Large-Order Dimensional Perturbation Theory for H_2^+

M. López-Cabrera, D. Z. Goodson, and D. R. Herschbach
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

J. D. Morgan, III
Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716
(Received 27 January 1992)

An asymptotic expansion for the electronic energy of H_2^+ is developed in inverse powers of D, the spatial dimension, and the singularity structure in the $D\to\infty$ limit is elucidated by analysis of the coefficients at large order ($\sim$30 to 45). For the ground state and several excited states, Padé-Borel summation yields an accuracy of eight or more significant figures.

PACS numbers: 31.20.Di

Dimensional perturbation and scaling techniques have recently yielded useful results for several daunting problems involving nonseparable dynamics or drastic correlations among strongly interacting particles. These include atomic Zeeman [1] and Stark [2] effects in very strong fields, correlation energy of two-electron [3–6] and many-electron [7] atoms, and the virial equations of state of a dense hard-sphere fluid [8]. The general approach involves transforming the Hamiltonian so that the spatial dimension appears only as a parameter, D, which is treated as a continuous variable [9–12]. Coefficients of perturbation expansions in powers of $\delta\equiv 1/D$ for energy eigenvalues $E(\delta)$ and other properties can be calculated exactly and to large order using an efficient recursive method [13]. However, for Coulombic systems such δ expansions usually diverge [14,15]. For He($1s^2$), the first few coefficients of the δ expansion of $E(\delta)$ decrease steadily, but beyond fifth order factorial divergence appears to set in [6]. This behavior is in accord with the suspected [16] presence of an essential singularity at $\delta=0$, in addition to known first- and second-order poles at $\delta=1$.

Here we report a study of the one-electron diatomic cation, H_2^+. With the assumption of fixed nuclei, this system is simpler than He since it involves only two internal degrees of freedom rather than three. By computing the coefficients of the δ expansion for $E(\delta)$ to $\sim$45th order, we have established major features of the singularity structure and find that Padé-Borel approximants [17] are well suited to summing the asymptotic expansion. For the ground-state electronic energy, this method can provide an accuracy of at least eight or nine significant figures. For certain excited states, we find even more accurate results by exploiting interdimensional degeneracies [18]. The energies of these excited states for $D=3$ are obtained by simply evaluating our ground-state expansion at higher dimensionalities.

We use a dimensional continuation of the Schrödinger equation [9] that generalizes the kinetic energy to a D-dimensional coordinate space but retains the potential energy in its three-dimensional form. This yields [19]

$$\left[-\frac{1}{2f}\frac{\partial^2}{\partial\rho^2}-\frac{1}{2f}\frac{\partial^2}{\partial z^2}+V_{\rm eff}\right]\Psi=fE\Psi\,, \tag{1}$$

with

$$V_{\rm eff}=\frac{(D-1)(D-3)}{8f\rho^2}-[\rho^2+(z-\tfrac{1}{2}R/f)^2]^{-1/2}-[\rho^2+(z+\tfrac{1}{2}R/f)^2]^{-1/2}. \tag{2}$$

In accord with the Born-Oppenheimer approximation, the internuclear distance R is a fixed parameter. The coordinate ρ specifies the radial distance of the electron from the internuclear axis and z the projection on the axis, measured from the midpoint of the nuclei. The dimensional scaling factor, $f=D(D-1)/6$, is chosen to insure correct behavior in the $D\to\infty$ limit [11] and the $D\to 1$ limit [14] and to reduce to unity at $D=3$. With $\tilde{R}=R/f$ treated as a dimension-independent parameter, the large-dimension limit provides a good approximation to the $D=3$ intermolecular potential [19]. In the $D\to\infty$ limit the derivative terms in Eq. (1) disappear, so the scaled energy fE in that limit is simply the minimum of $V_{\rm eff}$. For D large but finite, the electron is restricted to small harmonic oscillations about the minimum, which contribute to fE a term linear in δ. Anharmonic components of $V_{\rm eff}$ contribute higher-order terms, resulting in an asymptotic expansion of the energy in the form

$$E=\delta^2\sum_{k=0}^{\infty}E_k\delta^k \tag{3a}$$

$$=\delta^2\left[\frac{a_{-2}}{(1-\delta)^2}+\frac{a_{-1}}{1-\delta}+\sum_{k=0}^{\infty}E_k'\delta^k\right]. \tag{3b}$$

Equation (3b) displays explicitly the residues a_{-2} and a_{-1} of poles at $\delta=1$, which are a characteristic feature of Coulombic systems [14,16,20,21]. They result from the divergence of the expectation values of Coulomb potentials at particle coalescences. The summation over the $E_k'\equiv E_k-(k+1)a_{-2}-a_{-1}$ tends to be easier to evaluate than the original summation [6,22,23].

The residue a_{-2} can be computed exactly as the eigen-

value of a scaled one-dimensional system with the Coulombic potentials replaced by δ functions [20,21]. In principle, a_{-1} could be determined exactly from a first-order perturbation expansion about $\delta=1$, but here we obtain this residue more simply albeit approximately from Padé summation [6]. The E_k were computed recursively, using the moment method [13], to as high an order as round-off error allowed (up to $k\sim 45$, in the case of $\tilde{R}=1$ with quadruple-precision arithmetic), for eight values of $\tilde{R}<\tilde{R}_c=(\frac{27}{16})^{1/2}=1.299038$, the range in which $V_{\rm eff}(D\rightarrow\infty)$ has a single minimum [19].

Figure 1 shows that the ratios $|E_k'/E_{k-1}'|$ of successive coefficients increase linearly with k for the range of $\tilde{R}$ considered, once the perturbation expansion is carried to sufficiently high order. Hence the E_k grow as $k!$ and the radius of convergence of the expansion is zero, implying the presence of a singularity at $\delta=0$. To examine this singularity, we construct the Borel function, $F(\delta)$, according to [24]

$$E(\delta)=\delta^2\left[\frac{a_{-2}}{(1-\delta)^2}+\frac{a_{-1}}{1-\delta}+\int_0^\infty e^{-t}F(\delta t)dt\right]. \quad (4)$$

The expansion coefficients of the Borel function are $F_k=E_k'/k!$, so the ratios $|F_k/F_{k-1}|$ will converge to a constant, $1/r_0$, the reciprocal of the radius of convergence of the δ expansion of $F(\delta)$. We find from the Borel ratios that r_0 ranges from about 0.7 at $\tilde{R}=0.6$ to 0 at $\tilde{R}_c$, where the divergence becomes worse than factorial [15]. The F_k beyond lowest orders alternate in sign, so the singularity in $F(\delta)$ closest to the origin is at $\delta_0=-r_0$. If we assume that this is an algebraic singularity, proportional to $(\delta_0-\delta)^\sigma$, then the Borel ratios $|F_k/F_{k-1}|$ will converge at a rate proportional to $1/k$. Using the Neville-Richardson extrapolation of these ratios, we find that $\sigma=\frac{1}{2}$ and obtain an estimate for δ_0 that is convergent to about seven significant figures for the case $\tilde{R}=1$. A singularity analysis of quadratic Padé approximants [25] to the F_k confirms that the closest singularity to the origin is a square-root branch point on the negative real axis; the location is quite stable with increasing order and thereby gives a value for δ_0 convergent to about one additional figure. Table I gives numerical results for the singularity parameters a_{-2}, a_{-1}, and δ_0.

We thus infer that the Borel function has the form

$$F(\delta)=\alpha(\delta)(\delta_0-\delta)^{1/2}+\beta(\delta), \quad (5)$$

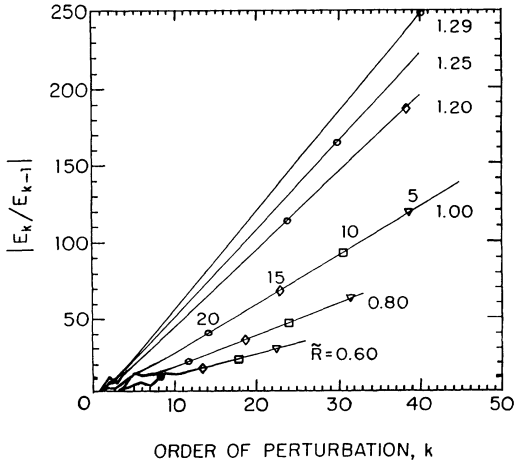

FIG. 1. Ratios of coefficients E_k of the δ expansion for various values of $\tilde{R}$. Round-off error in E_k is illustrated by the circles, diamonds, squares, and triangles, which indicate the orders at which the accuracy of the coefficients drops to twenty, fifteen, ten, and five significant figures, respectively.

where $\alpha(\delta)$ and $\beta(\delta)$ are nonsingular for $|\delta|\leq|\delta_0|$. According to Darboux's theorem [26], the large-order behavior of the δ expansion of the $F(\delta)$ is the same as that for a function with $\alpha(\delta)$ replaced by $\alpha_0\equiv\alpha(\delta_0)$. Hence we construct for E the functional form

$$E(\delta)=\delta^2\left[\frac{a_{-2}}{(1-\delta)^2}+\frac{a_{-1}}{1-\delta}+\eta(\delta)+\bar{E}(\delta)\right], \quad (6)$$

where

$$\eta(\delta)=\alpha_0\int_0^\infty e^{-t}(\delta_0-\delta t)^{1/2}dt. \quad (7)$$

$\eta(\delta)$ accounts for the large-order behavior of the δ expansion; any singularities of the remainder $\bar{E}(\delta)$ are subdominant. In the limit $\delta\rightarrow 0$, the function $\eta(\delta)$ has a branch point of the form $\delta^{1/2}\bar{\eta}(\delta)$, where $\bar{\eta}(\delta)$ is a single-valued function with an essential singularity at the origin. Since the radius of convergence for the expansion of E is zero, the standard proofs of Borel summability [24,27] do not apply. However, we find that the singularities of Padé approximants are consistent with this analysis. The approximants appear to trace out a branch cut along the negative real axis while also modeling, by

TABLE I. Parameters from singularity analysis of the D-dimensional ground-state energy of H_2^+.

Parameter	Value $\tilde{R}=0.8$	$\tilde{R}=1.0$	$\tilde{R}=1.2$	Method of calculation
a_{-2}	−5.411 464 478 65	−5.048 785 818 35	−4.743 709 235 01	Exact
a_{-1}	−1.059	−0.983 0	−0.909 4	Padé summation
δ_0	−0.474 795	−0.313 841 21	−0.197 516 618 76	Quadratic Padé analysis
		−0.313 841 1		Neville-Richardson extrapolation

means of coincident poles and zeros, an essential singularity at the origin.

By virtue of its simpler singularity structure, $F(\delta)$ ought to be better represented by Padé approximants than is $E(\delta)$, and indeed we find that Padé-Borel summation [17] of Eq. (3b) yields very accurate results and is superior to Padé summation. Removing the poles at $\delta=1$, by using Eq. (3b) instead of Eq. (3a), improves the results by about two significant figures. Incorporating the singularity at $\delta=0$ into the approximant, by using Padé-Borel summation instead of Padé summation, adds about one or two more significant figures. For a given value of the scaled internuclear distance $\tilde{R}$, excited-state energies are obtained by evaluating the ground-state energy at higher odd integer values of D, according to the interdimensional degeneracies identified by Herrick [18]. For example, if we evaluate the ground-state energy at $\delta=\frac{1}{5}$ with $R=\tilde{R}=1$, then we obtain the $2p\pi_u$ excited state with $R=[D(D-1)/6]\tilde{R}=10/3$. Figure 2 shows that extremely accurate results are obtained for excited states. Similar results are obtained for $\tilde{R}=0.8$ and 1.2, although in both cases the overall accuracy is slightly lower than for $\tilde{R}=1.0$. At $\tilde{R}=0.8$ the accuracy is degraded by round-off error in the E_k, while at 1.2 it is degraded by proximity to the symmetry-breaking point.

Since in our dimensional continuation the scaled $\tilde{R}$ $=6R\delta^2/(1-\delta)$ is fixed, the limit $\delta\rightarrow 0$ corresponds to the unscaled $R\rightarrow\infty$. The energy of H_2^+ as a function of $1/R$ has a complicated branch point singularity in this limit [29], attributed [30] to the fact that for $R\rightarrow\infty$ the electron is localized at only one of the protons, whereas at any finite R the wave function is symmetric to exchange of the protons. This link between the large-D and large-R limits suggests that techniques developed for the $1/R$ expansion [29,31] may be applied also to dimensional perturbation theory. The limit $\delta\rightarrow 1$ is analogous to the limit $R\rightarrow 0$. The expansion for the energy at small R is known to include logarithmic terms [32], which suggests that there is a weak logarithmic singularity at $\delta=1$ of the form $(1-\delta)^3\log(1-\delta)$. This singularity is not detected by the Padé analysis of the remainder sum in Eq. (3b).

In a similar treatment in progress for the two-electron atom, we have found qualitatively similar dimensional singularities. However, the Borel function appears to have a complex-conjugate pair of branch points slightly displaced from the negative real axis. Expressing the expansion in the form of Eq. (3b) and computing Padé-Borel approximants for the remainder again appears to be a very effective summation method.

We thank John Loeser, Tony Scott, and Don Frantz for enjoyable discussions, and Stella Sung for computational help. This work was supported by grants from the National Science Foundation and the Office of Naval Research, and by a Cray Research and Development grant.

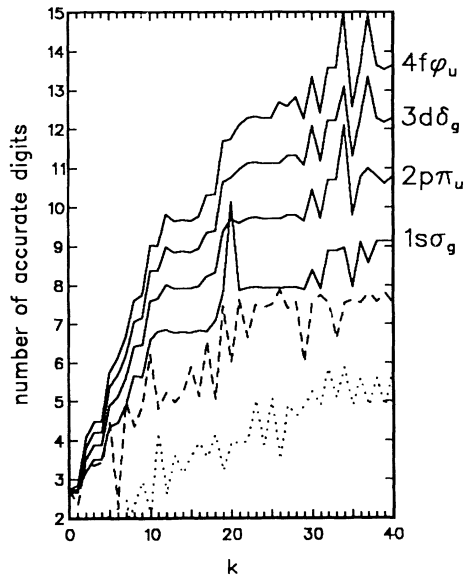

FIG. 2. Accuracy of summation approximants for the electron energy E as a function of the order k of the δ expansion. The solid curves show the Padé-Borel summation of Eq. (3b) for four eigenstates with $\tilde{R}=1$, which corresponds to $D=3,5,7,9$. The dashed and dotted curves show the Padé summation for the $1s\sigma_g$ state, the former using Eq. (3b) and the latter using Eq. (3a). The number of accurate digits is defined as $-\log_{10}|(E_{\text{approx}}-E_{\text{exact}})/E_{\text{exact}}|$, with E_{exact} calculated by conventional methods [28].

[1] C. M. Bender, L. D. Mlodinow, and N. Papanicolaou, Phys. Rev. A **25**, 1305 (1982).
[2] V. S. Popov, V. D. Mur, A. V. Shcheblykin, and V. M. Weinberg, Phys. Lett. A **124**, 77 (1987); V. S. Popov, V. D. Mur, and A. V. Sergeev, Phys. Lett. A **149**, 425 (1990); V. M. Vaĭnberg, V. S. Popov, and A. V. Sergeev, Zh. Eksp. Teor. Fiz. **98**, 847 (1990) [Sov. Phys. JETP **71**, 470 (1990)].
[3] J. G. Loeser and D. R. Herschbach, J. Phys. Chem. **89**, 3444 (1985); **86**, 3512 (1987).
[4] O. Goscinski and V. Mujica, Int. J. Quantum Chem. **29**, 897 (1986).
[5] D. Z. Goodson and D. R. Herschbach, J. Chem. Phys. **86**, 4997 (1987).
[6] D. Z. Goodson and D. R. Herschbach, Phys. Rev. Lett. **58**, 1628 (1987).
[7] J. G. Loeser, J. Chem. Phys. **86**, 5635 (1987).
[8] J. G. Loeser, Z. Zheng, S. Kais, and D. R. Herschbach, J. Chem. Phys. **95**, 4525 (1991).
[9] D. R. Herrick and F. H. Stillinger, Phys. Rev. A **11**, 42 (1975).
[10] L. D. Mlodinow and N. Papanicolaou, Ann. Phys. (N.Y.) **128**, 314 (1980); **131**, 1 (1981).
[11] D. R. Herschbach, J. Chem. Phys. **84**, 838 (1986).
[12] J. Avery, D. Z. Goodson, and D. R. Herschbach, Theor. Chim. Acta **81**, 1 (1991).

[13] J. P. Ader, Phys. Lett. **97A**, 178 (1983).
[14] D. J. Doren and D. R. Herschbach, Phys. Rev. A **34**, 2654 (1986).
[15] V. D. Mur, V. S. Popov, and A. V. Sergeev, Zh. Eksp. Teor. Fiz. **97**, 32 (1990) [Sov. Phys. JETP **70**, 16 (1990)].
[16] D. J. Doren and D. R. Herschbach, J. Chem. Phys. **87**, 433 (1987).
[17] S. Graffi, V. Grecchi, and B. Simon, Phys. Lett. **32B**, 240 (1970).
[18] D. R. Herrick, J. Math. Phys. **16**, 281 (1975); D. D. Frantz and D. R. Herschbach, J. Chem. Phys. **92**, 6668 (1990).
[19] D. D. Frantz and D. R. Herschbach, Chem. Phys. **126**, 59 (1988).
[20] M. López-Cabrera, Ph.D. thesis, The University of Michigan, Ann Arbor, 1991 (unpublished).
[21] D. Z. Goodson and M. López-Cabrera, in "Dimensional Scaling in Chemical Physics," edited by D. R. Herschbach, O. Goscinski, and J. Avery (Kluwer, Dordrecht, to be published), Chap. 4.1.
[22] D. J. Doren and D. R. Herschbach, Chem. Phys. Lett. **118**, 115 (1985); Phys. Rev. A **34**, 2665 (1986).
[23] D. Z. Goodson and D. R. Herschbach (to be published).
[24] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge Univ. Press, Cambridge, 1940).
[25] R. E. Shafer, SIAM J. Numer. Anal. **11**, 447 (1974).
[26] B. W. Ninham, J. Math. Phys. **4**, 679 (1963).
[27] A. D. Sokal, J. Math. Phys. **21**, 261 (1980).
[28] D. D. Frantz, D. R. Herschbach, and J. D. Morgan, III, Phys. Rev. A **40**, 1175 (1989).
[29] J. Čížek, R. J. Damburg, S. Graffi, V. Grecchi, E. M. Harrell, J. G. Harris, S. Nakai, J. Paldus, R. K. Propin, and H. J. Silverstone, Phys. Rev. A **33**, 12 (1986).
[30] J. D. Morgan, III and B. Simon, Int. J. Quantum Chem. **17**, 1143 (1980).
[31] E. Brézin and J. Zinn-Justin, J. Phys. (Paris), Lett. **40**, L511 (1979).
[32] W. Byers Brown and E. Steiner, J. Chem. Phys. **44**, 3934 (1966).