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Large-order dimensional perturbation theory for diatomic molecules within the Born-Oppenheimer approximation

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A renormalization of the D-dimensional Hamiltonian is developed to ensure that the large-D limit corresponds to a single well at any value of the internuclear distance R. This avoids convergence problems caused by a symmetry-breaking transition that is otherwise expected to occur when R is approximately equal to the equilibrium bond distance R_{eq}, with larger R giving a double well. This symmetry breaking has restricted the applicability of large-order perturbation theory in $1/D$ to cases where R is significantly less than R_{eq}. The renormalization greatly extends the range of R for which the large-order expansion can be summed. A numerical demonstration is presented for $H_2{}^+$. The $1/D$ expansions are summed using Padé-Borel approximants with modifications that explicitly model known singularity structure. [S1050-2947(98)06607-4]

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I. INTRODUCTION

In a previous study [1] it was demonstrated that large-order dimensional perturbation theory (DPT) could be used to calculate highly accurate electronic energy eigenvalues for $H_2{}^+$ within the Born-Oppenheimer approximation. Results were presented for internuclear distances $R=0.8$, 1.0, and 1.2. (We are expressing distances in units of Bohr radii and energies in hartree atomic units.) However, the method fails in practice as R approaches the equilibrium bond length $R_{\mathrm{eq}}\approx 1.997$ due to increasingly poor convergence of the summation approximants. Here we present a technique that makes it possible to extend that work to values of R at and beyond R_{eq} and, in principle, to many-electron diatomic molecules.

DPT is a semiclassical theory [2–4], in which differential operators in the Schrödinger equation disappear at zeroth order. In the usual formulation [5,6] the perturbation parameter is $\delta=1/D$, where D is the dimensionality of coordinate space, treated as a continuous variable. In the limit $\delta\to 0$ the system becomes localized at the minimum of an effective potential W that is the sum of the Coulomb potential and a repulsive centrifugal potential. First-order DPT corresponds to harmonic oscillation about this minimum. Higher orders systematically include anharmonic effects. Energy eigenvalues are obtained as asymptotic expansions in powers of δ. An advantage of this theory is that the energy expansion coefficients E_k can be efficiently computed to very high k using a recursive linear algebraic algorithm [7]. The energy expansions diverge as $k!$, but Padé or Padé-Borel approximants, with modifications that take into account the singularity structure of the energy function $E(\delta)$ [8–10], have yielded excellent results for a variety of systems [11].

Difficulties can arise when the extremum of W corresponding to the zeroth-order theory is not a unique global minimum or when a harmonic frequency of the first-order theory approaches zero. For $H_2{}^+$ at small R the effective potential has a symmetric global minimum, with the electron equidistant from each nucleus. As R increases, the symmetric extremum becomes a saddle point with a pair of unsymmetric minima on either side. Thus low-order perturbation theory allows the molecule to gracefully dissociate into a hydrogen atom and a free proton at large R. A number of studies [12–21] have now shown that the low-order theory can provide a reasonable qualitative, and even semiquantitative, model for diatomic molecules. However, it is difficult to systematically improve the accuracy of these calculations by going to higher order in the perturbation theory because of serious convergence problems. As R approaches the symmetry-breaking value the divergence of the E_k increases drastically [22,23]. For larger R one could, in principle, compute the expansion of W about one of the unsymmetric wells, but that would omit subdominant contributions that result from interaction with the degenerate solution at the other well. Although the subdominant terms go to zero faster than any power of δ, they can nevertheless be numerically significant for $\delta=1/3$ [18].

Our approach is to use a dimensional scaling of the parameter R that ensures that the symmetric extremum of W is a stable global minimum. In effect, we redefine the dimensional continuation of the Schrödinger equation so that the internuclear distance decreases somewhat as D increases above 3. Since the Hamiltonian remains correct at $D=3$, this procedure introduces no approximations into the analysis. We obtain an exact asymptotic expansion of the electronic energy within the Born-Oppenheimer approximation.

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II. THEORY

Our theory yields an asymptotic expansion for $E(\delta)$ about the infinite-dimensional limit $\delta\to 0$. However, the rate of convergence of summation approximants for the ground state can be increased by including information about the one-dimensional limit $\delta\to 1$. We begin this section with a review of dimensional scaling and the computation of large-dimensional expansions. Then we describe the one-dimensional solution, present our particular approach to the dimensional scaling, and discuss summation methods.

A. Analysis at the $D\to\infty$ limit

The first step in a large-D analysis is to express the Hamiltonian in terms of body-fixed coordinates. Then the dimension dependence will appear only as an explicit parameter in a centrifugal potential. Thus the electronic Hamiltonian has the form [14]

$$H = T + D^2 C(\delta) U + V, \tag{1}$$

where $\delta = 1/D$. V is the physical, three-dimensional Coulomb potential. The kinetic-energy operator has been separated into an effective kinetic-energy operator T, which is a sum of terms containing partial derivatives, and a centrifugal potential involving the operator U, which does not contain derivatives. C is a polynomial in δ such that $C(0)$ is nonzero and finite.

It is convenient to scale the electronic coordinates $\mathbf{r}_i$ with a dimension-dependent factor $f(\delta)$,

$$\mathbf{r}_i \to f\mathbf{r}_i, \tag{2}$$

where $f\propto D^2$ in the large-D limit but is otherwise arbitrary. T and U are homogeneous operators of degree -2 with respect to the $\mathbf{r}_i$. Therefore, the scaled Schrödinger equation for a homonuclear diatomic molecule is

$$[\, f^{-1} T + \tilde{C}(\delta) U + \tilde{V} - \tilde{E}]\Psi = 0, \tag{3}$$

where $\tilde{E} = fE$, $\tilde{C} = D^2 C/f$, and

$$\tilde{V} = \sum_{i<j} r_{ij}^{-1} - Z \sum_i \{[\rho_i^2 + (z_i - \tilde{R}/2)^2]^{-1/2} + [\rho_i^2 + (z_i + \tilde{R}/2)^2]^{-1/2}\}. \tag{4}$$

The r_{ij} are the interelectron distances while (ρ_i, z_i) is the radial and axial coordinate, respectively, for the ith electron in the cylindrical coordinate system about the internuclear axis centered at the midpoint. Z is the nuclear charge and

$$\tilde{R} = R/f \tag{5}$$

is a dimension-scaled internuclear distance. The parameter R is being treated differently from the coordinates $\mathbf{r}_i$ on account of the Born-Oppenheimer approximation.

Equation (3) is in a form suitable for semiclassical perturbation theory [2,3,5]. In the limit $D\to\infty$ the derivatives disappear and the system becomes localized at a minimum of the function

$$W_0 = \tilde{C}(0) U + \tilde{V}, \tag{6}$$

which corresponds to a stable, classical configuration of the particles. The repulsive centrifugal potential prevents the electrons from coalescing with nuclei.

This infinite-D limit is the zeroth order of an asymptotic expansion for the scaled energy

$$\tilde{E} = \sum_{k=0}^{\infty} \tilde{E}_k f^{-k/2}. \tag{7}$$

The zeroth-order coefficient $\tilde{E}_0$ is equal to the minimum of W_0. The first-order coefficient is

$$\tilde{E}_1 = \tilde{C}_1 + \sum_{i=1}^{N(N+3)/2} \left(n_i + \frac{1}{2} \right) \omega_i, \tag{8}$$

where N is the number of electrons, the ω_i are the frequencies for harmonic oscillations about the minimum of W_0, and $\tilde{C}_1$ is a zero-point-energy contribution from the δ dependence of $\tilde{C}$. The n_i are harmonic quantum numbers. The $\tilde{E}_{k>1}$ can be calculated recursively using any of several computational algorithms. With more than one degree of freedom, the matrix method of Dunn *et al.* [7,24] is particularly convenient. Once the $\tilde{E}_k$ are calculated, Eq. (7) can be reexpanded in powers of δ,

$$E = \delta^2 \sum_{k=0}^{\infty} E_k\ \delta^k. \tag{9}$$

B. Analysis at the $D\to 1$ limit

In the limit $D\to 1$ the Coulomb potential becomes a delta function, according to the relation [25–27]

$$\frac{D-1}{r} \to \delta(|x|), \tag{10}$$

with the one-dimensional Cartesian coordinate x replacing the radial coordinate r. Therefore, the dimensional scaling $\mathbf{r}_i \to (D-1)\mathbf{r}_i$ leads to the following Schrödinger equation for $D=1$:

$$\left\{ -\frac{1}{2} \sum_{i=1}^{N} \frac{\partial^2}{\partial x_i^2} - \sum_{i=1}^{N} [\delta(|x_i + \tilde{R}/2|) + \delta(|x_i - \tilde{R}/2|)] + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(|x_i - x_j|) \right\} \Psi = \frac{(D-1)^2}{4} E \Psi. \tag{11}$$

If Eq. (11) for a given eigenstate has a nonzero eigenvalue, then the energy function $E(\delta)$ will have a second-order pole at $\delta=1$ and the residue of the pole will be proportional to the one-dimensional eigenvalue. This pole will be the first term in a Laurent expansion about $\delta=1$ [28],

$$E(\delta)\sim\frac{a_{-2}}{(1-\delta)^2}+\frac{a_{-1}}{1-\delta}+a_0+a_1(1-\delta)+\cdots. \tag{12}$$

C. Dimensional scaling of internuclear distance

According to Eq. (5), we have $\tilde{R}\rightarrow 0$ in the limit $D\rightarrow\infty$. This would imply that our zeroth-order model for an N-electron molecule would be the same as that for an N-electron atom. Frantz and Herschbach [12] have shown that a more accurate zeroth-order approximation can be obtained by replacing the function $\tilde{R}(D)$ with the constant $\tilde{R}(D_{\text{ph}})$, where D_{ph} is the physical value of dimensionality. This treatment of $\tilde{R}$ amounts to redefining the dimensional continuation of the Hamiltonian. It is valid because H remains correct at $D=D_{\text{ph}}$. Typically one would choose $D_{\text{ph}}=3$, although it is possible to obtain energies of three-dimensional excited states by evaluating the ground-state energy at a higher value of D_{ph}, on account of exact interdimensional degeneracies [29,30].

In Ref. [1] our choice for the scale factor was $f=D(D-1)/6$, so as to have the desired behavior in both the $D\rightarrow\infty$ and $D\rightarrow 1$ limits and, for convenience, to have $f=1$ at $D=3$. Then we simply replaced $\tilde{R}$ with the constant R. Here we use the choice

$$f=\frac{(D+\beta)(D-1)}{(D_{\text{ph}}+\beta)(D_{\text{ph}}-1)}, \tag{13}$$

where β is an arbitrary parameter that is independent of D. This gives the desired behavior in both limits and it includes a free parameter that can be chosen so as to improve the convergence of the perturbation expansion.

We will treat $\tilde{R}$ as a dimension-independent constant, with its numerical value set equal to the desired physical value of internuclear distance at $D=D_{\text{ph}}$. We introduce the following notational convention: $\tilde{R}$ refers to the value of the internuclear distance at $D=D_{\text{ph}}$ while R refers to the value of internuclear distance at $D=3$. For example, suppose one wanted to calculate the energy of the excited state at $D=3$ that is degenerate with the $D=5$ ground state. Then R would be the internuclear distance for the excited state, with $D_{\text{ph}}=5$ and $\tilde{R}=2(5+\beta)R/(3+\beta)$.

For $H_2{}^+$ the operators in Eq. (3) can be written as [12]

$$T=-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2}+\frac{\partial^2}{\partial z^2}\right),\quad U=\frac{1}{8}\rho^{-2}, \tag{14}$$

$$\tilde{V}=-[\rho^2+(z-\tilde{R}/2)^2]^{-1/2}-[\rho^2+(z+\tilde{R}/2)^2]^{-1/2}, \tag{15}$$

where ρ is the radial distance of the electron from the internuclear axis and z is the projection onto the axis. The dimension-dependent factor in Eq. (3) is [31]

$$\tilde{C}(\delta)=(D-2)(D-4)/f=\frac{(1-2\delta)(1-4\delta)}{(1+\beta\delta)(1-\delta)}\tilde{C}_0, \tag{16}$$

where

$$\tilde{C}_0=(D_{\text{ph}}+\beta)(D_{\text{ph}}-1). \tag{17}$$

The zeroth-order result for the energy is $\tilde{E}_0=W_0(\rho_m,z_m)$, where (ρ_m,z_m) is an extremum of W_0. For small $\tilde{R}$ there is a global minimum corresponding to the symmetric configuration $z_m=0$. For large $\tilde{R}$, the function W_0 is a double well with equivalent unsymmetric minima corresponding to $z=\pm z_m\neq 0$ separated by a saddle point with $z=0$. The condition $\partial^2W_0/\partial z^2=0$ determines the critical value $\tilde{R}=\tilde{R}_c$,

$$\tilde{R}_c=\frac{3\sqrt{3}}{16}\tilde{C}_0. \tag{18}$$

for which the $z=0$ extremum becomes a saddle point [31]. Increasing β increases the centrifugal potential $\tilde{C}U$, which increases the effective potential energy of the unsymmetric configuration more than it does that of the symmetric configuration.

D. Summing the energy expansion

The asymptotic behavior of the δ expansion (9) is determined by the singularity structure of the function $E(\delta)$. The ground-state energy of a many-electron atom or molecule will in general have a second-order pole at $\delta=1$, due to the divergence of the expectation value of the Coulomb potential at particle coalescences [26,27]. It is helpful to explicitly remove this singularity structure from the energy expansion. To this end, we reexpand $E(\delta)$ as [32]

$$E(\delta)=\delta^2\left[\frac{a_{-2}}{(1-\delta)^2}+\frac{1}{1-\delta}E'(\delta)\right], \tag{19}$$

where

$$E'(\delta)=\sum_{k=0}^{\infty}E'_k\delta^k, \tag{20a}$$

$$E'_0=E_0-a_{-2},\quad E'_k=E_k-E_{k-1}-a_{-2}. \tag{20b}$$

The residue a_{-2} is the eigenvalue of the $D=1$ δ-function Hamiltonian. Note that $\delta(|x|)$ is normalized on the integration range $[0,\infty)$. Therefore, $\delta(|x|)=2\delta(x)$. It follows that for $H_2{}^+$ we have

$$\left\{-\frac{1}{2}\frac{d^2}{dx^2}-g[\delta(x-\tilde{R}/2)+\delta(x+\tilde{R}/2)]\right\}\Psi=\epsilon\Psi, \tag{21}$$

with

$$g=\frac{2(1+\beta)}{(D_{\text{ph}}+\beta)(D_{\text{ph}}-1)},\quad a_{-2}=\frac{4}{g^2}\epsilon. \tag{22}$$

Equation (21) was solved by Frost [33]. The two eigenvalues can be obtained from the transcendental equation

$$\kappa=g(1\pm e^{-\kappa\tilde{R}}), \tag{23}$$

with $\epsilon = -\kappa^2/2$. The plus sign corresponds to the ground state, which is symmetric, while the minus sign corresponds to the excited state, which is antisymmetric. The form of Eq. (19) ensures that $E'(\delta)$ is analytic at $\delta = 1$.

In general, δ expansions for Coulombic systems will also have a complicated singularity at $\delta = 0$, which leads to factorial increase of the E_k as k becomes large. This singularity is closely analogous to the singularity in quantum electrodynamics at the limit $e^2 \to 0$, where e is the unit of electric charge. The $e^2 \to 0$ singularity was explained by Dyson [34] as being caused by the instability of Coulombic systems at unphysical (negative) values of e^2. Popov and Sergeev [22,23] used a modified version of Dyson's analysis to show that the divergence of dimensional expansions is due to the instability of the minimum of W_0 in complex coordinate space. They were able to determine the asymptotic behavior of the δ expansion for $H_2{}^+$ by calculating the rate at which the system can tunnel out of the minimum of W_0 along a complex sub-barrier trajectory. The result for $0.2 < \tilde{R} < \tilde{R}_c$ is that

$$E_k/E_{k-1} \sim \delta_0^{-1} k, \tag{24}$$

where δ_0 is a constant that depends on $\tilde{R}$ according to the equations [35]

$$\delta_0 = \zeta - \operatorname{arctanh} \zeta, \tag{25}$$

$$\zeta = (1-3\tau)^{1/2}(1-\tau)^{-1}, \tag{26}$$

$$\frac{(\tau-1)^4}{\tau} = \left[\frac{(D_{\rm ph}+\beta)(D_{\rm ph}-1)}{4\tilde{R}}\right]^2, \quad 0 < \tau < 1/3. \tag{27}$$

To better characterize the singularity at $\delta = 0$, it is convenient to consider the Borel function $F(\delta)$ that is related to $E'(\delta)$ by the transform

$$E'(\delta) = \int_0^\infty e^{-t} F(\delta t)\, dt. \tag{28}$$

The asymptotic expansion of F is $\Sigma_{k=0}^{\infty} F_k \delta^k$, where $F_k = E_k/k!$. The location of the nearest singularity to the origin in $F(\delta)$ is given by $\lim_{k\to\infty} F_{k-1}/F_k$. It follows from Eq. (24) that this singularity is at the point $\delta = \delta_0$. Numerical analysis of our calculated values for E_k indicates that $F_{k-1}/F_k \sim \delta_0(1 + \frac{3}{2} k^{-1})$, which is consistent with a square-root branch point in $F(\delta)$ at δ_0.

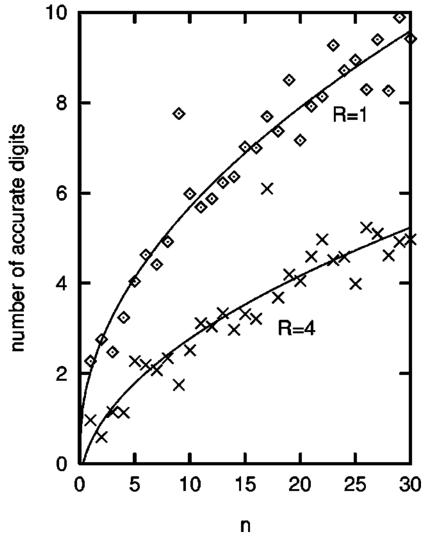

FIG. 1. Accuracy of summation approximants vs order n of the perturbation expansion for the ground-state energy of $H_2{}^+$ with $R=1$ (◇) and $R=4$ (×). The ordinate is $-\log_{10}|(E_{\rm approx} - E_{\rm exact})/E_{\rm exact}|$, which is a continuous measure of the number of accurate digits. The curves show fits according to Eq. (31).

Previously [1] we evaluated E' by numerical quadrature of Eq. (28) with Padé approximants substituted for F. Since Padé approximants are able to use combinations of poles and zeros to model square-root branch cuts, the convergence of this Padé-Borel summation is somewhat better than that obtained from evaluating E' by direct Padé summation. Here we will use an even better method. It follows from Darboux's theorem [36] that the asymptotic behavior of $F(\delta)$ will be equivalent to that of a function of the form $(1 - \delta/\delta_0)^{1/2} g + h$, where $g(\delta)$ and $h(\delta)$ are analytic for $\delta \leqslant \delta_0$. This suggests that we evaluate F using *Darboux approximants*

$$F_{[L,N/M]}(\delta) = \frac{P_L(\delta)}{Q_M(\delta)} + \frac{R_N(\delta)}{Q_M(\delta)}(1-\delta/\delta_0)^{1/2}, \tag{29}$$

where P_L, Q_M, and R_N are polynomials of degrees L, M, and N, respectively, which can be determined by solving a set of linear equations [9]. We substitute Eq. (29) into Eq. (28) and use numerical quadrature to obtain E'. Substituting this value into Eq. (19) yields a *Darboux-Borel* approximant, which we designate $S_{[L,N/M]}$. In practice we will use the diagonal staircase approximant sequence $S_{[0,0/0]}$, $S_{[0,0/1]}$, $S_{[1,0/1]}$, $S_{[1,1/1]}$, $S_{[1,1/2]}, \ldots$, denoting the elements of the sequence as S_n where $n = L+M+N+1$ is the order of the perturbation expansion.

III. NUMERICAL DEMONSTRATION

We consider two different perturbation theories for the ground-state electronic energy of $H_2{}^+$. The first uses single-well configurations at the $D\to\infty$ limit, with the electron equidistant from the nuclei. The second uses double-well configurations, with the electron closer to one nucleus than to the other.

A. Single-well expansion

According to Eq. (18), a large enough choice of the free parameter β will ensure $\tilde{R} < \tilde{R}_c$ for any value of the physical internuclear distance R. Furthermore, we find that the position δ_0 of the dominant singularity in the Borel function steadily moves away from the origin as β increases and this decreases the rate of increase of the E_k. In practice, however, for given R there is an optimal value for β beyond which the convergence of the summation approximants begins to slow. We attribute this to the β dependence of the harmonic frequencies.

Figure 1 shows the convergence of the approximant sequence S_n with $R=1$ and 4 and $D_{\rm ph}=3$. For $R=1$ we use

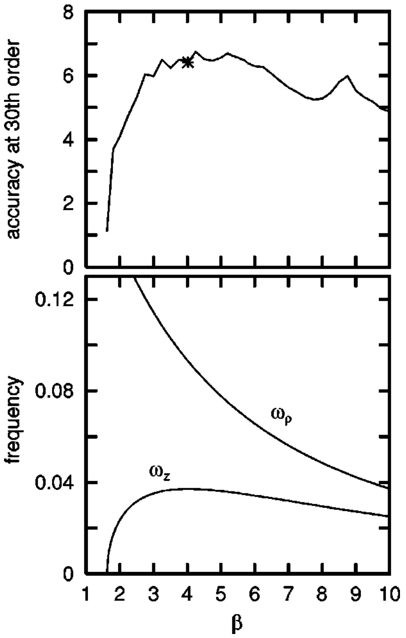

FIG. 2. Summation accuracy and large-dimensional harmonic frequencies vs the parameter β, with $R=3$. The ordinate is $\alpha(30)$, according to Eq. (31). The value of $\alpha(30)$ corresponding to the β that gives the maximum ω_z is indicated by an asterisk. The frequencies are in hartree atomic units.

$\beta=0$ and for $R=4$ we use $\beta=6.36$. In both cases the number of accurate digits as a function of order n of the perturbation expansion appears to increase according to the relation

$$\log_{10}|(S_n-E_{\text{exact}})/E_{\text{exact}}|\approx\alpha(n), \tag{30}$$

where α has the form

$$\alpha(n)=\alpha_0+\alpha_1 n^{1/2}. \tag{31}$$

The "exact" energies were obtained from Frantz's H2ION program [37], which takes advantage of the separability of the $H_2{}^+$ Hamiltonian, solving the separated differential equations using an iterative procedure [38,39].

In Fig. 2 we show the dependence of the harmonic frequencies and of the summation accuracy on the parameter β, in this case for $R=3$. As a measure of the accuracy, we use $\alpha(30)$. Using the fitted expression avoids the essentially random fluctuations that would result from showing the actual value of a given approximant. It is the antisymmetric normal mode that becomes unstable, with frequency $\omega_z=0$, when $\tilde{R}=\tilde{R}_c$, which in this case corresponds to $\beta\approx1.6$. ω_z reaches its maximum value at $\beta\approx4$ and then decreases only very slowly with increasing β. The summation accuracy behaves in a manner that is qualitatively similar to that of ω_z. There is a rapid drop in $\alpha(30)$ when ω_z approaches zero, but only a gradual decline at large β. This decline at large β is perhaps due to the decrease in ω_z and ω_ρ canceling out the beneficial effect of the slower divergence of the E_k.

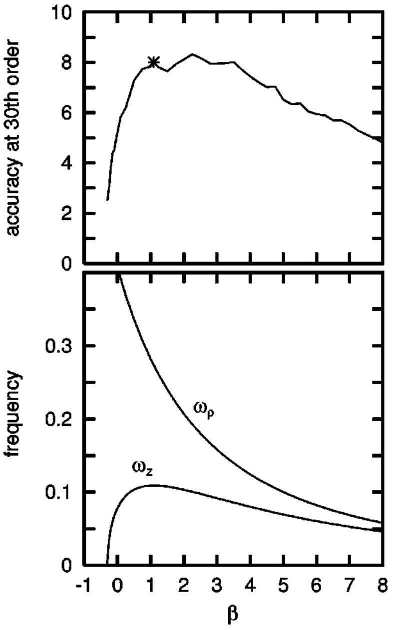

FIG. 3. Summation accuracy and large-dimensional harmonic frequencies vs the parameter β, with $R=1.75$. The ordinate is $\alpha(30)$, according to Eq. (31). The value of $\alpha(30)$ corresponding to the β that gives the maximum ω_z is indicated by an asterisk. The frequencies are in hartree atomic units.

It would seem that a safe choice for β is the value β_m corresponding to the maximum of ω_z. The explicit expression for ω_z is

$$\omega_z=2^{-1/2}\rho_m^{-2}(2\rho_m^2-\tilde{R}^2)^{1/2}(4\rho_m^2+\tilde{R}^2)^{-1/2}, \tag{32}$$

while ρ_m satisfies the equation

$$8\rho_m^4-\tilde{C}_0(\rho_m^2+\tilde{R}^2/4)^{3/2}=0. \tag{33}$$

The condition $\partial\omega_z/\partial\beta=0$ implies that

$$\tilde{C}_0=\frac{128}{(522+30\sqrt{57})^{1/2}}\tilde{R}, \quad \beta_m=\frac{\tilde{C}_0}{D_{\text{ph}}-1}-D_{\text{ph}}. \tag{34}$$

Figure 3 shows results for $R=1.75$, which is just slightly below $\tilde{R}_c$. Here the expansion for $\beta=0$ does converge, but the use of a positive β can greatly improve the convergence rate. As a general rule, we find for arbitrary R that $\beta=\beta_m$ gives very nearly the best convergence, unless $\beta_m<0$, in which case β should be set to zero.

The solid curve in Fig. 4 shows $\alpha(30)$ as a function of R. The curve was calculated using the optimal values for β (i.e., β_m or zero) and in general we determined the parameters α_0 and α_2 by least-squares fitting to the results from orders 1–30. However, for $R<1$ the convergence at very high orders is degraded by roundoff error in the E_k, which we calculated using quadruple-precision floating-point arithmetic. In the fittings we omitted any points at orders beyond that at which the accuracy of the convergence exceeds the precision of the E_k at that order. For example, at $R=0.25$ we used only the results through order 20.

B. Double-well expansion

For $\tilde{R}>\tilde{R}_c$ the large-D limit gives a pair of degenerate solutions corresponding to the two minima in the effective potential W_0. Electron exchange from tunneling between the

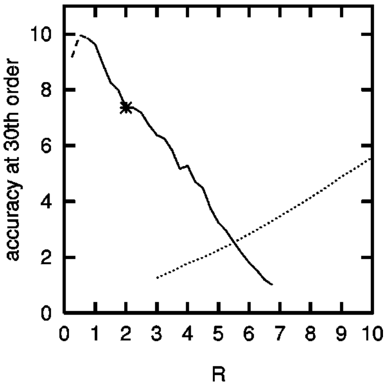

FIG. 4. Summation convergence vs internuclear distance R. The solid curve shows $\alpha(30)$, according to Eq. (31), using the single-well expansion with optimal β as described in the text. The point corresponding to the equilibrium bond distance is indicated by an asterisk. A dashed curve is used for $R<1$ because these results are estimates using a maximum order of less than 30. The dotted curve shows the accuracy of the double-well expansion, defined as $\alpha(30)$ with the exact mean energy of the lowest tunneling pair used for E_{exact} in Eq. (30).

minima gives rise to an energy splitting ΔE. Kais, Frantz, and Herschbach [18] used the instanton method to compute ΔE and derived the expression

$$\Delta E \sim 2\pi^{-1/2}(D-1)^{-1/2}\exp[-(D-1)(\tilde{R}-\ln 2\tilde{R})/2] \tag{35}$$

in the large-$\tilde{R}$ limit. In the limit $D\rightarrow\infty$ it is clear from Eq. (35) that ΔE is subdominant to the asymptotic expansion, going to zero faster than any power of δ.

The singularity structure of the energy function $E(\delta)$ is similar to that for the single-well expansion, consisting first of a second-order pole at $\delta=1$ whose residue corresponds to the solution of the $D=1$ δ-function Hamiltonian. A new complication arises, however, in the fact that the large-D limit now corresponds to the degenerate $1s\sigma_g$ and $2p\sigma_u$ tunneling pair, while for $D=1$ the $2p\sigma_u$ state is unbound for $R^{D=1}\leqslant 1$ (corresponding to $R^{D=3}\leqslant 3$ for $\beta=0$) [33]. In practice, it is found that the residue in the numerical $1/D$ series corresponds (approximately) to the $D=1$ $1s\sigma_g$ eigenvalue for small R (where the $2p\sigma_u$ state is unbound) and to the mean of the two $D=1$ eigenvalues for large R. For intermediate R, the residue lies somewhere between these two theoretical values, but we obtain adequate results by removing a second-order pole with residue $E_g^{D=1}$ when the $2p\sigma_u$ state is unbound at $D=1$ and residue $(E_g^{D=1}+E_u^{D=1})/2$ when both states are bound.

As in the single-well case, there is also an apparent square-root branch point singularity in the Borel function. Popov and Sergeev [22] have shown that its location δ_0 is given by [35]

$$\delta_0=2\left(\frac{\eta_0}{1-\eta_0^2}-\operatorname{arctanh}\,\eta_0\right), \tag{36}$$

where η_0 is the spheroidal coordinate for the frozen $D\rightarrow\infty$ geometry. This branch point agrees well with numerical estimates from the $1/D$ coefficients and we use it here in calculating Darboux-Borel approximants.

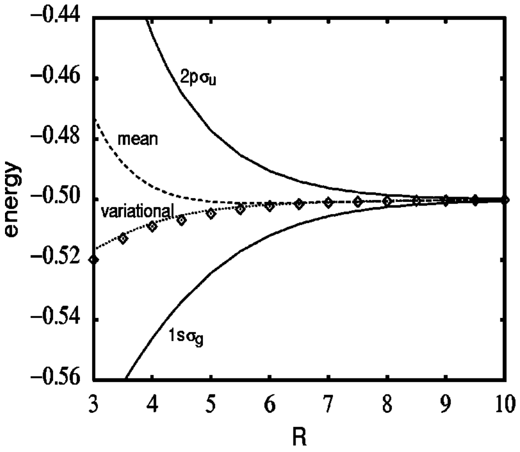

FIG. 5. $H_2{}^+$ total energies, in hartree atomic units, for the $1s\sigma_g$ and $2p\sigma_u$ states. The mean energy of these two states is shown as a dashed curve, while the dotted curve is the variational energy for a simple two-parameter wave function centered on only one of the nuclei. Points represent converged Darboux-Borel sums for the double-well $1/D$ expansion.

The energies obtained from the double-well $1/D$ expansion in this manner are shown in Fig. 5, along with the exact $1s\sigma_g$ and $2p\sigma_u$ energies and their average for comparison. It is seen that in the large-R limit, our results approach the mean energy quite accurately, but the deviation increases rapidly as R decreases.

This behavior can be understood as follows. Consider a variational wave function composed of a linear combination of atomic functions, centered on the two nuclei A and B [41]. Solving the secular equation leads to the pair of eigenvalues $E_\pm=(H_{AA}\pm H_{AB})/(1\pm S)$, where H_{AA} and H_{AB} are Hamiltonian matrix elements and $S=\langle A|B\rangle$ is the overlap integral. Since $H_{AB}<0$, the ground state is E_+. In the large-R limit, the overlap integral S vanishes and the pair of states $E_\pm$ are symmetrically split about H_{AA}. However, as A and B move closer together and S increases, the excited state E_- has a larger separation from H_{AA} than does the ground state E_+.

This phenomenon is illustrated in Fig. 5, where we also show the energy H_{AA} resulting from a simple two-parameter variational wave function comprised of hydrogenic $1s$ and $2p_z$ orbitals [42]. These energies follow (but lie slightly above) our $1/D$ results; a more complicated variational function (still centered on nucleus A) should exhibit even better agreement.

There are thus three sources of error in using the double-well $1/D$ expansion: the limited convergence of the $1/D$ series for $E(\delta)$, the limited accuracy (approximately 1–10 % in practice) of the semiclassical estimates for the energy splitting ΔE, and the complete neglect of the splitting asymmetry, which causes $E(\delta)$ to lie somewhat below than the mean energy of the tunneling pair.

We find that the Darboux-Borel approximants (or other approximants such as Padé-Borel) usually converge to one to four more digits than this splitting asymmetry, i.e., the summation is *precise* but not *accurate*, at least relative to the average of the $1s\sigma_g$ and $2p\sigma_u$ energies in Eq. (30). For this reason a scaling parameter $\beta=0$ is adequate, although in practice it also happens to yield the nearly optimal convergence. This is because the accumulation of roundoff error in the calculation of expansion coefficients is more severe for $\beta < 0$, while the branch point in the Borel function moves closer to the origin and thus has a greater dominance in the expansion coefficients for increasing $\beta > 0$. These two effects tend to worsen convergence for increasing $|\beta|$ (for both positive and negative β), resulting in the optimal parameter lying near $\beta = 0$.

For comparison with the summation accuracy of the single-well expansion, we take the difference between the converged Darboux-Borel sum and the average of the exact $1s\sigma_g$ and $2p\sigma_u$ energies. This reflects the error due to the neglect of the splitting asymmetry, which dominates any convergence difficulties. However, it neglects any errors in the calculation of ΔE, which in practice would limit the obtainable accuracy even further, to two or three digits at most using semiclassical expressions developed thus far [17]. We conclude that the accuracy at large R is at this point limited by the accuracy of the available expression for ΔE and not by the convergence of the δ expansion. The convergence at 30th order as a function of R is indicated by the dotted curve in Fig. 4.

IV. DISCUSSION

When the internuclear distance R becomes equal to the critical value $\tilde{R}_c$, the large-D effective potential W_0 undergoes a transition between a single well and a double well. In the original formulation of the dimensional scaling [12] (corresponding to setting our parameter β to zero), $\tilde{R}_c$ is equal to $9\sqrt{3}/8 \approx 1.949$. It is probably no coincidence that this value is very close to the $D=3$ equilibrium internuclear distance of 1.997. Tan and Loeser [14] have noted that $R = \tilde{R}_c$ maximizes the delocalization of electron probability between the nuclei (since W_0 flattens out in the vicinity of the minimum when $\partial^2 W_0/\partial z^2 \approx 0$) and according to an analysis of the electronic wave function by Feinberg and Ruedenberg [40], such delocalization maximizes the strength of the chemical bond. In fact, Tan and Loeser suggested using a dimensional scaling essentially equivalent to our Eq. (13) in zeroth-order DPT with β chosen to ensure that $\tilde{R} = \tilde{R}_c$. A similar approach was used in a recent study of $H_2{}^+$ without the Born-Oppenheimer approximation within first-order DPT [21].

Here, in contrast, we have shown that for *large-order* dimensional perturbation theory it is best to choose the dimensional continuation such that $\partial^2 W_0/\partial z^2$ is *maximized*, even though this gives a less accurate low-order theory. Our approach has much in common with various ''renormalized'' large-order perturbation theories that have been developed for anharmonic oscillators and for atoms [43–47]. For example, Killingbeck [43] showed that a summable large-order expansion could be obtained by partitioning the potential of a double-well anharmonic oscillator so that the zeroth-order limit corresponded to a single-well harmonic oscillator. A similar approach has been used [47] to calculate a large-order $1/D$ expansion for the ground-state energy of H^-. That system dissociates in the conventional large-D limit and a simple charge-renormalization procedure gave a stable large-D limit and a summable large-order expansion.

For $H_2{}^+$ we have carried out the renormalization through a coordinate scaling. (We initially attempted to treat this system using charge renormalization, but found that the convergence was very poor.) Coordinate scaling is a popular approach for renormalizing perturbation theories in which the Hamiltonian consists of operators that are homogeneous with different degrees [44–46]. Within the Born-Oppenheimer approximation the electron-nucleus potentials in molecular Hamiltonians are inhomogeneous and this leads to unphysical zeroth-order limits. We avoid this problem by replacing the scaled internuclear distance with a D-independent parameter that is numerically equal to the scaled parameter at $D=3$. Thus the renormalization of diatomic molecular Hamiltonians is essentially equivalent to a rescaling of the internuclear distance.

Our criterion for setting the renormalization parameter β is different. The usual approach [43,46] has been to use a variational principle to determine the optimal parameter value. Our choice of β so as to maximize the antisymmetric frequency ω_z is supported by the striking resemblance between the plots of ω_z and of the summation accuracies versus β in Figs. 2 and 3.

Dimensional perturbation theory appears to be a promising approach for describing many-electron effects such as electron correlation [48] and London dispersion forces [49]. Although we have formulated our theory for diatomic molecules with an arbitrary number of electrons, we have presented results only for the one-electron case $H_2{}^+$. Until recently, large-order $1/D$ expansions had only been calculated for problems with at most three degrees of freedom. However, such calculations with at least six degrees of freedom are now feasible using the linear algebraic algorithm of Dunn *et al.* [7]. Systems with more degrees of freedom can in principle be treated using a related algorithm that incorporates separability assumptions [50]. Many-electron molecules also undergo a symmetry-breaking transition as R ranges from the single-well united atom limit to the double-well separated atom limit. Therefore, we expect that our renormalization procedure will still be applicable. It is possible that the most straightforward dimensional continuation of the Hamiltonian, as developed in Ref. [14], will not be an appropriate starting point for a large-order perturbation expansion for molecules with more than two electrons due to the fact that at large-D there are internal coordinates that become redundant at $D=3$. In that case it would be necessary to use an alternative definition for the D-dimensional Hamiltonian without redundant coordinates to ensure that the energy expansion converges to the physical solution.

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