$1/R$ Expansion for H_2^+: Analyticity, Summability, Asymptotics, and Calculation of Exponentially Small Terms

Robert J. Damburg and Rafail Kh. Propin
Institute of Physics, Latvian Academy of Sciences, Riga, Salaspils, U.S.S.R.

and

Sandro Graffi
Dipartimento di Matematica, Università di Bologna, 40127 Bologna, Italy

and

Vincenzo Grecchi
Dipartimento di Matematica, Università di Modena, 41100 Modena, Italy

and

Evans M. Harrell, II
Department of Mathematics, Georgia Institute of Technology, Atlanta, Georgia 30332

and

Jiří Čížek and Josef Paldus
Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

and

Harris J. Silverstone
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218
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The $1/R$ perturbation series for H_2^+ has a complex Borel sum whose imaginary part determines the asymptotics of the perturbed energy coefficients $E^{(N)}$. The full asymptotic expansion for the energy includes complex, exponentially small terms:

$$E(R) \sim \sum E^{(N)}(2R)^{-N} + e^{-R/n}\sum a^{(N)}(2R)^{-N} + e^{-2R/n}\left[\sum d^{(N)}(2R)^{-N} + \log R \text{ terms}\right] \pm ie^{-2R/n}\sum c^{(N)}(2R)^{-N} + \dots .$$

The explicit imaginary terms cancel the implicit imaginary part of the Borel sum. An exact relation between the double-well gap series, $\exp(-R/n)\sum a^{(N)}(2R)^{-N}$, and the $i\exp(-2R/n)$ series is derived.

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This paper concerns the expansion[1,2] of the energy levels of the hydrogen molecular ion H_2^+, in inverse powers of twice the internuclear distance, $2R$. A standard textbook example of Rayleigh-Schrödinger perturbation theory (RSPT), H_2^+ displays not only all the subtle complications of the anharmonic oscillator, Zeeman effect, and LoSurdo-Stark effect,[3,4] but several surprising new ones.

The Hamiltonian for H_2^+ in atomic units is $H = -\frac{1}{2}\nabla^2 - |\vec{x}|^{-1} - |\vec{x}-\vec{R}|^{-1}$, where R is the internuclear distance. As $R \to \infty$, the bound states of H_2^+ converge to those of the hydrogen atom and admit the RSPT $1/2R$ series as an asymptotic expansion to all orders.[1,2,5,6] There are, however, the following known complications:

(1) The perturbation series diverges.[2,7-12]

(2) Since H_2^+ is a symmetric double well, its bound states are asymptotically doubly degenerate as $R \to \infty$, the gap being $O(\exp(-R/n))$.[13]

(3) All the terms in the ground-state perturbation expansion after the first few have the same sign (which may be general for double wells)[3,14]; thus the Borel sum (if it exists) is complex, and its relation to the original problem needs clarification.

(4) An approximate formula relating the rate of divergence of the RSPT series to the gap has been discovered numerically by Brézin and Zinn-Justin[15] (BZJ). The divergence rates for the anharmonic oscillator and the LoSurdo-Stark effect have been understood rigorously through the Borel summability[12,16] of the perturbation theory and dispersion relations.[7,9,11,17-19] However, H_2^+ is not directly Borel summable [(3) above].

Our main goals are a mathematical understanding of the Borel sum of the RSPT series and of its relevance to the asymptotics of the series; the systematic determination of the full $1/2R$ expansion including complex exponentially small contributions; and the derivation of the asymptotics of the RSPT series for which the BZJ formula is a first approximation.

To begin qualitatively, we note first that the ground-state RSPT series would have alternating signs if R were negative. In fact, the (physically interpretable) Hamiltonian, $K=-\frac{1}{2}\nabla^2-|\vec{x}|^{-1}+|\vec{x}+\vec{R}|^{-1}$, has the RSPT energy expansion $\sum E^{(N)}(-1)^N(2R)^{-N}$, where the $E^{(N)}$ come from the corresponding RSPT series for H_2^+, $E(R)\sim\sum E^{(N)}(2R)^{-N}$. Unlike the double-well oscillator,[20] and contrary to general expectation,[2] it turns out that *the Borel sum of the* H_2^+ *series for negative* R *is not even an eigenvalue of* K*, which is a stable, single-well problem.*[21] To understand the Borel sum, it is necessary to consider both Hamiltonians H and K simultaneously. Their perturbation theories are subtly interconnected.

We note second that the full asymptotic expansion for the energy, which we derive by a modified semiclassical technique,[22] has the form

$$E(R)\sim\sum E^{(N)}(2R)^{-N}+e^{-R/n}\sum a^{(N)}(2R)^{-N}+e^{-2R/n}\left[\sum d^{(N)}(2R)^{-N}+\log R\text{ terms}\right]\pm ie^{-2R/n}\sum c^{(N)}(2R)^{-N}+\dots,\qquad(1)$$

where R is taken as $R\pm i0$, and n is the principal quantum number. We find a remarkable result; that the "sum" of this explicitly complex expansion is real and continuous for R positive, because the imaginary part of the Borel sum of the RSPT series cancels the explicit imaginary series through order $\exp(-2R/n)$.

To continue more precisely, we first reformulate in scaled elliptic coordinates. The Schrödinger equation for H is equivalent to two coupled ordinary differential equations (o.d.e.'s) [$m=0,1,2\dots$ corresponds to $\exp(\pm im\phi)$]:

$$\left[-\frac{d^2}{dx_1^2}+\frac{1}{4}-\frac{\beta_1}{x_1}+\frac{m^2-1}{4x_1^2}+V_1(x_1,\beta_1+2\beta_2,r)\right]\Psi_1(x_1)=0,\qquad(2)$$

$$\left[-\frac{d^2}{dx_2^2}+\frac{1}{4}-\frac{\beta_2}{x_2}+\frac{m^2-1}{4x_2^2}+V_2(x_2,\beta_2,r)\right]\Psi_2(x_2)=0,\qquad(3)$$

where V_1 and V_2 are

$$V_1(x_1,\beta_1+2\beta_2,r)=-\frac{\beta_1+2\beta_2}{x_1+2r}+\frac{m^2-1}{4}\left[\frac{1}{(x_1+2r)^2}-\frac{2}{x_1(x_1+2r)}\right],\qquad(4)$$

$$V_2(x_2,\beta_2,r)=-\frac{\beta_2}{2r-x_2}+\frac{m^2-1}{4}\left[\frac{1}{(2r-x_2)^2}+\frac{2}{x_2(2r-x_2)}\right].\qquad(5)$$

Here $E=-\frac{1}{2}\gamma^{-2}$, $r=R/\gamma$, $\gamma=\beta_1+\beta_2$, $0\le x_1=r(\xi-1)<\infty$, $0\le x_2=r(\eta+1)\le 2r$. The usual elliptical coordinates are $1\le\xi<\infty$, $-1\le\eta\le 1$, and $0\le\phi<2\pi$. The boundary conditions are $\Psi_1(x_1)=O(x_1^{(m+1)/2})$ at zero, $\Psi_2(x_2)=O(x_2^{(m+1)/2})$ at zero, and $\Psi_2(x_2)=O((2r-x_2)^{(m+1)/2})$ at $2r$.

Although Eqs. (2) and (3) can be cast as eigenvalue equations for the separation constants β_1 and β_2,[22,23] it is more convenient *for proving analyticity and summability* to proceed as follows: Let $\lambda(\beta_1+2\beta_2,r)$ and $\mu(\beta_2,r)$ be the eigenvalues of the operators on the left-hand sides of Eqs. (2) and (3). Then $\beta_2=\beta_2(r)$ is defined implicitly by $\mu(\beta_2,r)=0$. In turn $\beta_1(r)$ is determined by $\lambda(\beta_1+2\beta_2(r),r)=0$. Then $r=f(R)$ is the inverse function of $R=r\gamma(r)$, so that $E(R)=-\frac{1}{2}[\gamma(f(R))]^{-2}$.

We get similar equations for the K problem, but instead of (4) and (5) (primes distinguish K from H)

$$V_1'(x_1,\beta_1',r')=+\frac{\beta_1'}{x_1+2r'}+\frac{m^2-1}{4}\left[\frac{1}{(x_1+2r')^2}-\frac{2}{x_1(x_1+2r')}\right],\qquad(6)$$

$$V_2'(x_2,\beta_1'+2\beta_2',r')=+\frac{2\beta_1'+\beta_2'}{2r'-x_2}+\frac{m^2-1}{4}\left[\frac{1}{(2r'-x_2)^2}+\frac{2}{x_2(2r'-x_2)}\right].\qquad(7)$$

Then $E'(R')=-\frac{1}{2}[\gamma'(f'(R'))]^{-2}$, where $R'=R\exp(\pm i\pi)$, and the other primed variables have their obvious meaning, e.g., $\gamma'(r')=\beta_1'+\beta_2'$. The boundary conditions are as for H.

Our main results are two rigorous propositions about summability and analyticity, and the quasisemiclassically obtained expansion (1). Details will appear later.[23]

Proposition 1.— (i) The perturbation series for β_2 is Borel summable not to $\beta_2(r)$, but to $\beta_1'(re^{-i\pi})$, the continuation (see below) of $\beta_1'(r')$ up to $r'=re^{-i\pi}$ $(r>0)$. [If the continuation is counterclockwise, the sum is $\beta_1'(re^{+i\pi})$.] (ii) The perturbation series for β_1 is Borel summable to $\beta_1(r,\beta_1'(re^{-i\pi}))$, i.e., the solution of $\lambda(\beta_1+2\beta_1'(re^{-i\pi}),r)=0$. (iii) The perturbation series for γ is summable not to $\gamma(r)$, but to $\gamma''(r)=\beta_1(r,\beta_1'(r^{-i\pi}))+\beta_1'(re^{-i\pi})$; therefore the $1/2R$ expansion for E is Borel summable not to $E(R)$ but to $E''(R)=-\frac{1}{2}[\gamma''(f''(R))]^{-2}$, where $f''(R)$ is the inverse function of $R=r\gamma''(r)$. Similar statements apply to K.

Proposition 2.— (i) The function $\beta_1'(r')$ is analytic for r' in $D_1=\{\infty>|r'|>M,\ |\arg r'|<3\pi/2$, cut on the negative r' axis$\}$, and continuous as $|r'|\to\infty$ within D_1. The function $\beta_1(r,\beta_1'(re^{-i\pi}))$ is analytic in the sector $D_2=\{\infty>|r|>M,\ -\pi/2<\arg r<3\pi/2$, cut along the entire real axis$\}$, and continuous as $|r|\to\infty$ in D_2. The same is true for $E''(R)$. (ii) As $r\to\infty$, $\mathrm{Im}\gamma''(r)\sim\pi a^{-2}(2r)^{4b}\times e^{-2r}$, where $b=\beta_2(\infty)=n_2+(m+1)/2$, and $a=n_2!(n_2+m)!$. If $\mathrm{Im}E''$ is the imaginary part of the Borel sum, then

$$\mathrm{Im}E''\sim\pi n^{-3}a^{-2}(2R/n)^{4b}\exp(-2R/n-2n),$$

where $n=n_1+n_2+m+1$, n_1 and n_2 being parabolic quantum numbers. (iii) We have

$$E^{(N)}=-\pi^{-1}\Big(\int_{-\infty}^{-\epsilon}+\int_{\epsilon}^{\infty}\Big)dx\,\mathrm{Im}E''(x)x^{N-1}+O(\epsilon^N)\sim-n^{N-3}a^{-2}e^{-2n}(N+4n_2+2m+1)!.$$

Proposition 3.— (i) Any eigenvalue $E(R)$ of H_2^+ admits the expansion (1) as $R\to\infty$. (ii) We have

$$\mathrm{Im}E''(R)=\mp e^{-2R/n}\sum(2R)^{-N}c^{(N)}$$

[note the sign, which makes the "sum" of (1) real and continuous on $R>0$]. (iii) We have

$$\mathrm{Im}\beta_1'(re^{-i\pi})=\pi(\Delta\beta_2)^2/q(r)+O(e^{-3r}),$$

where $2\Delta\beta_2$ is the double-well gap from Eq. (3), and $q(r)$ has an explicit $1/2r$ expansion computable directly from RSPT.

Outline of the proof of Propositions 1 and 2.[23] —Consider first the K version of Eq. (2) for $|\arg r'|<\pi$. The operator on the left is a real holomorphic family (of type A) of m-sectorial operators[24] $T_1(r',\beta_1')$ in $L^2(0,\infty)$, for $|\arg r'|<\pi$ and $\beta_1'\in C$, if defined on domain $H^2(0,\infty)$ with the boundary condition at 0. Any eigenvalue $\lambda'(r_1',\beta')$ is thus locally holomorphic in (r_1',β') in that region. By complex scaling,[25] one sees that λ' is actually locally holomorphic in the region $|\arg r'|<3\pi/2$ cut along the negative real axis and $\beta_1'\in C$. Since $|V_1'(e^{\theta}x_1,\beta_1',r')|$ tends to zero uniformly with respect to (θ,β_1') as $|r'|\to\infty$, it can be shown that the resolvent of $T_1(r',\beta_1')$ converges in norm to the unperturbed resolvent as $|r'|\to\infty$, provided that $|\arg r'|<3\pi/2$, $|\mathrm{Im}\theta|<\pi/2$, $\mathrm{Im}\theta\neq-\arg r'$. Therefore, as is well known,[24] $\lambda'(r',\beta_1')$ is analytic in (r',β_1') for r' in D_1, locally in β_1', and continuous as $|r'|\to\infty$. Given the analyticity in D_1, it can be proved by modifying the Morgan-Simon argument[2] that the perturbation expansion is strongly asymptotic[25] to $\lambda'(r',\beta_1')$ uniformly in β_1'. By the Watson-Nevanlinna theorem,[26] this implies summability to $\lambda'(r',\beta_1')$ in $|\arg r'|<\frac{3}{2}\pi-\epsilon$, $|r'|<B$, for some $B>0$. Now it can be verified that $\partial\lambda'(r',\beta_1')/\partial\beta_1'\neq0$ for β_1' near $\beta_1'(\infty)=n_2+(m+1)/2$ and r' in D_1. Hence, by the analytic implicit function theorem, the function $\beta_1'=\beta_1'(r')$ exists and is analytic in D_1, and it can also be verified that its perturbation expansion is Borel summable in D_1. Now, for $\arg r'=-\pi$, i.e., $r'=re^{-i\pi}$, $r>0$, and for all suitable β, the perturbation series of $\lambda'(r',\beta)$ coincides with that of $\mu(r,\beta)$. Therefore the Borel sum of the perturbation series for $\beta_2(r)$ is the function defined by $\lambda'(r',\beta)=0$, i.e., $\beta_1'(re^{-i\pi})$. Proposition 1 and assertions (i) and (ii) of Proposition 2 follow from a similar argument for Eq. (2). Now by Proposition 2 (ii), a standard approximate dispersion-relation argument,[3,11] and the Cauchy formula, we can write

$$\beta_2^{(N)}=\pi^{-1}\int_{\epsilon}^{\infty}r^{N-1}\,\mathrm{Im}\beta_1'(re^{-i\pi})\,dr+O(\epsilon^N).$$

Then by o.d.e. arguments typical of these problems,[13,27] it is seen that as $r\to\infty$,

$$\mathrm{Im}\beta_1'(re^{-i\pi})\sim\pi a^{-2}(2r)^{4b}e^{-2r}.$$

Similarly, $\mathrm{Im}\beta_1(r,\beta_1'(re^{-i\pi}))\sim\mathrm{Im}\beta_1'(re^{-i\pi})/r$, clinching Proposition 2(ii). Proposition 2(iii) then follows by an easy inversion.

Outline of the quasisemiclassical method.[22,23] —Consider first Eq. (3) in the rescaled variable $\eta=x_2/r-1$. We develop a recursive, perturbative, multistep procedure for the wave function, based in part on the Langer-Cherry refinement[28] of the JWKB method.[22]

Step 1.—Near $\eta=0$, Eq. (3) is Whittaker's equation. We put the solutions in the form $\Psi = (m!)^{-1}(d\phi/d\eta)^{-1/2}M_{b,m/2}(r\phi)$, where ϕ satisfies a Riccati equation, and $b = \beta_2(\infty) + \Delta b(r)$. The "index shift" $\Delta b(r)$ turns out to be $O(\exp(-r))$.

Step 2.—We develop ϕ in the form

$$\phi \sim \sum \phi^{(N)}(\eta)(2r)^{-N} + r^{-1}\Delta b \sum \theta^{(N)}(2r)^{-N}.$$

The boundary condition at 0 fixes both $\phi^{(N)}$ and the RSPT coefficients $\beta_2^{(N)}$. The boundary condition at $\eta = 2$ is then sufficient to determine the index shift Δb through $O(\exp(-r))$. The requirement that the Riccati equation be satisfied through $O(\exp(-r))$ then determines the $\theta^{(N)}$ (recursively) and also the ratio $q(r)$ of the double-well half-gap $\Delta\beta$ to Δb as an expansion in $1/2r$.

Step 3.—The same approach can be carried out to any order in $\exp(-r)$. There is in second exponential order an explicit imaginary contribution to β_2, which arises in a simple way from the asymptotics of the Whittaker M function. The imaginary series is the square of the real series of $O(\exp(-r))$ for the gap, divided by the series $q(r)$ in Step 2. This justifies the BZJ formula..

Step 4.—the same procedure is then applied to the K Hamiltonian Eq. (11) to get an expansion for $\beta_1'(re^{-i\pi})$. For argument $-(\pi - \epsilon)$, the expansion turns out to be the $1/2r$ series (whose Borel sum is β_1'). For argument $-(\pi + \epsilon)$, there is an additional imaginary series proportional to e^{-2r}. Since the Borel sum has a cut on the real axis where the imaginary part changes sign, while β_1' has a (continuous) direct analytic continuation, the imaginary series represents twice the imaginary part of the Borel sum $\beta_1'(re^{-i(\pi-0)})$; it is also -2 times the series of Step 3. Thus the imaginary series of Step 3 provides the counterterms that cancel the imaginary part of the Borel sum of the RSPT series for $\beta_2(r)$.

Step 5.—Analogously, we find an imaginary series for the discontinuity of $\beta_1(r, \beta_1'(re^{-i\pi}))$ on the negative r axis. It contains $\log r$ terms, which lead to $\log N$ terms in the asymptotics of the $\beta_1^{(N)}$ and $E^{(N)}$ (cf. $\log R$ for R small[29]).

Step 6.—Elementary algebraic operations turn results for $\beta_1 + \beta_2$ into results for $E(R)$.

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