

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1999 issue.

NOTES

On the use of algebraic approximants to sum divergent series for Fermi resonances in vibrational spectroscopy

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Čížek *et al.*¹ have suggested large-order Rayleigh–Schrödinger perturbation expansions as an alternative to variational methods for calculating molecular vibration energy levels. The energy $E(\lambda)$ of an anharmonic oscillator, considered as a function of the perturbation parameter λ , has a complicated singularity at the origin in the complex λ plane,^{2,3} and therefore has a zero radius of convergence. Nevertheless, Čížek *et al.* found in practice that the expansions could be summed with Padé approximants. Recently the computational cost of the perturbation theory was compared with that of variational diagonalization of the Hamiltonian for a model two-mode oscillator problem.⁴ It was found that perturbation theory had a significant advantage over variational calculations in the number of arithmetic operations needed to obtain a given level of accuracy. Scaling arguments indicate that this advantage can be even greater for rotating oscillators.⁵

However, there is a class of eigenstates for which the perturbation theory appears to fail: eigenstates involved in Fermi resonances, for which the wave functions show strong mixing of two or more of the unperturbed harmonic eigenfunctions. In the function $E(\lambda)$ the resonant states are connected by branch points, with the different eigenvalues residing on different Riemann sheets.³ The closer the degeneracy of the harmonic energies, the closer the branch point is to the origin, and hence the greater the effect on the convergence. Since Padé approximants are rational functions, which cannot explicitly model the multiple-valued nature of $E(\lambda)$, they can have serious convergence problems in such cases.

A simple solution to this problem is to use algebraic summation approximants. Consider an expansion $E(\lambda) = \sum_{n=0}^{\infty} E_n \lambda^n$. The conventional “linear” Padé approximant is a function $E_{[L,M]}(\lambda) = P_L(\lambda)/Q_M(\lambda)$ in terms of the polynomials P_L and Q_M , of degrees L and M , respectively, defined by the linear equation

$$P(\lambda) - Q(\lambda)E(\lambda) = O(\lambda^{L+M+1}). \quad (1)$$

Similarly, algebraic approximants $E_{[p_0, p_1, \dots, p_m]}$ of arbitrary degree m can be defined by

$$\sum_{k=0}^m A_k(\lambda) E_{[p_0, p_1, \dots, p_m]}^k(\lambda) = 0. \quad (2)$$

The $A_k(\lambda)$ are polynomials of degree p_k that satisfy

$$\sum_{k=0}^m A_k(\lambda) E^k(\lambda) = O(\lambda^q), \quad q = m + \sum_{k=0}^m p_k. \quad (3)$$

These approximants were proposed by Padé,⁶ but are not nearly as well known as the linear approximants ($m=1$). Quadratic approximants ($m=2$) have been used occasionally, especially for calculating the complex energies of unstable quasibound eigenstates,^{4,7} but higher-degree approximants have rarely been applied to physical problems. We have recently developed an algorithm for computing high-degree approximants^{8,9} and have analyzed some of their mathematical properties.⁹

Since Eq. (3) has m solutions for $E(\lambda)$, an algebraic approximant of degree $m > 1$ is a multiple-valued function with m branches. Square-root branch points occur at those values of λ for which two of the solutions become equal. For quadratic approximants, for example, the singular points are simply the zeros of the discriminant polynomial $A_1^2 - 4A_0A_2$. If none of the branch points are close to the origin or close to the physical value of λ , then linear approximants should be adequate. However, if it is necessary to model branch points and the number of resonant states connected by the branch points is N , then the degree of the approximants should be chosen to be equal to or greater than N .

We have computed perturbation series through 40th order for the molecules H_2O and H_2S , with the anharmonic oscillator Hamiltonians used by Čížek *et al.*¹ Table I compares the harmonic frequencies. For the ground states and for

TABLE I. Harmonic vibrational frequencies, in cm^{-1} .

	ω_1	ω_2	ω_3
H_2O	3832.0	1648.9	3942.6
H_2S	2721.9	1214.5	2733.3

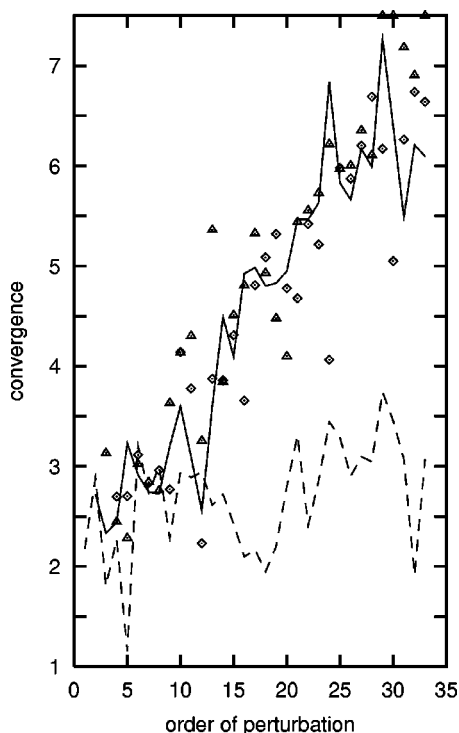


FIG. 1. Summation convergence vs order k of the perturbation expansion for the (200) state of H_2S . The ordinate is $-\log_{10}|(S_k - E)/E|$, which is a continuous measure of the number of converged digits, where S_k is the algebraic approximant corresponding to order k of the diagonal staircase approximant sequence and $E = 8522.5667 \text{ cm}^{-1}$ is the result to which 40th-order perturbation theory seems to converge. (The last digit in E is uncertain.) The degrees of the approximants are as follows: $m=1$ (---), $m=2$ (—), $m=3$ (Δ), $m=4$ (\diamond).

singly excited states the rate of convergence shows no appreciable dependence on m . However, for the (200) state of H_2S , which is strongly resonant with the nearly degenerate (002) state, the convergence is much more rapid for $m > 1$ than for $m=1$, as shown in Fig. 1. There seems to be an advantage to using $m \geq 3$ beginning at 30th order. The convergence behavior is similar for the (002) state. The branch point at which these two states become degenerate is at $\lambda = 0.60096 \pm 0.28837i$. (The physical solution corresponds to $\lambda = 1$.) For H_2O the $m=1$ approximants for the (200) state show no convergence problems. However, for the (400) state, in Fig. 2, which seems to involve a resonance of at least three states, they converge relatively slowly. The convergence is better for $m \geq 2$, with an advantage for $m \geq 3$ beginning at 26th order.

High-degree approximants have the additional advantage

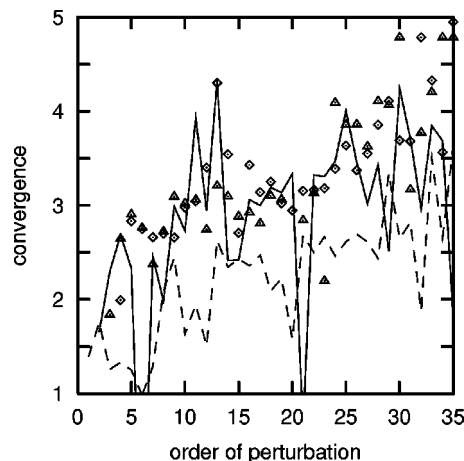


FIG. 2. Summation convergence vs order for the (400) state of H_2O . The ordinate is defined as in Fig. 1 and the converged energy is $E = 19538.4 \text{ cm}^{-1}$. (The last digit is uncertain.) The degrees of the approximants are $m=1$ (---), $m=2$ (—), $m=3$ (Δ), $m=4$ (\diamond).

of being able to model complicated singularities at the $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$ limits,^{9,10} which are generic features of anharmonic oscillator energies, but this advantage is realized only if the perturbation series is known to rather high order.⁹ For the 40th-order expansions considered here we find that the high-degree ($m \geq 3$) approximants noticeably outperform the quadratic approximants only for states involved in Fermi resonances. This indicates that the source of their advantage is not the behavior at $\lambda \rightarrow 0$ or $\lambda \rightarrow \infty$ but rather the accuracy with which they model the resonance branch points.

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