In this communication we demonstrate the effectiveness of the method of complete basis set (CBS) extrapolation of correlation energies based on the application of the Riemann zeta function. Instead of fitting the results obtained with a systematic sequence of one-electron bases with a certain functional form, an analytic re-summation of the missing contributions coming from higher angular momenta, $l$ is performed. The assumption that these contributions vanish asymptotically as an inverse power of $l$ leads to an expression for the CBS limit given in terms of the zeta function. This result is turned into an extrapolation method that is very easy to use and requires no “empirical” parameters to be optimized. The performance of the method is assessed by comparing the results with very accurate reference data obtained with explicitly correlated theories and with results obtained with standard extrapolation schemes. On average, the errors of the zeta-function extrapolation are several times smaller compared with the conventional schemes employing the same sequence of bases. A recipe for the estimation of the residual extrapolation error is also proposed.
1 Introduction

Extrapolation to the complete basis set (CBS) limit is an effective theoretical tool that allows to remove a significant fraction of the finite basis set error at essentially zero computational cost. This is illustrated well by the papers of Feller and collaborators\textsuperscript{1,2} who have shown that even the worst-performing extrapolation schemes are able to reduce the error of raw \textit{ab initio} values by approximately a factor of two.

Various extrapolation protocols have been proposed in the literature (see Refs.\textsuperscript{1,3–5} for a comprehensive review). One of the first formulas used for this purpose is a simple two-parameter exponential,\textsuperscript{6,7} later generalized to a three-parameter mixed exponential/Gaussian expression.\textsuperscript{8,9} Both of them are based on purely empirical arguments and it has been shown that they typically underestimate the CBS limit.\textsuperscript{10}

A majority of the extrapolation schemes used today assume that the results converge towards the CBS limit with the error decaying as an inverse power of the the largest angular momentum $L$ included in the basis set. This approach, grounded in numerical observations of Schwartz\textsuperscript{11,12} for the energy of the helium atom, was subsequently justified theoretically by Hill\textsuperscript{13} and other authors.\textsuperscript{14–16}

One of the most popular extrapolation schemes employed for the correlation energy is due to Helgaker et al.\textsuperscript{17,18} and relies directly on the $L^{-3}$ error formula. However, numerous generalizations and extensions of this scheme were proposed in the literature, e.g., the $L^{-\alpha}$ or $(L+1/2)^{-\alpha}$ formulae with an adjustable $\alpha$,\textsuperscript{19–21} expressions that additionally include higher inverse powers of $L$,\textsuperscript{112} or shifted formulae where some effective parameter is used instead of $L$.\textsuperscript{22}\textsuperscript{25} A different approach was proposed by Schwenke\textsuperscript{26} who calculated the CBS limit by scaling the difference between the results obtained in two largest basis sets. The scaling coefficient is determined “empirically” for a given level of theory and basis set family. Note that extrapolations are not limited to the correlation energy and are also frequently applied to other quantities such as polarizabilities\textsuperscript{27} or structural parameters.\textsuperscript{28}

In this work we consider a CBS extrapolation method that is fundamentally different
from the approaches described in the previous paragraphs. The performance of the proposed method is assessed by comparing the results with accurate reference data and with results obtained with standard extrapolation schemes. Finally, we put forward a simple recipe to estimate the residual extrapolation error.

2 Theory

Let us denote the energy calculated with a basis set including functions up to the angular momentum \( L \) by \( E_L \). The basic idea of the method advocated by us relies on the assumption that energy increments, \( \delta_l = E_l - E_{l-1} \), possess the following asymptotic form

\[
\delta_l \to a \cdot l^{-4} \quad \text{as} \quad l \to \infty, \tag{1}
\]

where \( a \) is a system-dependent numerical parameter. We adopt a convention \( E_{-1} = 0 \), so that \( \delta_0 = E_0 \). The formula (1) is asymptotically valid for spin-singlet electron pairs. A more general (and presumably more accurate) asymptotic expression takes also the triplet electron pairs into account and reads

\[
\delta_l \to a \cdot l^{-4} + b \cdot l^{-6} \quad \text{as} \quad l \to \infty. \tag{2}
\]

Here we concentrate mostly on Eq. (1), but at the end of this section the main results are generalized to take Eq. (2) into account. Note that for systems where all electron pairs are triplet-coupled, such as the quintet state of the helium dimer, one should set \( a = 0 \) in Eq. (2).

The exact energy, \( E_\infty \), can obviously be obtained by summing all energy increments and so one can split this summation into two parts

\[
E_\infty = \sum_{l=0}^{L} \delta_l + \sum_{l=L+1}^{\infty} \delta_l = E_L + \sum_{l=L+1}^{\infty} \delta_l, \tag{3}
\]
where $L$ is the maximal angular momentum that is feasible in practice. It is assumed that $L$ is large enough to make Eq. (1) a good approximation to $\delta_l$ for $l > L$. Under these conditions the CBS limit can be rewritten as

$$E_\infty = E_L + a \sum_{l=L+1}^\infty l^{-4}, \quad (4)$$

or

$$E_\infty = E_L + a \left[ \zeta(4) - \sum_{l=1}^L l^{-4} \right], \quad (5)$$

where $\zeta(s) = \sum_{n=1}^\infty n^{-s}$ is the Riemann zeta function, so that $\zeta(4) = \pi^4/90$. The parameter $a$ required in Eq. (5) can be fixed assuming that results from two consecutive basis sets, say, $E_L$ and $E_{L-1}$, are available. The optimal $a$ is then found straightforwardly as

$$a = L^4 (E_L - E_{L-1}). \quad (6)$$

Together with Eq. (5) this constitutes the basic two-point extrapolation scheme.

In the above analysis we have assumed that the values of $E_l$ obtained within a given basis set are exact. This is not strictly true in practice since the number of $s, p, d, \ldots,$ functions is always finite. Further in this work we do not assume that each component $E_l$ is radially saturated with high accuracy like, e.g., in the work of Moncrieff and Wilson, and expect the validity of the extrapolation for the conventional correlation consistent bases when the number of radial functions decreases with $l$. The error in $E_l$ usually converges rather quickly (at least for atoms) with the number of functions $n$ in the shell especially when the “radial” functions satisfy the nuclear cusp condition. The problem of radial incompleteness is also alleviated by using uncontracted and/or augmented basis sets.

When the results from three consecutive basis sets, $E_L$, $E_{L-1}$, and $E_{L-2}$, are available, the three-point extrapolation scheme based on Eq. (2) can be applied. In this case the
expression for the CBS energy limit reads

\[ E_\infty = E_L + a \left[ \zeta(4) - \sum_{l=1}^{L} l^{-4} \right] + b \left[ \zeta(6) - \sum_{l=1}^{L} l^{-6} \right], \tag{7} \]

where \( \zeta(6) = \pi^6/945 \), and the coefficients \( a, b \) are

\[ a = \frac{L^6 \left( E_L - E_{L-1} \right) - (L - 1)^6 \left( E_{L-1} - E_{L-2} \right)}{2L - 1}, \tag{8} \]
\[ b = L^6 \left( E_L - E_{L-1} \right) - aL^2. \tag{9} \]

In principle, for a sufficiently large \( L \) the three-point extrapolation should outperform the two-point method. The former not only accounts for the convergence of the correlation energy for the triplet electron pairs, but the \( l^{-6} \) term also serves as a subdominant term in the asymptotic expansion for the singlet pairs. On the other hand, the main disadvantage of the three-point formula is the fact that the results from the smallest \( L - 2 \) basis set may not be reliable enough. Additionally, the three-point formula may be more susceptible to over-parametrization, numerical noise, and small irregularities in the basis set sequence.

The method considered here bears some similarities to the convergence acceleration technique employed by Drake and Yan\textsuperscript{33} in calculations of three-electron atomic integrals over exponential functions. Its particular variant, Eqs. (5) and (6), has also been applied by Moncrieff and Wilson\textsuperscript{30} to extrapolate the second-order (Møller-Plesset) correlation energies for 14-electron diatomics computed using specially designed universal Gaussian basis sets.

In the next section the results obtained with help of Riemann extrapolations are compared with the following conventional formulas\textsuperscript{17,18}

\[ E_L = E_\infty + A \cdot L^{-3}, \tag{10} \]
\[ E_L = E_\infty + A \cdot L^{-3} + B \cdot L^{-5}. \tag{11} \]

The parameters \( E_\infty, A, B \) are adjusted to match the results obtained with a sequence of
two or three basis sets. The extrapolation formula $E_L = E_\infty + A(L + 1/2)^{-4} + A(L + 1/2)^{-6}$ proposed by Martin\textsuperscript{19} has also been tested, but we have found it inferior in comparison to Eqs. (10) and (11).

It is also interesting to compare the two-point zeta-function extrapolation with the conventional formula (10) under the assumption that Eq. (1) strictly holds for each $l \geq L$. In such case the zeta-function formula gives the exact result given by Eqs. (4) or (5). Employing the asymptotic expansion\textsuperscript{33} of the infinite sum in Eq. (4), the limit $E_\infty$ can be rewritten as $E_\infty = E_L + \frac{1}{3}a \cdot L^{-3} - \frac{1}{2}a \cdot L^{-4} + \mathcal{O}(L^{-5})$. The extrapolation formula (10) also can be rewritten in an analogous form, $E'_\infty = E_L - a \cdot L^{-4} [1 - L^3 (L - 1)^{-3}]^{-1}$ which for large $L$ can be expanded as $E'_\infty = E_L + \frac{1}{3}a \cdot L^{-3} - \frac{2}{3}a \cdot L^{-4} + \mathcal{O}(L^{-5})$. By combining the obtained expressions for $E_\infty$ and $E'_\infty$ one can show that the error of the conventional extrapolation, $\epsilon_L = E_\infty - E'_\infty$, behaves asymptotically as $\epsilon_L = \frac{1}{6}a \cdot L^{-4} + \mathcal{O}(L^{-5})$. Thus, the extrapolation (10) contains the $L^{-4}$ error coming from inexact summation of the $l^{-4}$ term. This error is absent in the zeta-function method which can be viewed as a mathematical rationale behind the improved effectiveness of the zeta-function extrapolations.

3 Numerical results

3.1 Correlation energies

To investigate the performance of the extrapolation scheme defined by Eqs. (5)-(9), we performed finite basis set calculations for several systems where benchmark-quality results at various levels of theory are known. Literature sources of the reference values (which are all accurate to $1 \mu$H or better) and basis sets used in this work are summarized in Table I. Uncontracted Gaussian-type basis sets are used throughout the present work. For neon atom we employ Slater-type orbitals (STOs) basis sets optimized for the purposes of this work according to the scheme detailed in Refs.\textsuperscript{35,36} All basis sets can be obtained from the authors upon request. The internuclear distance in $\text{H}_2$ molecule is set to 1.4 a.u. and the
geometry of $H_3^+$ is the equilateral triangle with the side length of 1.65 a.u. All orbitals were active in the correlated calculations except for the neon atom where 1s core orbital was frozen. Calculations reported in this subsection were performed with help of the GAMESS program package.\textsuperscript{37}

The results of the two-point and three-point zeta-function extrapolations for the helium atom, beryllium atom (STOs basis set), carbon atom, hydrogen molecule (basis set of Mielke et al.\textsuperscript{38}), and trihydrogen cation ($H_3^+$) at the FCI level of theory are given in Table 2. Analogous results at the MP2 and CCSD levels of theory for the beryllium atom and lithium hydride molecule (LiH) are summarized in Table 3. In Table 4 we show values of the perturbative triples correction obtained for the neon atom

$$E_{(T)} = E_{\text{CCSD(T)}} - E_{\text{CCSD}},$$

(12)

where $E_{\text{CCSD}}$ and $E_{\text{CCSD(T)}}$ are the correlation energies obtained from the CCSD\textsuperscript{39} and CCSD(T) methods,\textsuperscript{40} respectively. For comparison, the corresponding results obtained at the MP2 level of theory are also reported in Table 4.

The results given in Tables 2 and 3 indicate a good performance of both the two-point and the three-point zeta-function extrapolations. On average, the errors are reduced by a factor of 3–4 compared with the conventional schemes employing the same number of basis functions. The gains are usually larger for smaller basis sets; for example, the quality of the results obtained even with the most crude $L = 2, 3$ zeta-function extrapolation compares favourably with raw results from basis sets as large as $L = 5, 6$. In some cases the three-point zeta-function method does not lead to any improvement over its two-point counterpart. This may be due to increased susceptibility of the former to small irregularities in the basis set sequence or simply is an indication that the convergence with respect to the angular momentum has already been reached and other factors are limiting the accuracy at this point (such as the “radial” convergence).
Similar conclusions apply also to the results for the neon atom presented in Table 4. For the $E_{(T)}$ component of the correlation energy the two-point $L = 6, 7$ zeta-function extrapolation outperforms any other scheme giving an error of only about 0.002 mH (which is very close to the estimated accuracy of the benchmark value).

In many applications, especially in those that aim at high accuracy of the results, it is important to provide a reliable estimate for the error of the extrapolated value. The simplest solution is to take the difference between the extrapolated value and the result in the largest basis set available. This conservative approach has been used in the literature numerous times, but in the case of the zeta-function method it leads to gross overestimations. Let us consider a more general approach where the residual extrapolation error, $\sigma_L = |E_{\text{exact}} - E_\infty|$, is estimated as

$$\sigma_L = C_L |E_L - E_\infty|, \quad (13)$$

where $C_L$ is a numerical parameter. By using the results from Tables 2-4 we can find “empirical” values of $C_L$ that can be used to estimate the error of future applications. To this end, we demand that for each extrapolated value from Tables 2-4 the error calculated from Eq. (13) is not smaller than the true error. In the case of the two-point zeta-function extrapolation one finds

$$C_3 = 0.113, \quad C_4 = 0.135, \quad C_5 = 0.136, \quad C_6 = 0.094, \quad C_7 = 0.094,$$

Note that the fact that $C_3 < C_4$ does not imply that the $L = 2, 3$ extrapolation gives, on average, smaller errors than $L = 3, 4$ extrapolation. The latter extrapolation would still be significantly more reliable simply because $|E_4 - E_\infty|$ is much smaller than $|E_3 - E_\infty|$, cf. Eq. (13). The error bars obtained with help of the constants $C_L$ can be additionally tightened if the value of $\sigma_L$ is interpreted statistically as the standard deviation, i.e., one demands that in about 68% of cases the true error is smaller than $\sigma_L$, in about 95% of cases the
true error is smaller than $2\sigma_L$, and so forth (assuming that the error distribution is normal). However, a further justification of this approach requires a larger statistical sample than available here and shall be considered in future works. One may note that another popular method of estimating the extrapolation error, namely taking the difference between the last two extrapolated results, was found by us to underestimate the error in several cases and we do not recommend its use in combination with the zeta-function method.

### 3.2 Other quantities

To check the applicability of the zeta-function method to extrapolation of properties other than the energy we selected static dipole polarizabilities of the helium atom and of the hydrogen molecule, and the exchange splitting in the hydrogen molecule. The latter quantity is defined as a difference between the energies of the ground ($^1\Sigma_g^+$) and the first excited state ($^3\Sigma_u^+$) of this system. Here we consider a scaled quantity defined as

$$\Delta E = e^{2R} R^{-5/2}(E_u - E_g),$$

where $E_g$ and $E_u$ are the energies of the ground and excited states, respectively, and $R$ is the internuclear distance ($R = 8.0$ was adopted in the calculations). The static dipole polarizabilities were calculated with help of the Dalton program package. Doubly-augmented Gaussian-type basis sets of Woon and Dunning were used in polarizability calculations for the hydrogen molecule.

The data provided in Tables 5 and 6 reveal that extrapolation of properties is a considerably more difficult task than of the correlation energies. Nonetheless, zeta-function extrapolations still give considerably better results than the conventional extrapolations with the same number of points. The only exception is the two-point extrapolation for the helium atom, but even in this case the differences are marginal. Overall, the extrapolated values converge less regularly to the CBS limit compared with the results for the correlation ener-
gies discussed in the previous section. This suggests that the lack of radial saturation may be responsible for the remaining basis set incompleteness error, despite doubly-augmented basis sets were used in the calculations.

4 Conclusions

We have studied the performance of the complete basis set extrapolation that is based on analytic re-summation of the missing energy increments using the Riemann zeta function. The performance of the proposed method has been assessed by comparing with accurate reference data obtained with explicitly correlated theories and with results obtained with standard extrapolation schemes. For extrapolation of the correlation energies we recommend the simplest two-point zeta-function formula due to its reliability, ease of use, and regular convergence of the results. This scheme outperforms the standard extrapolation methods in most cases studied here and, on average, allows to reduce the residual extrapolation errors several times. We have also proposed a reliable method of estimating the remaining extrapolation error.

In the future this work can be extended in several directions. For example, separate treatment of singlet and triplet electron pairs can be performed, and an analogous separation can be made for the core and valence electron pairs. It is also possible to generalize the zeta-function method to extrapolate relativistic and quantum electrodynamics corrections that are known to converge pathologically slowly\cite{16,47} with respect to the basis set size.

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Riemann extrapolation
L-3 extrapolation

Median extrapolation errors for the electronic correlation energies
(parts per thousand)
L=2,3, L=3,4, L=4,5
Table 1: Literature sources of benchmark values and of basis sets employed in this work. The abbreviation HF stands for Hartree-Fock.

| Element | Benchmark Source | Basis Set, Notes |
|---------|------------------|------------------|
| He      | Nakashima et al. (FCI limit) | Cencek et al. (dXZ) |
|         | Lehtola (HF limit) |                  |
|         | Pachucki and Sapirstein (static polarizability) |                  |
| Be      | Przybytek et al. (MP2 and CCSD limits) | Prascher et al. (aug-cc-pwCVnZ) |
|         | Pachucki and Komasa (FCI limit) | Lesiuk et al. (Slater-type basis set) |
| C       | Strasburger (FCI limit) | Kendall at al. (aug-cc-pCVXZ) |
|         | Bunge (HF limit) |                  |
| H₂      | Pachucki (FCI limit) | Mielke et al. (aug-mcc-pVXZ) |
|         | Mitin (HF limit) |                  |
|         | Rychlewski (static polarizability) | Woon and Dunning (d-aug-cc-pVXZ) |
| Ne      | Köhn (CCSD(T) limit) | this work (Slater-type basis set) |
|         | Flore (MP2 limit) |                  |
| LiH     | Bukowski et al. (MP2 and CCSD limits) | Prascher et al. (aug-cc-pwCVnZ) |
| H₃⁺     | Pavanello et al. (FCI limit) | Mielke et al. (aug-mcc-pVXZ) |
|         | Jensen et al. (HF limit) |                  |
Table 2: Extrapolation errors (in $\mu$H) in the FCI correlation energy for the helium atom, beryllium atom, carbon atom, hydrogen molecule ($H_2$), and trihydrogen cation ($H_3^+$). The values of $-E_L$ (in mH) are given in the second column. The reference values of the correlation energy are $E_\infty(\text{He}) = -42.044 381$ mH, $E_\infty(\text{Be}) = -94.332 459$ mH, $E_\infty(\text{C}) = -156.287$ mH, $E_\infty(\text{H}_2) = -40.846 348$ mH, and $E_\infty(\text{H}_3^+) = -43.463 500$ mH.

| $L$ | $-E_L$ | $\text{Eq. (5)}$ | $\text{Eq. (10)}$ | $\text{Eq. (7)}$ | $\text{Eq. (11)}$ |
|-----|--------|------------------|------------------|------------------|------------------|
| He  |        |                  |                  |                  |                  |
| 2   | 40.018 397 | —                | —                | —                | —                |
| 3   | 41.173 663 | 171.0            | 384.3            | —                | —                |
| 4   | 41.597 808 | 58.8             | 137.1            | 21.4             | 82.9             |
| 5   | 41.785 680 | 27.2             | 61.6             | 11.3             | 32.1             |
| 6   | 41.881 296 | 14.4             | 31.7             | 5.6              | 14.7             |
| 7   | 41.934 921 | 8.6              | 18.3             | 3.5              | 8.0              |
| Be  |        |                  |                  |                  |                  |
| 2   | 85.976 344 | —                | —                | —                | —                |
| 3   | 91.479 502 | -383.7           | 632.4            | —                | —                |
| 4   | 92.994 102 | 50.2             | 329.6            | 194.6            | 263.3            |
| 5   | 93.608 566 | 63.4             | 175.8            | 70.1             | 115.7            |
| 6   | 93.902 091 | 70.5             | 123.7            | 75.5             | 93.9             |
| C   |        |                  |                  |                  |                  |
| 2   | 132.539 255 | —                | —                | —                | —                |
| 3   | 145.933 543 | 2240.9           | 4713.9           | —                | —                |
| 4   | 151.028 728 | 600.1            | 1540.3           | 53.8             | 844.9            |
| H$_2$ |        |                  |                  |                  |                  |
| 2   | 39.834 097 | —                | —                | —                | —                |
| 3   | 40.449 439 | 24.2             | 137.8            | —                | —                |
| 4   | 40.652 767 | 7.7              | 45.2             | 2.2              | 24.9             |
| 5   | 40.737 378 | 4.7              | 20.2             | 3.2              | 10.4             |
| 6   | 40.779 706 | 0.8              | 8.5              | -1.8             | 1.8              |
| H$_3^+$ |        |                  |                  |                  |                  |
| 2   | 42.370 983 | —                | —                | —                | —                |
| 3   | 43.051 539 | -0.2             | 125.4            | —                | —                |
| 4   | 43.271 252 | -8.6             | 31.9             | -11.4            | 11.4             |
| 5   | 43.354 056 | +7.4             | 22.6             | +15.5            | 18.9             |
Table 3: Extrapolation errors (in \( \mu \text{H} \)) in the MP2 and CCSD correlation energies for the beryllium atom and for the lithium hydride (LiH) molecule. All abbreviations are the same as in Table 2. The reference values of the MP2 correlation energy are \( E_\infty(\text{Be}) = -76.358249 \text{mH} \) and \( E_\infty(\text{LiH}) = -72.8895 \text{mH} \), and of the CCSD correlation energy are \( E_\infty(\text{Be}) = -93.6645 \text{mH} \) and \( E_\infty(\text{LiH}) = -82.9901 \text{mH} \).

| \( L \) | \(-E_L\) | Eq. (5) | Eq. (10) | Eq. (7) | Eq. (11) |
|---|---|---|---|---|---|
| \( E_{\text{MP2}}(\text{Be}) \) | | | | | |
| 2 | 63.574069 | — | — | — | — |
| 3 | 70.880240 | 1052.8 | 2401.7 | — | — |
| 4 | 73.672818 | 132.3 | 647.6 | -174.2 | 263.3 |
| 5 | 74.849721 | 58.5 | 273.7 | 21.2 | 127.8 |
| \( E_{\text{MP2}}(\text{LiH}) \) | | | | | |
| 2 | 55.999799 | — | — | — | — |
| 3 | 66.006642 | +821.9 | 2669.5 | — | — |
| 4 | 69.669343 | -129.6 | 546.4 | -446.4 | 81.2 |
| 5 | 71.128900 | -36.9 | 229.9 | -10.0 | 106.4 |
| \( E_{\text{CCSD}}(\text{Be}) \) | | | | | |
| 2 | 84.563558 | — | — | — | — |
| 3 | 90.325338 | -149.1 | 914.7 | — | — |
| 4 | 92.237729 | -320.1 | 32.8 | -377.0 | -160.5 |
| 5 | 92.895696 | -40.3 | 80.0 | 101.3 | 98.4 |
| \( E_{\text{CCSD}}(\text{LiH}) \) | | | | | |
| 2 | 68.961499 | — | — | — | — |
| 3 | 78.630548 | -1496.9 | 288.3 | — | — |
| 4 | 81.216330 | -590.4 | -113.3 | -288.6 | -201.2 |
| 5 | 81.902675 | 241.7 | 367.2 | 662.9 | 554.8 |
Table 4: Extrapolation errors of the $E_{(T)}$ and $E_{MP2}$ components of the correlation energy for the neon atom. All values are given in mH and the abbreviations are the same as in Table 2. The reference results are $E_{(T)} = -6.501$ mH and $E_{MP2} = -320.223$ mH.

| $L$ | $E_L$ | Eq. (5) | Eq. (10) | Eq. (7) | Eq. (11) |
|-----|-------|---------|---------|--------|---------|
| 2   | -4.277| —       | —       | —      | —       |
| 3   | -5.788| -0.202  | 0.077   | —      | —       |
| 4   | -6.185| -0.048  | 0.026   | 0.003  | 0.014   |
| 5   | -6.336| -0.021  | 0.007   | -0.007| -0.000  |
| 6   | -6.401| -0.002  | 0.010   | 0.010  | 0.011   |
| 7   | -6.435| +0.002  | 0.009   | 0.006  | 0.008   |

| $E_{MP2}$ |
|-----------|
| 2         | 246.555  |
| 3         | 287.239  |
| 4         | 303.478  |
| 5         | 310.424  |
| 6         | 313.898  |
| 7         | 315.887  |

Table 5: Extrapolation errors (in $\mu$H) in the static dipole polarizability of the helium atom and the hydrogen molecule ($R = 1.4$) calculated at the FCI level of theory. The values of the polarizability calculated in the basis set $L$ are given in the second column. The reference values are $\alpha(\text{He}) = 1.383192174455(1)$ a.u. and $\alpha_{||}(\text{H}_2) = 6.3873188$ a.u.

| $L$ | $\alpha_L$ | Eq. (5) | Eq. (10) | Eq. (7) | Eq. (11) |
|-----|------------|---------|---------|--------|---------|
| 2   | 1.385972   | —       | —       | —      | —       |
| 3   | 1.384154   | -138.7  | +196.9  | —      | —       |
| 4   | 1.383522   | -247.8  | -131.1  | -284.1 | -203.0  |
| 5   | 1.383314   | -134.7  | -96.6   | -77.5  | -83.1   |
| 6   | 1.383244   | -57.7   | -45.0   | -4.8   | -15.4   |
| 7   | 1.383216   | -27.3   | -22.4   | -0.7   | -5.2    |

| $\alpha_{||}(\text{H}_2)$ |
|--------------------------|
| 1 | 6.463948 |
| 2 | 6.407661 |
| 3 | 6.394838 |
| 4 | 6.390487 |
| 5 | 6.389139 |
Table 6: Scaled exchange splitting in the hydrogen molecule ($R = 8.0$) defined according to Eq. (14) calculated at the FCI level of theory. All values are given in the atomic units and the abbreviations are the same as in Table 2. The reference value is $\Delta E = 1.736967949(9)$ a.u.

| $L$ | $\Delta E$ | Eq. (5) | Eq. (10) | Eq. (7) | Eq. (11) |
|-----|------------|---------|----------|---------|----------|
| 2   | 1.6825     | —       | —        | —       | —        |
| 3   | 1.6999     | -0.0266 | -0.0298  | —       | —        |
| 4   | 1.7142     | -0.0096 | -0.0123  | -0.0040 | -0.0084  |
| 5   | 1.7203     | -0.0091 | -0.0102  | -0.0089 | -0.0094  |
| 6   | 1.7246     | -0.0058 | -0.0065  | -0.0034 | -0.0044  |