

Application of the Cauchy integral formula as a tool of analytic continuation for the resummation of divergent perturbation series

Cite as: J. Chem. Phys. **150**, 031101 (2019); <https://doi.org/10.1063/1.5083191>

Submitted: 29 November 2018 . Accepted: 04 January 2019 . Published Online: 16 January 2019

Zsuzsanna É. Mihálka, Ágnes Szabados , and Péter R. Surján 



View Online



Export Citation



CrossMark

PHYSICS TODAY
WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY
 **MASTERBOND**
ADHESIVES | SEALANTS | COATINGS



Application of the Cauchy integral formula as a tool of analytic continuation for the resummation of divergent perturbation series

Cite as: J. Chem. Phys. 150, 031101 (2019); doi: 10.1063/1.5083191

Submitted: 29 November 2018 • Accepted: 4 January 2019 •

Published Online: 16 January 2019



View Online



Export Citation



CrossMark

Zsuzsanna É. Mihálka,^{1,2} Ágnes Szabados,¹  and Péter R. Surján^{1,a)} 

AFFILIATIONS

¹Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, 112, P.O. Box 32, H-1518 Budapest, Hungary

²George Hevesy Doctoral School of Chemistry, ELTE Eötvös Loránd University, 112, P.O. Box 32, H-1518 Budapest, Hungary

^{a)}Electronic mail: surjan@chem.elte.hu

ABSTRACT

Previous attempts to the resummation of divergent power series by means of analytic continuation are improved applying the Cauchy integral formula for complex functions. The idea is tested on divergent Møller-Plesset perturbation expansions of the electron correlation energy. In particular, the potential curve of the LiH molecule is computed from single reference MPn results which are divergent for bond distances larger than 3.6 Å. Preliminary results for the Hartree-Fock molecule are also tabulated.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5083191>

I. INTRODUCTION

The Cauchy integral formula¹

$$\oint \frac{E(z)}{z - z_1} dz = 2\pi i E(z_1) \quad (1)$$

for a complex function $E(z)$ which is analytic on and inside the boundary of the integration contour connects the values $E(z)$ on the contour to the values $E(z_1)$ inside the contour. In that sense, it can be applied as a tool for analytic continuation.

In perturbation theory,² one may consider the non-Hermitian eigenvalue problem

$$H(z)\Psi(z) = (H^0 + zW)\Psi(z) = E(z)\Psi(z), \quad (2)$$

where z is a complex perturbation parameter, the physical situation corresponding to the value $z = 1$. Rayleigh-Schrödinger perturbation theory (RSPT) consists of expanding the complex function $E(z)$ in Taylor series in terms of z . This power series will be convergent for those values z whose modulus is smaller than the convergence radius $|z_0|$. In the domain $|z| < |z_0|$, the

function $E(z)$ is analytic.¹ The convergence radius is determined by the location of the singularity of $E(z)$ closest to the origin. In problems of chemical physics, the singularities are typically branching points appearing in complex conjugated pairs (z_0, z_0^*) (see Fig. 1).

Quantum chemical applications of RSPT in the Møller-Plesset (MP) partitioning, when the Fockian is chosen as the zero order Hamiltonian, aim to approach the total energy treating electron correlation as a perturbation. These calculations, especially when performed in large basis sets and/or for molecular systems far from their equilibrium structures, frequently run into the problem of divergence.

Treating divergent perturbation series is an old, but still open problem.³⁻⁸ In a previous paper,⁹ we proposed a procedure to scale down the divergent series by small real numbers to make it convergent. In the knowledge of scaled, converged values, an extrapolation technique was used to estimate the exact infinite order result. Very recently,¹⁰ we generalized this procedure by using complex scaling parameters and applying analytic continuation by solving the Laplace equation.

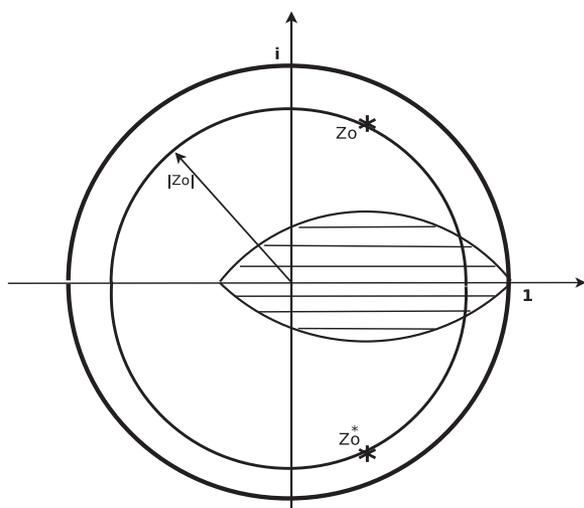


FIG. 1. Schematic contours on the complex plane exhibiting the (outer) unit circle, the location of the closest singularities z_0, z_0^* , the convergence radius $|z_0|$, the domain of convergence (inner circle), and an area bordered by an artificial contour to be used for the application of the Cauchy integral formula (shaded domain).

The aim of this paper is to use, instead of the laborious numerical solution of the Laplace equation, Cauchy's integral formula [Eq. (1)], which we found to be a much more robust procedure for analytic continuation of complex functions.

It has to be noted that analytic continuation is not the only method to resum divergent PT series. Besides the references given above, we mention the Levin–Weniger transformation^{11,12} as an important resummation tool, with which a few comparative calculations will also be presented in this paper.

II. THEORY

Suppose that we know individual terms of an infinite series, convergent or divergent,

$$E_n = \sum_{i=0}^n E^{(i)} \quad (3)$$

up to a certain order n . We are interested in the limit of this series, E , when $n \rightarrow \infty$. One can formally write it as a power series introducing parameter z as

$$E_n(z) = \sum_{i=0}^n z^i E^{(i)}, \quad (4)$$

the physical situation corresponding to the value $z = 1$. In general, complex values for z are permitted. Assume further that (4) is an expansion of some complex function $E(z)$ around the origin $z = 0$. As known, this expansion is convergent in the $n \rightarrow \infty$ limit for those values of z for which $|z| < |z_0|$, where z_0 is the location of the singularity of $E(z)$ closest to the origin, in other words, within the convergence radius (the inner circle

in Fig. 1). The “physical” series (3) is convergent if $|z_0| > 1$, while the case in Fig. 1 illustrates a divergent situation.

Even if the series (3) is divergent, we can always scale individual members of the series by z , meeting criterion $|z| < |z_0|$. For these values, we can sum up (4), and if n is sufficiently large, we can determine the unknown complex function $E(z)$ to a given numerical accuracy within the convergence radius. Then the question arises whether we can extrapolate function $E(z)$ to the point $z = 1$ by means of analytic continuation techniques.

In this paper, we apply the Cauchy integral formula (1) as a tool for analytic continuation. To do this, we set up the following procedure:

1. Choose a value for n , as large as possible, and determine individual terms of series (3). In the quantum chemical practice, this could mean performing MPn calculations.
 2. Design a contour on the complex plane so that a significant part of it embeds z values within the convergent region $|z| < |z_0|$, but extending it to contain the point $z = 1$ of physical interest (the contour enclosing the shaded area in Fig. 1). The overlap of this shaded domain and the convergent domain can be called the trusted region. This contour should not enclose any singularity to ensure that function $E(z)$ is analytic inside. The shape of the contour is otherwise arbitrary.
 3. Choose many values of z_1 within the trusted domain and sum up Eq. (4) for these values. In practice, the radius of the inner circle is chosen somewhat less than $|z_0|$ to ensure fast convergence of the $E_n(z_1)$ values. These summed values represent the unknown function $E(z_1)$ up to some numerical accuracy.
- The reference points inside the trusted region were chosen as $z_1 = x + iy$, where (x, y) are the points of a grid starting at $x = x_{\min}$, with a uniform grid length of 0.01 in both x and y directions. x_{\min} was between 0.6 and 0.65, and points too close (closer than 0.01) to the contour were left out. This resulted in 40–50 reference points. The reason for not choosing reference points in the entire trusted region is that points farther from our point of interest $z = 1$ are less sensitive to the value of $f(z = 1)$.

4. Knowing $E(z)$ within the trusted domain, the next step is to initialize $E(z)$ on that part of contour of the shaded domain which is out of the trusted region, including the point $z = 1$. This can be done by any extrapolation procedure, and when the cycle of this iteration procedure converges, the initial values have little importance. We have used a simple polynomial extrapolation procedure by fitting a 5th order polynomial to 6 points in the trusted region.⁹ Having done this, we have values for $E(z)$ all along the boundary of the shaded domain: accurate, summed values within the trusted region and approximate extrapolated values outside. The latter ones were represented by 8–10 selected points including the point of interest $E(z = 1)$. They are initialized by the extrapolation just mentioned and used as the parameters of optimization described under step 7.

- In the knowledge of the values $E(z)$ on the boundary, invoke Eq. (1) to evaluate values $E(z_1)$, for several values z_1 in the trusted region. To evaluate the contour integral, we used polynomial interpolation between the selected points, which ensures the continuity of $E(z)$ along the contour.
- Compare the results of this integration to the scaled (numerically exact) results obtained in step 3 and form a measure of the error by the square root of the average of squared deviations.
- Modify values $E(z)$ on the contour outside the trusted region so that the error of step 6 should decrease. This is an optimization procedure what we have carried out with the BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm.¹³ As optimizable parameters of BFGS, we selected the values of $E(z)$ at 8-10 points on the boundary (these are the values initialized under step 4). The gradient vector provided to BFGS was obtained from a numerical finite difference procedure.

At the end of this procedure, one has converged values for $E(z)$ within the shaded domain as well as on its boundary, including $E(z = 1)$. This latter value can be considered as a resummation of the original, eventually divergent series (3).

III. RESULTS

In this section, we shall apply this procedure to extrapolate and resum MP_n values obtained for the correlation energy of quantum chemical systems.

A. The dissociation of the LiH molecule

We begin with the calculation of the potential curve of the LiH molecule using single reference MP perturbation theory to account for correlation effects. The correlation energy is defined as the difference between the exact and the Hartree-Fock (HF) energy.

Relying on RSPT and using MP partitioning, and denoting the i th order contribution to the total electronic energy by $E^{(i)}$, the Hartree-Fock energy is given by $E_{\text{HF}} = \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle = E^{(0)} + E^{(1)}$. If the “ z -dependent” correlation energy is $E_{\text{corr}}(z) = E(z) - \langle \Psi^{(0)} | \hat{H}(z) | \Psi^{(0)} \rangle$ (which for $z = 1$ coincides with the usual definition of E_{corr}), then the power series expansion of $E_{\text{corr}}(z)$ is given by

$$\sum_{i=2} E^{(i)} z^i. \quad (5)$$

The resummation technique described in Sec. II was applied to this series.

For the LiH molecule, high order PT calculations were carried out at several different geometries (i.e., at different $R_{\text{Li-H}}$ distances) in the 6-311G** basis set. The MP series turned out to be convergent at $z = 1$ for all $R_{\text{Li-H}}$ bond lengths that were less than 3.55 Å and divergent for bond lengths greater than 3.6 Å. In the former cases, the method could be still tested by choosing the convergence radius to be $r_0 = 0.7$ and only using the power series expansion for $|z| \leq r_0$. In the latter

cases, the convergence radius was estimated from the terms of divergent series by finding the largest values of $|z|$ for which the scaled results turn converged.^{9,10}

For all geometries considered, the contour was chosen to be a right-angled triangle with vertices at 0, 1 and 0.2i. This means that the vertical leg of the triangle was completely inside the trusted region in each case, and no singularity was present inside this triangle. (This could be in principle checked by the method proposed by Goodson^{14,15} using quadratic Padé approximants. In the present case, the success of the analytic continuation procedure indicates the absence of any singularity inside the contour.) Table I contains the results of the proposed analytic continuation method for the series in Eq. (5). MP_5 and MP_6 refer to the total correction at fifth and sixth order, respectively, i.e., $\sum_{i=2}^n E^{(i)}$ for $n = 5$ and $n = 6$. Full configuration interaction (FCI) denotes the exact correlation energy that can be obtained in a given basis set. Table I contains also the radii r_0 used at different geometries. The data for $R_{\text{Li-H}} \geq 3.75$ Å show that larger bond lengths generate smaller convergence radii. (The seemingly contradictory value of r_0 for $R_{\text{Li-H}} \leq 3.5$ Å is intentional, as for small $R_{\text{Li-H}}$ values, r_0 was chosen artificially small, to test the extrapolation procedure.)

Figure 2 shows the potential curve calculated for the LiH molecule. Around equilibrium, MP_5 , MP_6 , and the energies obtained via the proposed method are close to the FCI energy; at this scale, the lines apparently coincide. At longer distances, the MP_5 and MP_6 energies start to deviate from the exact energy, the difference becoming visible on the scale of Fig. 2 as well. The difference of the results of the procedure described in Sec. II (denoted by “Cauchy”) from the FCI energies is still small enough that the plot does not show it. Therefore it is helpful to plot the deviation (with respect to the FCI) of these energies (see Fig. 3). The differences near

TABLE I. Correlation energy of the LiH molecule at several geometries and at various orders of MP PT and their resummed value. Energies are in mE_h . (For the meaning of r_0 , see the text.)

$R_{\text{Li-H}}/\text{Å}$	r_0	E_{MP5}	E_{MP6}	E_{FCI}	E_{Cauchy}
0.9	0.7	-51.680	-51.868	-51.968	-51.965
1.0	0.7	-50.433	-50.602	-50.690	-50.688
1.1	0.7	-49.302	-49.459	-49.542	-49.539
1.2	0.7	-48.317	-48.468	-48.550	-48.548
1.3	0.7	-47.485	-47.634	-47.721	-47.718
1.4	0.7	-46.800	-46.952	-47.049	-47.045
1.5	0.7	-46.258	-46.420	-46.532	-46.527
1.6	0.7	-45.857	-46.034	-46.170	-46.164
1.7	0.7	-45.594	-45.794	-45.961	-45.955
1.8	0.7	-45.464	-45.694	-45.905	-45.896
1.9	0.7	-45.459	-45.727	-45.994	-45.983
2.0	0.7	-45.570	-45.884	-46.225	-46.209
2.5	0.7	-47.611	-48.300	-49.393	-49.332
3.0	0.7	-51.760	-53.152	-56.111	-55.982
3.5	0.7	-57.978	-60.651	-66.860	-67.094
3.75	0.95	-62.019	-65.713	-73.498	-73.499
4.0	0.94	-66.842	-71.966	-80.532	-80.491
4.5	0.86	-79.382	-89.369	-94.401	-93.660

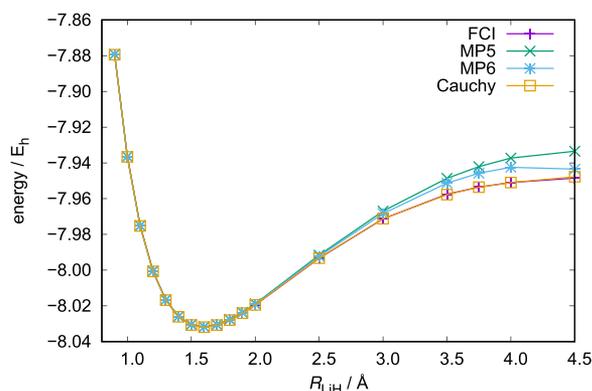


FIG. 2. Potential curve for the LiH molecule, 6-311G** basis set.

equilibrium can be seen in the inset. In this case, the “Cauchy” method yields very accurate results. At larger distances, numerical errors appear in the order of the magnitude of 1 mE_h . Note also that this technique does not yield variational results.

The non-parallelity error (NPE) of the Cauchy method was calculated according to

$$\text{NPE} = \sqrt{\frac{\sum_{j=1}^K (\Delta E_j - \overline{\Delta E})^2}{K-1}}, \quad (6)$$

where ΔE_j is the difference between the Cauchy and the FCI energies at the j th geometry, while $\overline{\Delta E}$ is the average of these differences. In other words, we define NPE as the variance of the energy differences taken at K different geometries sampled uniformly with a step of 0.5 \AA . The NPE of the curve “Cauchy” in Fig. 2 is 0.28 mE_h , to be compared with the NPE of MP5 and MP6 curves (6.12 mE_h and 3.22 mE_h , respectively).

To check the stability of our results with respect to the location and number of reference points applied in the optimization procedure, we report the following example. At 4.0 \AA

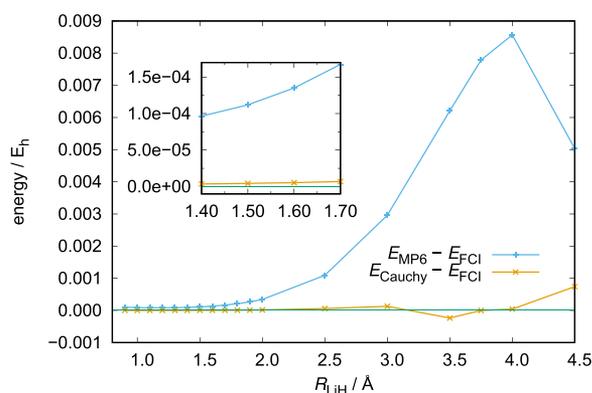


FIG. 3. Deviation from the exact (FCI) results of the MP6 and Cauchy method for the LiH molecule at different geometries (6-311G** basis set).

Li-H distance, we set the reference points in three different ways:

- (i) As originally, i.e., $x_{\min} = 0.65$ and grid length is 0.01 .
- (ii) Points are located in the same area, but denser: $x_{\min} = 0.65$ and grid length is 0.001 .
- (iii) Points are located in a larger area, with density as in (i): $x_{\min} = 0.01$ and grid length is 0.01 . The method yields in these three cases the following estimations for the correlation energy (in mE_h): (i) -80.491 , (ii) -80.751 , and (iii) -80.546 , respectively.

We have also performed single-point calculations (LiH, 4.0 \AA) with the Levin and Weniger transformations of the MPn series. Of several variants, we have selected Eq. (10) of Cizek *et al.*,⁸ which defines Levin and Weniger transformations at various levels, depending on parameters n , l of the formula. As indicated in the last-but-one line of Table I, the FCI correlation energy at this bond length is 80.53 mE_h , while the present analytic continuation predicts 80.49 mE_h . This is to be compared with the results of Levin and Weniger transformations which were found to vary between 59.69 and 86.03 mE_h for parameters $n = 4$ and $1 \leq l \leq 12$ [see their meaning in Eq. (10) in Ref. 8]. The transformations by Levin and Weniger deviate little. Both transformations, therefore, predict the correct order of magnitude of the correlation energy in spite of the fact that the MPn series is rapidly divergent at this geometry. In the present case, the analytic continuation technique served a more accurate estimation.

B. Results for the HF molecule

The same process was carried out for the HF molecule, using a smaller (6-31G**) basis set at different bond lengths. For every $R_{\text{H-F}}$ distance, the contour of integration was chosen to be a right-angled triangle with vertices at 0 , 1 and $0.i$. Table II contains the calculated energies for a few chosen geometries, as well as the convergence radii of the MPn series.

At distances of 0.82539 \AA , 0.91710 \AA , and 1.83420 \AA , the MP series converged, and the choice for r_0 was 0.85 . Far from equilibrium, the error of the Cauchy method becomes greater. This can be explained by the decrease of the convergence radius: the smaller the r_0 is, i.e., the further the $z = 1$ is from the trusted region, the harder the analytic continuation is to carry out.

To conclude, numerical results show that Cauchy’s integral formula can be trustworthily applied as a tool for analytical continuation aiming at resummation of divergent perturbational series. This means, e.g., that molecular potential curves can be approximated from single reference MPn calculations. Higher numerical accuracy of the method when the PT series is convergent is regarded as a numerical test. When resumming divergent data, millihartree accuracy can be expected. The significant advantage of this technique over the procedure suggested in Ref. 10 is that there is no need to solve the Laplace equation at each iteration step. Consequently, once the PT energy terms are available, the procedure is practically costless. At the present stage, the

TABLE II. Energies and energy differences obtained for the HF molecule in the 6-31G** basis set. Energies are in mE_h. r_0 is the radius used for the trusted domain.

$R_{\text{H-F}} (\text{Å})$	r_0	E_{MP5}	E_{Cauchy}	E_{FCI}	$E_{\text{FCI}} - E_{\text{MP5}}$	$E_{\text{FCI}} - E_{\text{Cauchy}}$
0.825 39	0.85	-187.020	-187.443	-187.446	-0.425	-0.003
0.917 10	0.85	-191.556	-192.087	-192.085	-0.529	-0.003
1.834 20	0.85	-250.757	-256.210	-256.211	-5.455	-0.001
2.292 75	0.80	-308.228	-308.336	-308.356	-0.128	-0.021
2.751 30	0.70	-382.505	-352.345	-354.731	27.774	-2.385

method is not yet practical since large order PT results (occasionally a few dozen MPn terms, extracted from a FCI run) have been used. Currently we are investigating possibilities to extrapolate (and eventually resum) based on low order MP results, rendering practical applicability to these techniques.

ACKNOWLEDGMENTS

This work was completed in the ELTE Excellence Program (No. 783-3/2018/FEKUTSRAT) supported by the Hungarian Ministry of Human Capacities and was partly supported by Grant No. NKFIH-K115744. Z.É.M. acknowledges Grant No. ÚNKP-18-3 from the New National Excellence Program of the Ministry of Human Capacities.

REFERENCES

¹L. V. Ahlfors, *Complex Analysis: An Introduction to the Theory of Analytic Functions of One Complex Variable*, International Series in Pure and Applied Mathematics (McGraw-Hill, 1979).

²T. Kato, *Perturbation Theory for Linear Operators* (Springer, Berlin, 1966).

³J. Čížek and E. R. Vrscaj, *Int. J. Quantum Chem.* **21**, 27 (1982).

⁴L. Skála, J. Čížek, V. Kapsa, and E. J. Weniger, *Phys. Rev. A* **56**, 4471 (1997).

⁵G. A. Artega, F. M. Fernández, and E. A. Castro, *Large Order Perturbation Theory and Summation Methods in Quantum Mechanics*, Volume 53 of Lecture Notes in Chemistry (Springer, Berlin, 1990), p. 1.

⁶E. J. Weniger, J. Čížek, and F. Vinette, *J. Math. Phys.* **34**, 571 (1993).

⁷J. Čížek, V. Spirko, and O. Bludsky, *J. Chem. Phys.* **99**, 7331 (1993).

⁸J. Čížek, J. Zamastil, and L. Skála, *J. Math. Phys.* **44**, 962 (2003).

⁹Z. E. Mihalka and P. R. Surjan, *Phys. Rev. A* **96**, 062106 (2017).

¹⁰Z. E. Mihalka, P. R. Surjan, and Á. Szabados, *Theor. Chem. Acc.* **137**, 149 (2018).

¹¹E. J. Weniger, *J. Comput. Phys. Rep.* **10**, 189–371 (1989).

¹²D. Roy, R. Bhattacharya, and S. Bhowmick, *Comput. Phys. Commun.* **93**, 159–178 (1996).

¹³R. Fletcher, *Comput. J.* **13**, 317 (1970).

¹⁴D. Z. Goodson, "Resummation methods," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 743–761 (2012).

¹⁵D. Z. Goodson, *J. Chem. Phys.* **112**, 4901 (2000).