

## LETTER TO THE EDITOR

# Calculation of Stark effect energy shifts by Padé approximants of Rayleigh–Schrödinger perturbation theory

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**Abstract.** Padé approximants give Stark effect energies for excited states of hydrogen that are considerably more accurate than simple perturbation theory. In one example, Padé approximants for an  $n = 25$  state lie within the experimental uncertainty, while simple perturbation theory lies outside. In a second example, Padé approximants for an  $n = 30$  state fall inside the theoretical ionisation width, while simple perturbation theory falls outside. This behaviour appears to be general.

Recent experiments by Koch (1978), Littman *et al* (1978), Zimmerman *et al* (1979), Freeman *et al* (1978), Freeman and Economou (1979), Feneuille *et al* (1979), Beyer and Kleinpoppen (1978), and other workers have sparked interest in calculating the energy shifts of highly excited states of hydrogen and other atoms in an electric field  $F$ . At least six methods are currently being used: (1) Breit–Wigner analysis of the Weyl ‘ $m$  function’, asymptotic expansion coefficient or phaseshift of numerical or semi-numerical solutions for the resonant energy  $E(F) = E_R(F) - i\Gamma(F)/2$  of the Schrödinger equation (Hehenberger *et al* 1974, Damburg and Kolosov 1976, Hatton 1977); (2) variational solution (Herrick 1976, Froelich and Brändas 1975); (3) complex coordinate methods (Reinhardt 1976, Brändas and Froelich 1977, Cerjan *et al* 1978); (4) classical methods (Banks and Leopold 1978a, b, 1979); (5) numerical diagonalisation of the energy matrix (Littman *et al* 1978, Zimmerman *et al* 1979); and (6) Rayleigh–Schrödinger perturbation theory (RSPT) (Silverstone 1978, Silverstone *et al* 1979). Methods (1), (2), (3) and (5), which must treat each state and each field strength as an entirely separate calculation, are somewhat cumbersome, as is (4), unless the suggested formulae, which represent fits to the numerical solutions, are used. Method (6), RSPT, is more easily used, but it produces a divergent asymptotic power series whose ‘best’ partial sum may not be sufficiently accurate.

The purpose of this letter is to report that Padé approximants of the perturbation series can greatly accelerate the ‘apparent convergence’ to within experimental accuracy (or sometimes to within the field-ionisation linewidth  $\Gamma$ ) for many states of experimental interest. A number of cases we have analysed, two of which are presented in this letter, lead us to conclude that diagonal or paradiagonal sequences of Padé approximants generally give significantly more precise results for the hydrogen Stark problem than do RSPT partial sums.

The method of Padé approximants has been employed previously in several other areas of atomic physics (Gillespie 1977, Cohen and McEachran 1978, Ortolani and

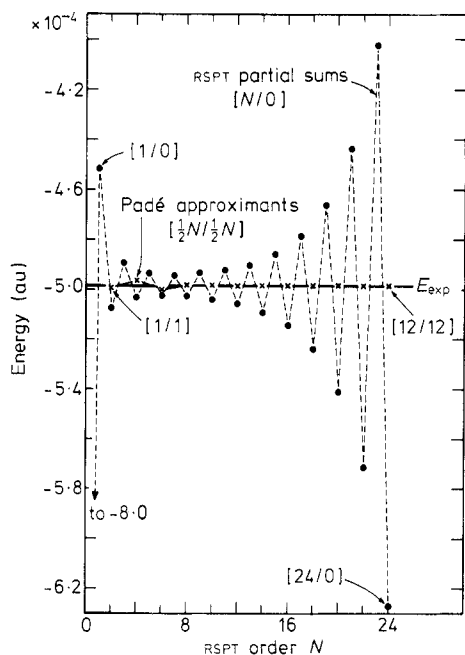
Turchetti 1978) and in studies of quantum-mechanical perturbation theory (reviewed by Baker 1975 and Killingbeck 1977; see also Amos 1978). The Padé approximant (see, for example, Baker 1975)  $[L/M]$  to  $E_R(F)$  is the quotient of two polynomials of degrees  $L$  and  $M$  in  $F$ , whose power series agrees with that of  $E_R(F)$  through order  $L+M$ . It is easy to calculate  $[L/M]$  recursively via Wynn's identity (see Baker 1975),

$$[L/M+1] = [L/M] + \{([L+1/M] - [L/M])^{-1} + ([L-1/M] - [L/M])^{-1} - ([L/M-1] - [L/M])^{-1}\}^{-1} \quad (1)$$

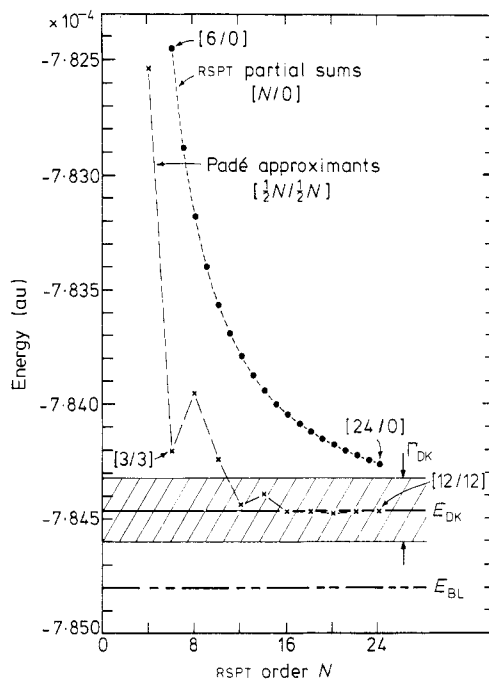
from the  $[L/0]$ , which are also the partial sums of the perturbation series,

$$[L/0] = \sum_{k=0}^L E_R^{(k)} F^k \quad (2)$$

and from the auxiliary conditions (see Baker 1975, p 76),  $[L/-1] = \infty$  and  $[-1/M] = 0$ . Thus a calculation of the Padé approximants  $[L/M]$  with  $L+M \leq N$  requires only the knowledge of the coefficients  $E_R^{(k)}$  of RSPT through order  $N$ . Since the coefficients are



**Figure 1.** Full line: measured energy (Koch 1978) for the  $n=25$  state of hydrogen  $(n_1, n_2, |m\rangle) = (21, 2, 1)$  in an electric field  $F=2514(3) \text{ V cm}^{-1}$ ;  $E_{\text{exp}} = -4.9866(29) \times 10^{-4} \text{ au}$ . Circles: Rayleigh-Schrödinger perturbation theory summed to order  $N$ . Crosses: Padé approximants  $[\frac{1}{2}N/\frac{1}{2}N]$ .  $E_{\text{exp}} - [12/12] = 0.4 \pm 2.9 \times 10^{-7} \text{ au}$ , where the error is caused predominantly by uncertainty in the measured value of  $F$ .



**Figure 2.** Full line: energy of the  $n=30$  state of hydrogen  $(n_1, n_2, |m\rangle) = (0, 29, 0)$  in an electric field  $F=800 \text{ V cm}^{-1}$ , computed by the phaseshift method (Damburg and Kolosov 1976 and private communication);  $E_{\text{DK}} = -7.844648 \times 10^{-4} \text{ au}$ . The theoretical width  $\Gamma_{\text{DK}}$  from this calculation is also shown. Broken line: energy for the same state and  $F$  computed by the classical method (Banks and Leopold 1979). Circles: Rayleigh-Schrödinger perturbation theory summed to order  $N$ . Crosses: Padé approximants  $[\frac{1}{2}N/\frac{1}{2}N]$ .

now available to rather high order (Silverstone 1978, Silverstone *et al* 1979), calculation of a large array of Padé approximants for the hydrogen Stark problem (Koch 1978) is possible.

The perturbation series here were generated by an adaptation of § 7 of Silverstone (1978).

We select two excited states of the hydrogen atom to discuss in detail. The ( $n = 25$ ,  $n_1 = 21$ ,  $n_2 = 2$ ,  $|m| = 1$ ) state is one for which accurate experimental values of the energy shift are known (Koch 1978). This state is typical of  $n_1 > n_2$  states for which the divergent perturbation series is oscillatory. On the other hand, the ( $n = 30$ ,  $n_1 = 0$ ,  $n_2 = 29$ ,  $|m| = 0$ ) state is typical of  $n_2 > n_1$  states for which the perturbation series is monotonic. Accurate values of the energy shift and width for this latter state (among others) have been calculated by Damburg and Kolosov (1976 and private communication) using method (1) and by Banks and Leopold (1978a, b, 1979, and private communication) using method (4).

The  $N$ th-order partial sums of RSPT (indicated by full circles in figures 1 and 2), the diagonal Padé approximants [ $\frac{1}{2}N/\frac{1}{2}N$ ] (indicated by crosses), and the experimental or theoretical energy (indicated by horizontal lines) are shown in figures 1 and 2 and in

**Table 1.** Energy of two excited states of hydrogen in an electric field, calculated by perturbation theory and by Padé approximants, in au.

Order $N$	$n = 25, n_1 = 21, n_2 = 2, m = 1$		$n = 30, n_1 = 0, n_2 = 29, m = 0$	
	RSPT partial sum	Padé approximant [ $\frac{1}{2}N/\frac{1}{2}N$ ]	RSPT partial sum	Padé approximant [ $\frac{1}{2}N/\frac{1}{2}N$ ]
0	-0.000800000	-0.000800000	-0.000555556	-0.000555556
1	-0.000451665		-0.000758580	
2	-0.000507404	-0.000499715	-0.000774258	-0.000775570
3	-0.000489537		-0.000778713	
4	-0.000503325	-0.000496455	-0.000780724	-0.000782546
5	-0.000493588		-0.000781797	
6	-0.000502731	-0.000500602	-0.000782453	-0.000784207
7	-0.000494270		-0.000782883	
8	-0.000503030	-0.000498629	-0.000783183	-0.000783951
9	-0.000493837		-0.000783401	
10	-0.000504004	-0.000498629	-0.000783566	-0.000784237
11	-0.000492550		-0.000783693	
12	-0.000505839	-0.000498703	-0.000783794	-0.000784443
13	-0.000490156		-0.000783876	
14	-0.000509025	-0.000498698	-0.000783943	-0.000784386
15	-0.000485996		-0.000783999	
16	-0.000514503	-0.000498790	-0.000784046	-0.000784469 <sup>a</sup>
17	-0.000478795		-0.000784087	
18	-0.000524028	-0.000498703	-0.000784121	-0.000784464
19	-0.000466156		-0.000784152	
20	-0.000540891	-0.000498703	-0.000784179	-0.000784478
21	-0.000443557		-0.000784202	
22	-0.000571133	-0.000498703	-0.000784223	-0.000784468
23	-0.0004023		-0.00078424	
24	-0.000627	-0.000498703	-0.00078426	-0.000784468

<sup>a</sup> There is some uncertainty in the underlined digits.

table 1. For the oscillatory case, the sequence of diagonal Padé approximants (other sequences, such as paradiagonal sequences, behave similarly) yields an improvement of four significant figures over the best partial sum (sixth order)—well within the experimental uncertainty. The Padé approximants retain numerical significance even when the partial sums are rapidly pulling away, as one can see by comparing [12/12] with the 24th-order partial sum, the last one we could fit on figure 1. For the monotonic case, the gain in significant figures is less, but the improvement is still significant. Here we stopped at 24th order because of round-off error in the 25th-order term. This is also approximately where the terms stop decreasing and start increasing in magnitude. (Note that the scales for figures 1 and 2 are considerably different.)

We can further justify the use of Padé approximants here by comparison with a standard textbook application of Padé approximants: to sum the asymptotic expansion  $x^{-1} e^{-x} \sum n! (-x)^{-n}$  for the exponential-type integral (see Baker 1975). The resonance energy for hydrogen in the Stark effect has been shown (Silverstone 1979) to be asymptotically equal to a sum of exponential-type integrals, the asymptotic expansions for which give an asymptotic expansion for the RSPT  $E_R^{(k)}$ . The usefulness of Padé approximants for the exponential-type integral would accordingly be expected to carry over to the Stark case. There is, however, a slight weakness to the argument as applied to the large values of  $n_1$  and  $n_2$  used here: a much higher order of perturbation theory would be required for the  $E_R^{(k)} F^k$  to behave asymptotically as if from an exponential-type integral.

In summary, the combination of the Padé technique with Rayleigh–Schrödinger perturbation theory, as is suggested by the asymptotics of the Stark effect, but as is more convincingly demonstrated practically and graphically by figures 1 and 2, is a powerful, accurate, and practical method for calculating Stark effect energy shifts.

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## References

- Amos A T 1978 *J. Phys. B: Atom Molec. Phys.* **11** 2053  
 Baker G A Jr 1975 *Essentials of Padé Approximants* (New York: Academic Press)  
 Banks D and Leopold J G 1978a *J. Phys. B: Atom. Molec. Phys.* **11** L5  
 — 1978b *J. Phys. B: Atom. Molec. Phys.* **11** 37  
 — 1979 submitted for publication  
 Beyer H-J and Kleinpoppen H 1978 *Int. J. Quantum. Chem. Symp.* **11** 271  
 Brändas E and Froelich P 1977 *Phys. Rev. A* **16** 2207  
 Cerjan C, Hedges R, Holt C, Reinhardt W P, Schreiber K and Wendoloski J J 1978 *Int. J. Quantum Chem. Symp.* **14** 393  
 Cohen M and McEachran R P 1978 *Int. J. Quantum Chem. Symp.* **12** 59  
 Damburg R J and Kolosov V V 1976 *J. Phys. B: Atom. Molec. Phys.* **9** 3149  
 Feneuille S, Liberman S, Pinard J and Taleb A 1979 *Phys. Rev. Lett.* **42** 1404  
 Freeman R R and Economou N P 1979 *Phys. Rev. A* submitted for publication  
 Freeman R R, Economou N P, Bjorklund G G and Lu K T 1978 *Phys. Rev. Lett.* **41** 1463  
 Froelich P and Brändas E 1975 *Phys. Rev. A* **12** 1  
 Gillespie G H 1977 *Phys. Rev. A* **16** 1728  
 Hatton G J 1977 *Phys. Rev. A* **16** 1347  
 Hehenberger M, McIntosh H V and Brändas E 1974 *Phys. Rev. A* **10** 1494

- Herrick D R 1976 *J. Chem. Phys.* **65** 3529  
Killingbeck J 1977 *Rep. Prog. Phys.* **40** 963  
Koch P M 1978 *Phys. Rev. Lett.* **41** 99  
Littman M G, Kash M M and Kleppner D 1978 *Phys. Rev. Lett.* **41** 103  
Ortolani F and Turchetti G 1978 *J. Phys. B: Atom. Molec. Phys.* **11** L207  
Reinhardt W P 1976 *Int. J. Quantum Chem. Symp.* **10** 359  
Silverstone H J 1978 *Phys. Rev. A* **18** 1853  
— 1979 submitted for publication  
Silverstone H J, Adams B G, Čížek J and Otto P 1979 submitted for publication  
Zimmerman M L, Littman M G, Kash M M and Kleppner D 1979 *Phys. Rev. A* submitted for publication