Asymptotic behavior of the ground-state-energy expansion for H_2^+ in terms of internuclear separation

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The asymptotic behavior of the coefficients a_n in the expansion of the ground-state energy of the hydrogen molecular ion in terms of the inverse powers of the internuclear separation is found to be $a_n = -(n+1)!2^{-n}e^{-2}[1+2n^{-1}-20n^{-2}-45n^{-3}+O(n^{-4})]$. The first two terms of this numerically obtained expression agree with the "asymptotic conjecture" involving the lowest excitation energy of H_2^+

In a recent article, Morgan and Simon[1] studied extensively the behavior of diatomic potential-energy curves for internuclear separation R. In particular, they examined an expansion of the ground-state energy of the hydrogen molecular ion of the form

$$E(R) \simeq -\sum_{n=0}^{\infty} a_n R^{-n}, \quad (1)$$

where the potential-energy curve $E=E(R)$ is given as the lowest eigenvalue of the Hamiltonian $\hat{H}$,

$$\hat{H} = \tfrac{1}{2}\hat{p}^2 - Z_1/r - Z_2/|\vec{R}-\vec{r}| , \quad (2)$$

with $Z_1 = Z_2 = 1$. In addition to a number of other interesting theorems, Morgan and Simon[1] proved (Theorem 4.1) that the coefficients a_n in the expansion (1) satisfy the condition

$$|a_n| < A^{n+1} n! \quad (3)$$

for a suitably chosen constant A, and they computed the first 45 coefficients a_n in expansion (1). On the basis of the numerical values of the a_n they conjectured that the series (1) is neither convergent nor Borel summable, and that the asymptotic behavior of the coefficients a_n is given by the formula

$$a_n \simeq -C_0(n+1)!\,2^{-(n+1)}, \quad (4)$$

where $0.24 < C_0 < 0.30$.

Very recently, Brezin and Zinn-Justin[2] reexamined the asymptotic behavior of the coefficients a_n. Relying on its analogy with a simple one-dimensional double-well problem, they proposed the asymptotic formula for these coefficients

$$a_n \simeq -\int_0^{\infty} dR\, R^{n-1}[\tfrac{1}{2}\Delta E(R)]^2, \quad (5)$$

where $\Delta E(R)$ designates the splitting between the two lowest-lying energy levels of H_2^+. Since[8] $\Delta E \sim 4Re^{-R-1}$, this formula implies immediately the behavior given by Eq. (4) with

$$C_0 = 2e^{-2} = 0.270\,670\,57. \quad (6)$$

Brezin and Zinn-Justin verified Eq. (6) numerically, using the values of coefficients a_n determined by Morgan and Simon,[1] and were able to suggest further that

$$\bar{a}_n = 2e^{-2}[1 + 2n^{-1} + O(n^{-2})], \quad (7)$$

where

$$\bar{a}_n = -a_n 2^{n+1}/(n+1)!\,. \quad (8)$$

The purposes of this work are (i) to show that a modification of the asymptotic analysis and what appear to be more accurate values[3] of the a_n lead to significantly improved agreement with Eq. (6), and (ii) to extend the asymptotic formula (7) from two to four terms. The third term is particularly interesting because it is in disagreement with the simplest application of the conjecture (5), emphasizing the value and role of such numerical analyses in verifying and extending heuristic analysis.

We calculated the a_n by perturbation theory and by applying the techniques of the $so(4,2)$ algebra[4] to the Hamiltonian (2) with arbitrary Z_1 and Z_2. Originally, we only determined 20 coefficients[5] but, stimulated by the above-mentioned papers,[1,2] we have calculated the first 45 coefficients.

For the asymptotic analysis of the coefficients a_n, Brezin and Zinn-Justin employed Neville's table.[6,7] The oscillations in the third column of their Table I (see Ref. 2) seem to indicate that the odd and even coefficients have a slightly different behavior, while having the same asymptotic expansion. This conclusion is also supported by considering a hypothetical case $Z_1 = -Z_2$. We therefore decided to analyze the odd and even coefficients separately using the following modified form of the Neville table:

$$\bar{a}_n^k = [n\bar{a}_n^{k-1} - (n-2k)\bar{a}_{n-2}^{k-1}]/2k, \quad (9)$$

where

$$\bar{a}_n^0 \equiv \bar{a}_n .$$

As is well known, the coefficients $\bar{a}_n^k$ should approach the same limit as the coefficients $\bar{a}_n \equiv \bar{a}_n^0$, but with deviations of the order of $n^{-(k+1)}$. It must be stressed, however, that great care must be exercised when performing such an analysis, since one loses the numerical accuracy as k is increased and, furthermore, the onset of the regular "asymptotic behavior" of $\bar{a}_n^k$ with respect to n is shifted to larger-n values with increasing k.

Since we are only interested in the asymptotic behavior of the series (1), we will only present the coefficients for $n \geqslant 30$. The values of these coefficients, as obtained from our $so(4,2)$-based computations,[3-5] are given in Table I. For greater convenience, we present the transformed coefficients $\bar{a}_n$, Eq. (8), scaled by the factor C_0^{-1}, Eq. (6); i.e., the coefficients $\bar{a}_n e^2/2$. These coefficients should be accurate to at least eleven decimal points. We observe that these numbers do indeed approach unity. However, the convergence is very slow, and even for $n = 44$—the largest coefficient available—the difference is greater than 3×10^{-2}.

Clearly, a much more rapid convergence will be obtained for the $\bar{a}_n^k$ coefficients, which are easily calculated using the recursive relationship given in Eq. (9). These values are plotted for $k = 2$, 3, 4, and 5 in Fig. 1, and for $k = 4$ and 5 are given in a more accurate form in Table II. We see, from Fig. 1, that with increasing k we indeed get closer and closer to the limiting value of C_0, Eq. (6), while the coefficients $\bar{a}_n^k$ with even-k values approach this limit from below, and those with odd-k from above, thus bracketing the desired limit. We also see that the regular "asymptotic behavior" is shifted towards the higher-n values as we increase k. This is particularly apparent

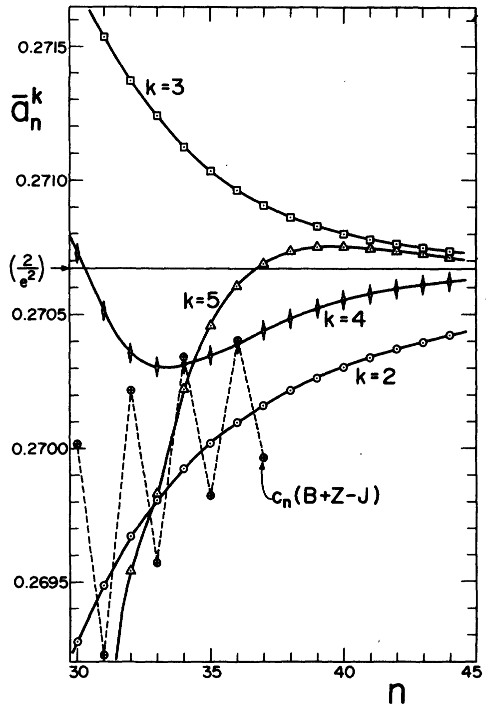

FIG. 1. The dependence of the modified Neville table coefficients $\bar{a}_n^k$, Eq. (9), on n for $k = 2$, 3, 4, and 5. For the sake of comparison, the c_n coefficients of Brezin and Zinn-Justin (Ref. 2) [corresponding to an unmodified Neville table with $k = 2$] are also shown and interconnected by a dashed line [these points are designated by $c_n(B+Z-J)$]. The solid horizontal line corresponds to the limiting value C_0 for the coefficients $\bar{a}_n \equiv \bar{a}_n^0$, given by Eq. (6) [Ref. 2].

TABLE I. The values of the coefficients $\bar{a}_n$, Eq. (7) scaled by the factor $e^2/2$ for $n = 30$ through 44.

n	$\bar{a}_n e^2/2$
30	1.042 461 310 881 8
31	1.041 922 086 586 8
32	1.041 363 012 841 5
33	1.040 786 259 610 2
34	1.040 202 682 982 1
35	1.039 613 135 782 7
36	1.039 024 700 484 7
37	1.038 437 512 230 6
38	1.037 856 243 745 0
39	1.037 280 640 979 4
40	1.036 713 804 462 3
41	1.036 155 275 674 7
42	1.035 607 111 217 5
43	1.035 068 753 995 9
44	1.034 541 557 697 9

TABLE II. The values of the coefficients $\bar{a}_n^4$ and $\bar{a}_n^5$, Eq. (7), for $n = 30$ through 44.

n	$\bar{a}_n^4$	$\bar{a}_n^5$
30	0.270 728	0.267 346
31	0.270 517	0.268 626
32	0.270 357	0.269 541
33	0.270 308	0.269 829
34	0.270 317	0.270 222
35	0.270 351	0.270 459
36	0.270 397	0.270 605
37	0.270 443	0.270 691
38	0.270 486	0.270 735
39	0.270 522	0.270 751
40	0.270 553	0.270 753
41	0.270 577	0.270 746
42	0.270 597	0.270 736
43	0.270 611	0.270 725
44	0.270 624	0.270 715

for the $\bar{a}_n^5$ coefficients, for which this regular behavior starts only at about $n=40$. Thus, with the available set of coefficients $\bar{a}_n \equiv \bar{a}_n^0$, it would be meaningless to proceed any further in the Neville table. For $k=5$ and $n=44$, we thus obtain the constant C_0, Eq. (6), with a better accuracy than 5×10^{-5}. (It is interesting to note that we obtain an even more accurate value for C_0 with $k=6$, since $\bar{a}_{44}^6 = 0.270\,658\,7$, which is closer to C_0 than 2×10^{-5}. However, we do not feel that the series $\bar{a}_n^6$ reaches the regular asymptotic behavior before $n=44$, and thus restrict ourselves to $k\leqslant 5$.)

For the sake of comparison, we have also plotted in the same figure the coefficients c_n given by Brezin and Zinn-Justin.[2] These coefficients correspond to the $k=2$ value in the unmodified Neville table. This plot clearly reveals the oscillatory behavior mentioned above.

Being encouraged by the excellent agreement of our asymptotic analysis with the general ansatz for the $\bar{a}_n$ coefficients given by Eqs. (4) and (6), we proceeded to determine the coefficients A_i in the expansion

$$\bar{a}_n = 2e^{-2}(1 + A_1 n^{-1} + A_2 n^{-2} + A_3 n^{-3} + \cdots)\,, \qquad (10)$$

generalizing Eq. (7). By the analogous procedure described above, based on the modified Neville table, we found the following values and bounds for the first three coefficients, viz.,

$$\begin{aligned} A_1 &= 2.000 \pm 0.003\,,\\ A_2 &= -20.00 \pm 0.05\,,\\ A_3 &= -45 \pm 1\,. \end{aligned} \qquad (11)$$

It is interesting to note that using the expansion[8]

$$\Delta E = 4\,\mathrm{R}e^{-R-1}\left(1 + \frac{1}{2R} - \frac{25}{8R^2} + \cdots\right), \qquad (12)$$

in Eq. (5), proposed by Brezin and Zinn-Justin,[2] we obtained, in addition to the correct value for C_0, as do these authors, also the value $A_1 = 2$, which is in good agreement with our analysis, while the subsequent A_i coefficients ($i \geqslant 2$), determined in this way, do not agree with the above given values [note that Eqs. (5) and (12) yield $A_2 = 26$]. However, this disagreement is not surprising, since the right-hand side of Eq. (5) represents only the leading term of a more complex expansion. Moreover, the expression (12) for ΔE is only approximate, since it should also contain the terms with higher positive powers of R and larger negative exponents in the exponential function.[9] Consequently, even the general form of the ansatz (10) can only be approximate.

To conclude, we note that our coefficient values $\bar{a}_n$ and the modified Neville table yield an excellent verification for the first two terms of the ansatz (10), particularly of the leading term $2e^{-2}$. The more general case, where $Z_1 \neq Z_2$, is currently being analyzed and will be described elsewhere. Also, for the case $Z_1 = Z_2$, a special program is being written which will enable us to go beyond $M=44$ in expansion (1).

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[1]J. D. Morgan, III and B. Simon, Int. J. Quantum Chem. (in press), and references therein, namely: B. Simon, Commun. Math. Phys. 55, 259 (1977); 58, 205 (1977); M. Reed and B. Simon, *Methods of Modern Mathematical Physics*, Vol. IV, *Analysis of Operators* (Academic, New York, 1978), and E. Harrell, Commun. Math. Phys. 60, 73 (1978). We are also grateful for an access to yet unpublished results by J. Avron, E. Harrell, I. Herbst, and B. Simon.

[2]E. Brezin and J. Zinn-Justin, J. Phys. (Paris) 40, L511 (1979); see also: E. Brezin, J. C. Le Guillon, and J. Zinn-Justin, Phys. Rev. D 15, 1544 (1976); 15, 1558 (1976); E. Brezin, G. Parisi, and J. Zinn-Justin, Phys. Rev. D 16, 408 (1977); E. B. Bogomolny and V. A. Fateyev, Phys. Lett. B71, 93 (1977) and references therein, where the quantum-field theory aspects of the "double-well" problems are pointed out.

[3]J. Čížek, M. Clay, and J. Paldus (unpublished).

[4]J. Čížek and E. Vrscay, in *Group Theoretical Methods in Physics*, edited by R. T. Sharp and B. Kolman (Academic, New York, 1977), p. 155; J. Čížek and J. Paldus, Int. J. Quantum Chem. 12, 875 (1977); E. Vrscay, M. Math. thesis, University of Waterloo, 1977 (unpublished); J. Čížek, B. G. Adams, and J. Paldus, Phys. Scri. 21, 364 (1980); J. Avron, B. G. Adams, J. Čížek, M. Clay, M. L. Glasser, P. Otto, J. Paldus, and E. Vrscay, Phys. Rev. Lett. 43, 691 (1979) and references therein.

[5]M. R. Clay, M. math. thesis, University of Waterloo,

1979 (unpublished).

[6]The method of the Neville table is identical to the method introduced by Bender and Wu (Ref. 7) in their pioneering paper on perturbation theory at large order.

[7]C. M. Bender and T. T. Wu, Phys. Rev. 184, 1231 (1969).

[8]R. J. Damburg and R. Kh. Propin, J. Phys. B 1, 681 (1968).

[9]A. A. Ovchinnikov and A. D. Sukhanov, Dok. Akad. Nauk SSSR 157, 1092 (1964) [Sov. Phys. Dokl. 9, 685 (1965)].