

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

Zsuzsanna É. Mihálka<sup>1</sup> and Ágnes Szabados and Péter R. Surján<sup>2</sup>

<sup>1</sup>Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, and George Hevesy Doctoral School of Chemistry, ELTE Eötvös Loránd University, H-1518 Budapest 112, P.O.B. 32, Hungary

<sup>2</sup>Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, H-1518 Budapest 112, P.O.B. 32, Hungary <sup>a)</sup>

Previous attempts to the resummation of divergent power series by means of analytic continuation are improved applying 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 HF molecule are also tabulated.

## I. INTRODUCTION

The Cauchy integral formula<sup>1</sup>

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

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<sup>2</sup>, 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<sup>1</sup>. 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

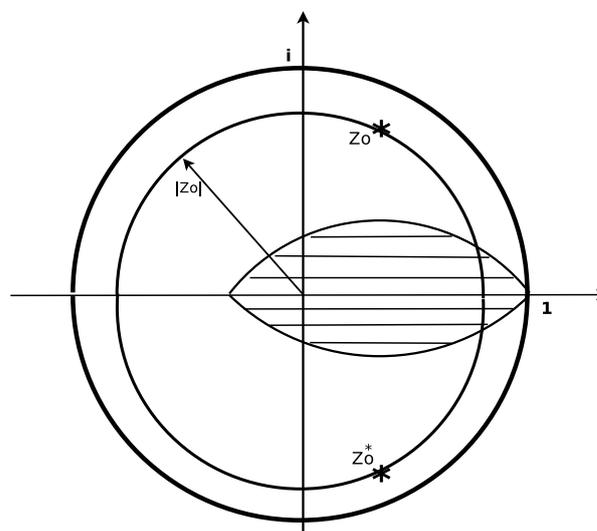


FIG. 1. Schematic contours on the complex plane exhibiting the (outer) unit circle, the location of the closest singularities  $z_0, z_0^*$ , the convergence radius  $|z_0|$ , the domain of convergence (inner circle), and an area bordered by an artificial contour to be used for the application of the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

their equilibrium structures, frequently run into the problem of divergence.

Treating divergent perturbation series is an old, but still open problem<sup>3–8</sup>. In a previous paper<sup>9</sup>, 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<sup>10</sup>, we generalized this procedure by using complex scaling parameters and applying analytic continuation by solving the Laplace equation.

The aim of this paper is to use, instead of the laborious

<sup>a)</sup>Electronic mail: surjan@chem.elte.hu

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<sup>11,12</sup> as an important resummation tool, with which a few comparative calculations will also be presented in this paper.

## II. THEORY

Suppose 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 MP $n$  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 has to be designed so that it should not embed any singularity, function  $E(z)$  remaining 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 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<sup>9</sup>. 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.
5. 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.

6. Compare the results of this integration to the scaled (numerically exact) results obtained in step 3. above, and form a measure of the error by the square root of the average of squared deviations.
7. 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 algorithm<sup>13</sup>. 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.

#### III.1. 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 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  $E_{\text{corr}}$ ), 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 Sect. 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  $R_{\text{Li-H}}$

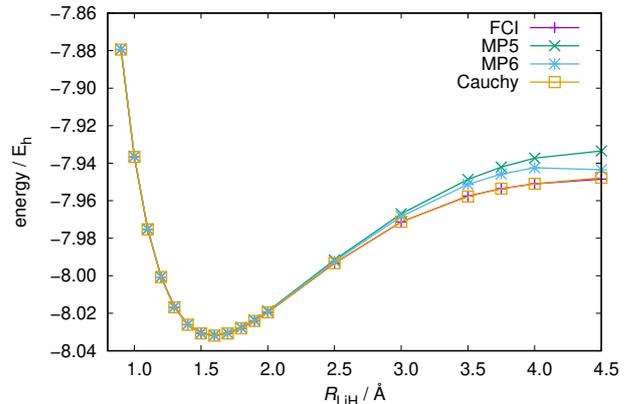


FIG. 2. Potential curve for the LiH molecule, 6-311G\*\* basis set.

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<sup>9,10</sup>.

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<sup>14,15</sup> 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). MP5 and MP6 refer to the total correction at fifth and sixth order, respectively, i.e.  $\sum_{i=2}^n E^{(i)}$  for  $n = 5$  and  $n = 6$ . 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.)

Fig. 2 shows the potential curve calculated for the LiH molecule. Around equilibrium, MP5, MP6 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 MP5 and MP6 energies start to deviate from the exact energy, the difference becoming

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 text.)

$R_{\text{Li-H}}/\text{\AA}$	$r_0$	$E_{\text{MP5}}$	$E_{\text{MP6}}$	$E_{\text{FCI}}$	$E_{\text{Cauchy}}$
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

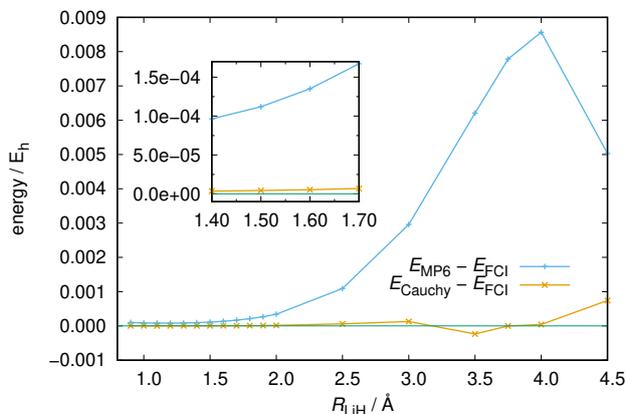


FIG. 3. Deviation from the exact (FCI) results of the MP6 and Cauchy method for the LiH molecule at different geometries (6-311G\*\* basis set).

visible on the scale of Fig. 2 as well. The difference of the results of the procedure described in Sect. 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 (w.r.t. to the FCI) of these energies (see Fig. 3). The differences near equilibrium can be seen in the inset. In this case, the "Cauchy" method yields very accurate results. At larger distances, numerical errors ap-

pear in the order of 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  $\Delta E_j$  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  $0.5 \text{ \AA}$ . 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  $4.0 \text{ \AA}$  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,  $4.0 \text{ \AA}$ ) with the Levin and Weniger transformations of the MPn series. Of several variants, we have selected Eq. (10) of Cizek et al.<sup>8</sup>, which defines Levin and Weniger transformations at various levels, depending on parameters  $n, l$  of the formula. As indicated in 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.<sup>8</sup>). 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.

### III.2. 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  $0.1i$ . Table II contains the calculated energies for a few chosen geometries, as well as the convergence radii of the MP $n$  series.

At distances of 0.82539 Å, 0.91710 Å and 1.83420 Å, 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  $r_0$  is, i.e. the further  $z = 1$  is from the trusted region, the harder is to carry out analytic continuation.

In concluding, 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 MP $n$  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.<sup>10</sup> 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 method is not yet practical, since large order PT results (occasionally a few dozen of MP $n$  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 (783-3/2018/FEKUTSRAT) supported by the Hungarian Ministry of Human Capacities, and was partly supported by the grant NKFIH-K115744. Zs. É. M. acknowledges the Grant ÚNKP-18-3 New National Excellence Program of the Ministry of Human Capacities.

- <sup>1</sup>L.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.
- <sup>2</sup>T. Kato. *Perturbation Theory for Linear Operators*. Springer, Berlin, 1966.
- <sup>3</sup>J. Čížek and E. R. Vrcsay. *Int. J. Quantum Chem.*, 21:27, 1982.
- <sup>4</sup>L. Skála, J. Čížek, V. Kapsa, and E. J. Weniger. *Phys. Rev. A*, 56:4471, 1997.
- <sup>5</sup>G. A. Arteca, F. M. Fernández, and E. A. Castro. *Lecture Notes in Chemistry, Large Order Perturbation Theory and Summation Methods in Quantum Mechanics*, volume 53, page 1. Springer, Berlin, 1990.
- <sup>6</sup>E.J. Weniger, J. Čížek, and F. Vinette. *J. Math. Phys.*, 34:571, 1993.
- <sup>7</sup>J. Čížek, V. Spirko, and O. Bludsky. *J. Chem. Phys.*, 99:7331, 1993.
- <sup>8</sup>J. Čížek, J. Zamastil, and L. Skála. *J. Math. Phys.*, 44:962, 2003.
- <sup>9</sup>Zs.E. Mihalka and P.R. Surjan. *Phys. Rev. A*, 96:062106, 2017.
- <sup>10</sup>Zs.E. Mihalka, P.R. Surjan, and Á. Szabados. *Theoretical Chemistry Accounts*, 137:149, 2018.
- <sup>11</sup>E. J. Weniger. *JComputer Physics Reports*, 10:189–371, 1989.
- <sup>12</sup>D. Roy, R. Bhattacharya, and S Bhowmick. *Computer Physics Communication*, 93:151–178, 1996.
- <sup>13</sup>R. Fletcher. *Computer J.*, 13:317, 1970.
- <sup>14</sup>David Z. Goodson. Resummation methods. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2:743–761, 2012.
- <sup>15</sup>D.Z. Goodson. *J. Chem. Phys.*, 112:4901, 2000.

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

$R_{\text{H-F}} / \text{\AA}$	$r_0$	$E_{\text{MP5}}$	$E_{\text{Cauchy}}$	$E_{\text{FCI}}$	$E_{\text{FCI}} - E_{\text{MP5}}$	$E_{\text{FCI}} - E_{\text{Cauchy}}$
0.82539	0.85	-187.020	-187.443	-187.446	-0.425	-0.003
0.91710	0.85	-191.556	-192.087	-192.085	-0.529	-0.003
1.83420	0.85	-250.757	-256.210	-256.211	-5.455	-0.001
2.29275	0.80	-308.228	-308.336	-308.356	-0.128	-0.021
2.75130	0.70	-382.505	-352.345	-354.731	27.774	-2.385