C_2O_3 (*9*) when compared to power series expansions with the same number of parameters.

The purpose of this paper is to give a theoretical justification, if not a formal proof, of the superiority of the Padé and Borel effective Hamiltonian representations of the exact energy eigenvalues of molecular rovibrational Hamiltonians. This will be done by considering the behavior of the power series expansions in the complex (J, K) plane and in particular by considering the cases $J(J+1) < 0$ and $K^2 < 0$.

Formally, the convergence properties of a given series expansion

$$f(x) = \sum_{n=0}^{\infty} \alpha_n x^n \tag{1}$$

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are determined by the radius of convergence, ρ, of the series. The series is convergent for all $|x| < \rho$ and divergent for all $|x| > \rho$. For $|x| = \rho$ the series may either converge or diverge. Furthermore, ρ is simply equal to the distance to the nearest singularity in the function $f(x)$ *in the complex plane.*

A simple example is provided by the series

$$\frac{1}{1+x} = \sum_{n=0}^{\infty} (-1)^n x^n. \tag{2}$$

As this function is singular at $x = -1$, $\rho = 1$ for this series.

In this work we consider two representative one dimensional problems: (a) the rotational levels of a diatomic molecule, for which the usual series expansion is in terms of $J(J+1)$, and (b) the rotational levels of a quasilinear molecule with a bending coordinate, for which a power series in K^2 is often used.

2. DIATOMIC MOLECULES

For a diatomic molecule the Schrödinger equation is given by

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} + 2\mu\left[E - V(r) - \frac{J(J+1)}{2\mu r^2}\right]\psi = 0, \tag{3}$$

and solutions are characterised in terms of the rotational quantum number J. Perturbative solutions of Eq. (3) give a power series in $J(J+1)$,

$$E(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 - LJ^4(J+1)^4 + PJ^5(J+1)^5, \tag{4}$$

were terms up to 10th order have been retained.

Table I gives values for these constants for H_2 determined by fitting the observed (*10*) rotational levels of the vibrational ground state and pure rotational data (*11, 12*). It is notable that the ratios between neighboring constants in the power series expansion are all similar (to within 30%)

$$\frac{D}{B} \simeq \frac{H}{D} \simeq \frac{L}{H} \simeq \frac{P}{L} \simeq 1 \times 10^{-3}. \tag{5}$$

TABLE I

Rotational Constants (in cm^{-1}) for H_2

	I	II	III	IV
B	59.330075(21)	59.334604(22)	59.334633(18)	59.334455(1)
10^2 D	4.54710(3)	4.56890(1)	4.56918(11)	4.568436(3)
10^5 H	4.4999(3)	4.88853(2)	4.8997(29)	4.89390(3)
10^8 L	3.858(7)	6.139(2)	6.343(32)	6.5088(7)
10^{10} P	0.155(4)	0.546(6)	0.716(12)	0.9212(4)

Note. (I) Power series fit of all laboratory data of Refs. (*10–12*), (II) power series fit to the rotational data up to $J = 15$, (III) fit of Jennings *et al.* to their rotational and corrected Orion data using a power series with geometric corrections (*12*), (IV) Padé fit to all the laboratory data. (Values in parentheses give one standard deviation in units of the final digit).

This behavior is suggestive of a geometric series for which the ratio of neighboring terms is a constant.

The equivalent Padé representation to the power series (*4*) is given by

$$E(J) = \frac{(BH^2 - BDL)J(J+1) - \alpha J^2(J+1)^2 + \beta J^3(J+1)^3}{H^2 - DL + (LH - DP)J(J+1) + (L^2 - HP)J^2(J+1)^2},$$

$$\alpha = -BHL + DBP - D^2L + DH^2,$$

$$\beta = BL^2 - 2DHL + D^2P + H^3 - BHP. \tag{6}$$

Table I presents four different fits to the available rotational levels of the vibrational ground state of H_2. The columns in Table I are given in order of increasing accuracy of the fits. The fits to all data (columns I and IV) were obtained by weighting the rotational data of Refs. (*11, 12*) 1000 times higher than the rovibrational data of Ref. (*10*). The Padé formula (column IV) reproduces these data with a standard deviation 30 times smaller than the polynomial expansion of Eq. (4) (column I).

Indeed the observed H_2 data are reproduced more accurately than the power series expansion by the simpler, sixth-order Padé expression

$$E(J) = BJ(J+1) - \frac{DJ^2(J+1)^2}{1 + (H/D)J(J+1)}. \tag{7}$$

If $J(J+1)$ is replaced by $-J(J+1)$ in Eq. (7), then this formula passes through a singularity near $J = 25$ for the rotational constants of Table I. Furthermore, the geometric properties of Eq. (5) means that this singularity will persist at higher, possibly all, orders.

Until now, the use of Padé rather than polynomial expansions has been justified on purely phenomonological grounds. However the observations above suggest that the exact solutions of Eq. (3) have a singularity for $J \sim 25$ if one takes $J(J+1) < 0$. If this is so then there is a sound theoretical reason for employing effective Hamiltonians with similar singularities.

It is possible to get some idea of the behavior of Schrödinger equation (*1*) for negative $J(J+1)$ by analysing the behavior of the effective potential

$$U_{\mathrm{eff}}(r) = V(r) + \frac{J(J+1)}{2\mu r^2} \tag{8}$$

for certain model potentials. For potentials such as the Kratzer,

$$V(r) = \frac{A}{r^2} - \frac{B}{r}, \tag{9}$$

and the spherical oscillator,

$$V(r) = \frac{A}{r^2} + Br^2, \tag{10}$$

the leading term in $1/r$ is of the same order as the rotational term. For these potentials there is a critical value of J for which U_{eff} with $J(J+1)$ negative switches from the $+\infty$ to $-\infty$ at $r = 0$. With these potentials, one can thus prove the existence of a singularity for $J(J+1) < 0$.

The model potentials discussed above probably give a poor representation of diatomic systems at very short bondlengths. To study this, it is therefore necessary to consider realistic potential functions for which solutions must be obtained numerically.

We have therefore performed a number of calculations on H_2 by direct numerical integration (*13*) of an accurate ab initio potential (*14*). The results for $J(J+1) < 0$ are summarized in Table II. As the ab initio potential is only defined for r greater than 0.5 a_0, it was necessary for us to extrapolate this potential to $r = 0$. Several ways of doing this were tried. Column II in Table II shows the results obtained using a Kratzer potential with $A = 0.23034E_h$ and $B = 0.22364E_h$ and column III shows the results of using

$$V(r) = a\exp(-br) + c, \tag{11}$$

with $a = 4917E_h$, $b = 7.62a_0^{-1}$, and $c = -0.5011E_h$. Extrapolations based on the united atom limit yielded qualitatively similar results.

Table II, column I presents the predictions of the Padé model using the empirically determined constants of Table I for $J(J+1) < 0$. Up to $J \sim 18$ the Padé results clearly give a good approximation to the numerically exact solutions. For higher J the numerical results become increasingly sensitive to the details of the potential at small r and the Padé results clearly show a singularity between J equal to 25 and 26.

TABLE II

Rotational Energy Levels for H_2 with $J(J+1)$ Replaced by $-J(J+1)$

J	I	II	III
1	−118.8	−118.9	−118.9
2	−357.6	−357.7	−357.7
3	−718.7	−718.8	−718.8
4	−1 205.4	−1 205.5	−1 205.5
5	−1 822.5	−1 822.8	−1 822.8
6	−2 567.5	−2 567.9	−2 567.9
7	−3 475.3	−3 475.9	−3 475.9
8	−4 529.1	−4 530.1	−4 530.0
9	−5 750.7	−5 752.2	−5 752.2
10	−7 156.0	−7 158.5	−7 158.5
11	−8 765.0	−8 769.4	−8 769.4
12	−10 603.3	−10 611.3	−10 611.7
13	−12 703.5	−12 718.8	−12 718.8
14	−15 108.6	−15 139.1	−15 139.1
15	−17 876.2	−17 938.6	−17 938.6
16	−21 085.3	−21 218.7	−21 218.8
17	−24 848.6	−25 151.5	−25 152.8
18	−29 332.8	−30 100.1	−30 120.8
19	−34 798.2	−100 473.4	−38 063.5
20	−41 677.3	−278 745.0	−55 358.1
21	−50 752.1	−637 912.8	−78 554.1
22	−63 609.0	−1 111 058.6	−105 189.1
23	−84 056.4		−134 679.3
24	−124 193.9		−166 814.4
25	−254 400.5		−201 521.5
26	+1 101 357.6		−238 800.4

Note. Column (I) is from Padé expression (*6*) with constants fitted to the observed levels with positive $J(J+1)$. The other columns were obtained by direct numerical integration of Eq. (3) using (II) a Kratzer potential (*9*) and (III) an exponential (*11*) for the potential with $r < 0.5a_0$.

3. QUASILINEAR MOLECULES

For quasilinear molecules the important quantum number is K, the projection of the total angular momentum, J, onto the linear molecule axis. Effective Hamiltonians for quasilinear systems are usually expressed in terms of K^2, and it is the behavior of these Hamiltonians with $K^2 < 0$ that we wish to consider.

For our purposes it is sufficient to consider the one-dimensional Thorson–Nakagawa model (*15*)

$$\frac{d^2\psi}{du^2} + \frac{1}{u}\frac{d\psi}{du} - \frac{K^2}{u^2}\psi + (E + V(u))\psi = 0$$

$$V(u) = u^2 + \frac{4G}{B + u^2}, \tag{12}$$

where the parameters are as defined by Ref. (*15*).

For quasilinear molecules with a small barrier to linearity, there is a singularity for *every* $K^2 < 0$, starting from $K = 0$. This means there is a cut on the complex K^2 plane which starts at $K = 0$ and extends along the negative real axis.

There is thus a qualitative difference between the diatomic case considered above, for which reliable power series solutions can be obtained below some critical value of J, and the quasilinear molecule for which the radius of convergence in K^2 is 0. This major difference is due to differences in the potential at $r = 0$ (or $u = 0$): for quasilinear molecules the effective potential will always tend to $-\infty$ as $u \to 0$ for $K^2 < 0$, whereas for the diatomic case this behavior is only found at above the critical value of J.

The Borel Hamiltonian (*5*) is an example of an effective Hamiltonian which displays a cut similar to that described. The Borel expression uses the integral properties of $n!$ to write the expansion as an integral. For example, solutions of Eq. (12) can be approximated, to fourth-order, by

$$E(K) = \int_0^\infty \frac{AK^2e^{-t}}{1 + (D/A)K^2t}\,dt = AK^2 \sum_{n=0}^{\infty} (-1)^n K^{2n}\left(\frac{D}{A}\right)^n n!, \tag{13}$$

where A and D are the rotational constants of the diatomic analog of the solutions of Eq. (12), see Polo (*16*). As A and D are positive, the integral clearly passes through a singularity for all values of $K^2 < 0$. This explains why Borel Hamiltonians have been found to be so good for fitting the rotational energy levels of quasilinear molecules (see, e.g., Ref. (9)). Furthermore, the constants A, D_K, H_K, L_K, . . . , for quasilinear molecules such as C_3O_2, $(HF)_2$, and HNCS have often been observed to have a factorial, $n!$, behavior. This behavior is clearly mimicked by the Borel representation.

4. CONCLUSIONS

We have suggested that the convergence properties of effective Hamiltonians need to be analyzed in terms of their behavior in the complex plane. Unlike conventional polynomial expansions, the behavior of two effective Hamiltonians, the Padé with $J(J + 1)$ and the Borel with K^2, is shown to be in accord with the properties of the rotational levels they are designed to represent. This gives substantiation for the suggestion (*3*) that these Hamiltonians be used and an explanation for the superior fits generally obtained with these Hamiltonians as compared to more conventional models.

Perhaps the most challenging case to analysis is for asymmetric tops with large amplitude motion. We believe that analysis similar to that applied here can be used to explain the anomalous behavior of the $J(J + 1)$ power series for molecules such as Ar-HCN (*17*) and N_2F_4. We are presently studying the Ar-HCN case for which the critical value of J appears to be as low as 10. The study of the singularities in such molecules will lead us to better effective Hamiltonians, better fits of the observed data, and hence a better understanding of the behavior of molecular energy levels as a function of rotational quantum numbers.

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