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The inverse boundary value problem – application in many-body perturbation theory

Péter R. Surján · Zsuzsanna É. Mihálka · Ágnes Szabados

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Abstract An algorithm is discussed to find boundary values to partial differential equations in the knowledge of the solution of that equation inside a part of the domain enclosed by the boundary. The method is used as a tool of analytic continuation to complement a method proposed recently (Mihálka and Surján, *Phys. Rev. A.* 96, 062106, 2017) for finding resummed values of divergent perturbation series.

Keywords partial differential equation · boundary value problem · Rayleigh Schrödinger perturbation theory · resummation of divergent series · Møller-Plesset partitioning

1 Introduction

In a recent paper [1], we introduced an *a posteriori* scaling of individual terms $E^{(n)}$ of a series

$$E(z) \;=\; \sum_{n=0}^{\infty} z^n E^{(n)}, \tag{1}$$

Péter R. Surján, Ágnes Szabados

Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, H-1518 Budapest 112, P.O.B. 32, Hungary

E-mail: surjan@chem.elte.hu, szabados@chem.elte.hu

Zsuzsanna É. Mihálka

Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, and Doctoral School of Chemistry, ELTE Eötvös Loránd University, H-1518 Budapest 112, P.O.B. 32, Hungary

E-mail: mihalka@coulson.chem.elte.hu

which for $z = 1$ recovers the original (eventually divergent) series, but for $|z| < |z_0|$ produces a convergent one if $|z_0|$ is the radius of convergence. $E^{(0)}$ is identified as the eigenvalue of H^0, and $E^{(n)}$ denotes the n-th order contribution to $E(z = 1)$. In applications to theoretical chemistry, terms $E^{(n)}$ can be resulted from a perturbation theory (PT) calculation e.g., for the correlation energy in the Møller-Plesset (MP) partitioning. Perturbation parameter z is only a formal tool in such calculations, usually set equal to 1. In the present context it is explicitly used as a scaling parameter to generate the sum $E(z)$ within the convergent domain.

The idea followed in Ref.[1] was based on function $E(z)$ being analytic along a path from a point z (with $|z| < |z_0|$) to the point $z = 1$. In such a case analytic continuation techniques can be used to extrapolate the values $E(z)$ in the "trusted region" (i.e., for $|z| < |z_0|$) to $z = 1$ which is the point of physical interest.

So far we have used simple extrapolation procedures via fitting by polynomials or Padé approximants as analytic continuation tools. In this work, we investigate a more sophisticated technique that utilizes some mathematical properties of analytic functions. The procedure can be applied to regularize divergent perturbation series that often emerge when calculating electron correlation energy with the Hartree-Fock reference state in the MP partitioning.

2 The background problem: convergence issues in PT

Consider the Hamiltonian split into a zero order part H^0 and a perturbation W as

$$H(z) \;=\; H^0 \;+\; z\, W, \tag{2}$$

where the scaling parameter z is, in general, a complex number with $z = 1$ corresponding to the physical situation. The eigenproblem

$$H(z)\, \Psi(z) \;=\; E(z)\, \Psi(z) \tag{3}$$

implies that both the eigenvectors $\Psi(z)$ and the eigenvalues $E(z)$ are z-dependent. Applying Rayleigh-Schrödinger PT (see, e.g., Ref.[2]) one expands $E(z)$ into an infinite power series according to Eq.(1).

Permitting complex values for z opens a possibility for a mathematical analysis to investigate convergence issues. If the complex function $E(z)$ is analytic, i.e., free from any singularities in a disk $|z| < |z_0|$

on the complex $z = x + iy$ plane, then $E(z)$ can be expanded into a convergent power series for any values z on this disk. Therefore, the convergence radius of PT, $|z_0|$, is determined by the location of the singularity of $E(z)$ closest to the origin. Such analyses were systematically applied by Goodson[3], who proposed to locate the singularities (which are typically branchings when $E(z)$ is obtained from a secular equation of $H(z)$) by fitting quadratic Padé approximants to the $E^{(n)}$ values. In Ref.[1], we emphasized that values $E(z)$ can be obtained at no further cost once the PT contributions $E^{(n)}$ are available, by scaling the n-th order term by z^n *a posteriori*, cf. Eq.(1). The estimation for the convergence radius $|z_0|$ is given by the largest modulus $|z|$ for which the scaled sum is convergent.

3 Analytic continuation and the Laplace equation

Assume we have selected many points z in the trusted region ($|z| < |z_0|$) in which the scaled values $E(z)$ of Eq.(1) are thus available, including complex values of z. The $E(z)$ values, although obtained from scaling the terms of a divergent series $E^{(n)}$, represent well the analytic function $E(z)$ to a desired numerical accuracy. We consider the case when the true function $E(z)$ has no singularity from the right of the trusted region (the case of back-door intruders, see. e.g. [4]). The case of front-door intruders will be mentioned later.

Let us decompose $E(z)$ to its the real ($u(z) = u(x, y)$) and imaginary ($v(z) = v(x, y)$) parts ($z = x + iy$):

$$E(z) \;=\; u(x, y) \;+\; i\; v(x, y). \tag{4}$$

If the function $E(z)$ is analytic in the domain of interest, both $u(x, y)$ and $v(x, y)$ are harmonic functions[5] satisfying the two-dimensional Laplace equations

$$\Delta u \;=\; 0 \;\text{ and }\; \Delta v \;=\; 0. \tag{5}$$

The Laplace equation is known to have a unique solution within a closed domain if the values of the solution are available along the boundary of that domain[6].

The present situation is illustrated schematically in Fig.1. We have determined $|z_0|$ by the above scaling procedure, which marks the trusted region (the inner disc in gray in the Figure). The arrow on the Figure from the trusted region to $z = 1$ simply indicates that we aim to perform an analytic

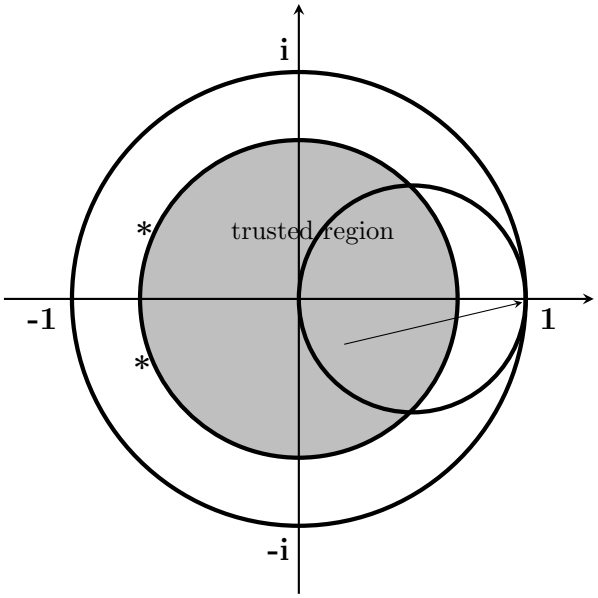

Fig. 1 Scheme for analytic continuation. The asterisks indicate singularities of $E(z)$, the gray disc shows the trusted region. The smallest, off-centered circle, referred to as the working region, whose perimeter intentionally embeds the point $z = 1$, represents the boundary within which the Laplace equation is solved.

continuation of $E(z)$ from the trusted region to the point of physical interest. For this aim, we investigate the following procedure.

A new closed boundary is marked on the complex plane with a substantial overlap with the trusted region in a way that its boundary passes through the point $z = 1$. This domain is symbolized by the smaller off-centered circle in Fig.1. In case we knew the values of $u(x, y)$ all along the boundary of this domain, values of $u(x, y)$ could be determined inside the domain from the Laplace equation (5). In the present case, however, we only know $u(x, y) = Re\{(E(z)\}$ in a part of the area enclosed in the boundary, i.e., for all x, y within the shaded region, but we do not know $u(x, y)$ along the boundary outside the trusted region.

Finding the missing boundary values can be called as the *inverse boundary value problem.*

Practically, we set up the following procedure:

1. find the trusted region by scaling the PT terms by z^n
2. draw a closed domain (hereafter: the working domain) including many points in the trusted region and its boundary passing through $z = 1$ (the shape needs not be a circle)

3. initialize the unknown boundary values, e.g., by some extrapolation procedure
4. solve the Laplace equation numerically inside the boundary
5. calculate a measure of the error as a root-mean-square difference between the computed and known values of $u(x, y)$ for all x, y points in the overlap of the trusted region and the working domain
6. optimize the unknown (initialized) boundary values by minimizing the above error.

Once this procedure is carried out until convergence, we have an estimation for the boundary values of the working domain, including the point $(x, y) = (1, 0)$ which is of our interest. As an eigenvalue of a Hermitean operator, $E(z)$ is real for real z, thus $E(z = 1) = u(1, 0)$ is the estimation of the true eigenvalue of $H(z = 1)$, that is, a resummation of the original, eventually divergent, PT series.

The above procedure can be repeated for the imaginary part $v(x, y)$ and the satisfaction of the Cauchy-Riemann equations can also be checked. This is merely for control purposes, since $v(x, y) = 0$ on the real axis thus it has no contribution to the physical energy E(1).

Utilization of the Laplace equation as a tool of analytic continuation has been previously proposed in Ref.[7] in a quite different context. In that approach the solution of the Laplace equation is approximated as a linear combination of logarithmic functions (recall that $-\frac{1}{2\pi}\log(r)$ is the fundamental solution of the Laplace equation in two dimensions).

The case of a front-door intruder has to be mentioned. In this situation the branching points closest to the origin, whose location determines a convergence radius, appear at the right of the trusted domain. In order to apply the present procedure, one has to more carefully devise the working domain in which the Laplace equation is to be solved, to avoid the singularities.

4 Numerical example

As a preliminary numerical illustration, we consider the case of the symmetrically stretched water molecule in the 6-31G* basis set[8] at $R(OH)$ being 2.25 times of the Hartree-Fock equilibrium distance. At this geometry, the Møller-Plesset PT is divergent for this system. The large order results are illustrated in Fig. 2, exhibiting also a few low-order results, the exact (frozen core) full configuration interaction (FCI) level, as well as the value we obtained from the present Laplace-equation-based analytic continuation

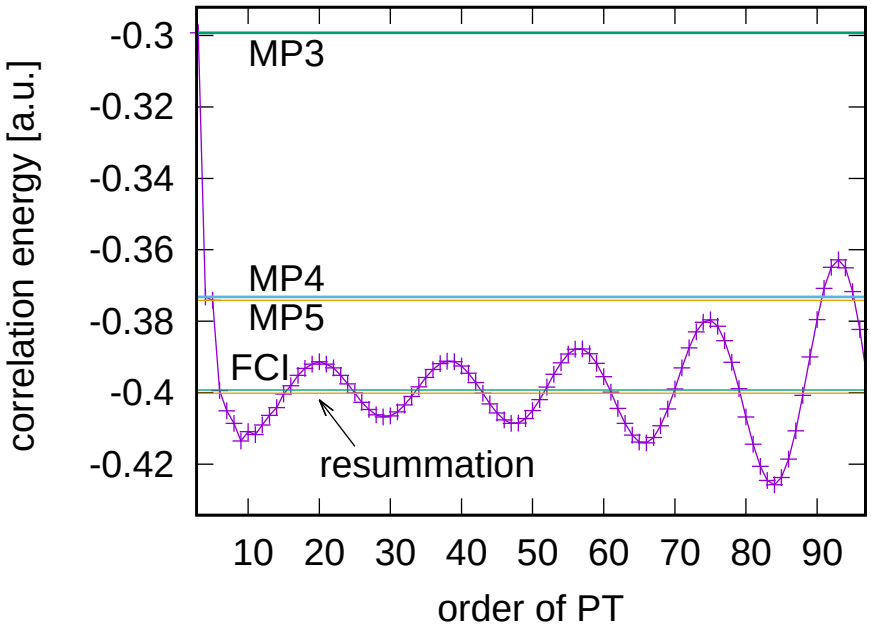

Fig. 2 Convergence pattern of the MP perturbation series for the correlation energy for the water molecule at 2.25 equilibrium distance. A few low-order results are marked with horizontal lines, as well as the exact (FCI) level and the estimation obtained by the present Laplace-equation-based analytic continuation resummation method

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Table 1 Correlation energy and energy error (deviation from the FCI energies) of the symmetrically stretched water molecule at various orders of MP PT and their resummed value [a.u.]

method	E_{corr}	energy error
MP2	-0.299483	0.099773
MP3	-0.299209	0.100047
MP4	-0.373205	0.026051
MP5	-0.374127	0.025129
AnalCont	-0.400171	-0.000915
FCI	-0.399256	0.0

technique. To illustrate the results by numbers, the low-order MP results as well as the resummed value for the electron correlation energy are also collected in Table 1.

Boundary values, following the recipe described in the previous Section, were iteratively determined with stopping the iteration at a root-mean-square error of $1.41002 \cdot 10^{-4}$. The grid size for solving the Laplace equation was $1.000 \cdot 10^{-2}$ in the direction of the x axis, and $9.804 \cdot 10^{-4}$ in the direction of the y axis.

The message of the figure and the table is clear. The MPn series is divergent, and the error of low-order results is quite large. The MP6 value is accidentally quite close to full CI, but after that heavily divergent oscillatory pattern is seen. Using these divergent numbers in the scaling procedure, and performing their resummation by analytic continuation using the Laplace-equation, we obtain the resummed value whose error is less than a millihartree. Since this value is obtained from a numerical procedure, it is not necessarily an upper bound, and in the case investigated here, the resummed energy is slightly below FCI.

The technique described in this paper is appropriate for testing rather than being practical, since large-order PT results were admitted to enter the scaling procedure. In the future, it has to be investigated what can be done if only low-order results are available. Work in this line is in progress.

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