Accurate non-covalent interaction energies via an efficient MP2 scaling procedure

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Using the observed proportionality of CCSD(T) and MP2 correlation interaction energies [I. Grabowski, E. Fabiano, F. Della Sala, Phys. Chem. Chem. Phys. 15, 15485 (2013)] we propose a simple scaling procedure to compute accurate interaction energies of non-covalent complexes. Our method makes use of MP2 and CCSD(T) correlation energies, computed in relatively small basis sets, and fitted scaling coefficients to yield interaction energies of almost complete basis set limit CCSD(T) quality. Thanks to the good transferability of the scaling coefficients involved in the calculations, good results can be easily obtained for different intermolecular distances.

I. INTRODUCTION

Non-covalent interactions play a fundamental role in chemistry and chemical-physics because of their importance in many phenomena including, among others, biochemistry, solvation, supermolecular organization, and molecular recognition. For this reason they have been subject of intense research\textsuperscript{1-4}. However, because the strength of non-covalent interactions is one or two order of magnitude smaller than that of typical covalent interactions, ranging from few tens to few tenths of kcal/mol, special care is required for accurate quantitative studies.

From a computational point of view this implies the need for high-level correlated wave function methods, being capable to describe correlation effects with good accuracy\textsuperscript{5,6}. Additional computational issues, such as the basis set superposition and the basis set incompleteness errors, must be properly taken into account as well\textsuperscript{6-8}. Finally, it must be considered that, because of the rather weak nature of non-covalent bonds, the description of non-covalent complexes cannot be restricted to the equilibrium geometry, but, in many cases, must be extended to include a more or less extended portion of the potential energy surface (PES).

Actually the method of choice for an accurate computational description of non-covalent complexes is the coupled cluster single and double with perturbative triple (CCSD(T)) approach\textsuperscript{9-15} with a complete basis set (CBS) description\textsuperscript{9}. This method provides in fact interaction energies with subchemical accuracy and yields errors often below 1 kcal/mol\textsuperscript{15}. Nevertheless, the CCSD(T) method is computationally very demanding, scaling as $\mathcal{O}(N^7)$, thus its applicability is limited to small complexes. On the other hand, lower level approaches, such as Møller-Plesset second-order perturbation theory (MP2)\textsuperscript{16,17} or even CCSD(T) calculations with a relatively small basis set, fail to describe various types of non-covalent interactions with the necessary accuracy. Therefore, continuous effort is dedicated to the development of new methods able of providing reliable results for non-covalent complexes at a reduced computational cost.

Recently one step in this direction has been performed by proposing a simple non-empirical scaling procedure for MP2 interaction energies which allows to obtain a full dissociation curve of CCSD(T) quality at the cost of a single CCSD(T) calculation\textsuperscript{18}. This method is based on an observed proportionality of the MP2 and CCSD(T) interaction energies which is maintained, with almost a constant factor, over a wide range on inter-molecular distances. Thus, accurate dissociation curves can be computed, with a precision of few hundreds of mHa, for many non-covalent complexes with a reduced effort. However, for high accuracy the proposed scaling procedure still requires one CCSD(T)/CBS calculation, which may be out of reach for larger scale applications.

In this paper we address this latest issue and propose a new methodology which joins the above mentioned scaling procedure with a basis set extrapolation scheme, so that finally highly accurate interaction energies can be computed by the sole requirement of relatively low-level calculations (e.g. MP2 and/or CCSD(T) with moderate basis sets). In this way a practical and efficient tool for large-scale application can be obtained.

II. METHOD

The main quantity of interest in this work is the correlation interaction energy. For calculations carried out with method X and using the basis set aug-cc-pV$n$Z it is denoted $\mathcal{E}^{(n)}_{X}$ and defined as the difference of the correlation energies ($E^{(n)}_{c,X}$, calculated using method X and basis set aug-cc-pV$n$Z, with $n=2,3,4,5$ i.e. D,T,Q,5) for a complex $AB$ and its constituent fragments $A$ and
According to Ref.\textsuperscript{17} the CCSD(T) correlation interaction energy of a non-covalent complex at any intermolecular separation $R$ is related to the MP2 correlation interaction energy by the simple equation

$$
\mathcal{E}_{\text{CCSD(T)}}^{(n)}(R) \approx c_n^{(n)} \mathcal{E}_{\text{MP2}}^{(n)}(R),
$$

where the factor $c_n^{(n)}$ is evaluated as

$$
c_n^{(n)} = \frac{\mathcal{E}_{\text{CCSD(T)}}^{(n)}(\tilde{R})}{\mathcal{E}_{\text{MP2}}^{(n)}(\tilde{R})},
$$

with $\tilde{R}$ being any reference point (for example, but not necessarily, the equilibrium inter-molecular separation $R_0$). Equations (2) and (3) allow to compute a full PES (with $N$ points) of CCSD(T) quality at the cost of a single CCSD(T) calculation (at distance $\tilde{R}$) and several (i.e. $N$) MP2 calculations.

When the CBS limit is considered, which formally corresponds to $n = \infty$, the scaling factor of Eq. (4) shall be computed as $c^{(\infty)} = \mathcal{E}_{\text{CCSD(T)}}^{(\infty)}/\mathcal{E}_{\text{MP2}}^{(\infty)}$, where both $\mathcal{E}_{\text{CCSD(T)}}^{(\infty)}$ and $\mathcal{E}_{\text{MP2}}^{(\infty)}$ have to be obtained via appropriate extrapolation formulas (e.g. Refs.\textsuperscript{26,40}). However, the bottleneck of this computational approach is certainly the calculation of $\mathcal{E}_{\text{CCSD(T)}}^{(\infty)}$. To avoid this we consider an alternative way to compute $c^{(\infty)}$. To this end we assume that the basis set evolution of the proportionality factor $c_n^{(n)}$ is described by the ansatz

$$
c_n^{(n)} = c^{(\infty)} + An^{-\alpha},
$$

where $A$ and $\alpha$ are assumed to be two system-dependent constants (note that they do not depend on $n$). A rationalization for this ansatz is given in A. A graphical impression of its accuracy for some typical non-covalent complexes is presented in Fig. 1. This figure shows in fact, for some selected complexes, the evolution of the values of the scaling factors $c_n^{(n)}$ with the basis set as well as the fit obtained via Eq. (4). We see that the postulated power behavior reproduces very well the trend of the computed scaling factors from $1/n = 0.5$ (aug-cc-pVDZ) to $1/n = 0$ (CBS limit).

In practice, we apply Eq. (4) for two given values of $n$ (we use $n = 2$ and $n = 3$) so that the CBS proportionality factor is given by the simple two-point formula

$$
c_{\text{approx}}^{(\infty)} = \frac{c^{(3)}3^{\alpha} - c^{(2)}2^{\alpha}}{3^{\alpha} - 2^{\alpha}},
$$

where the only unknown parameter, so far, is $\alpha$. Equation (5) allows to obtain an estimate for $c^{(\infty)}$ avoiding the computationally expensive calculation of $\mathcal{E}_{\text{CCSD(T)}}^{(\infty)}$, requiring at most the evaluation of $\mathcal{E}_{\text{CCSD(T)}}^{(3)}$, which is necessary to obtain $c^{(3)}$ from Eq. (4). On the other hand, the value of $\alpha$ should be, in principle system dependent. However, following Ref.\textsuperscript{28}, we will fix it by fitting to some appropriate training set (see later on). Hence, Eq. (4) becomes a universal formula for obtaining $c_{\text{approx}}^{(\infty)}$.

Using Eq. (5) it is possible to obtain a good approximation of $\mathcal{E}_{\text{CCSD(T)}}^{(\infty)}$ in a very efficient way via Eq. (2). Nevertheless, two possible variants can be considered:

- In a first approach, that we denote M1, we will use the best estimate available for $\mathcal{E}_{\text{MP2}}^{(\infty)}$ in practice, a cubic extrapolation formula\textsuperscript{9,28} using aug-cc-pVQZ and aug-cc-pV5Z data (other extrapolation formulas will not be considered here, since they will yield only slightly different results). Hence, the M1 correlation interaction energy is computed as

$$
\mathcal{E}_{\text{M1}}^{(\infty)} = c_{\text{approx}}^{(\infty)} \mathcal{E}_{\text{MP2}}^{(\infty)} \frac{5^3 - 2^3}{3^3 - 4^3},
$$

where $c_{\text{approx}}^{(\infty)}$ is given by Eq. (5) with $\alpha$ fitted on a training set to reproduce reference values of the $c$ coefficient at the reference CBS limit. Within this approach, to compute a full PES of $N$ points with CCSD(T)/CBS quality, the most computationally intensive steps required are one CCSD(T)/aug-cc-pVTZ calculation and $N$ MP2 calculations with large basis set (aug-cc-pV5Z in our case), one for each point of the PES.

- A cheaper method, which will be denoted M2, can be obtained using a simpler formula to evaluate $\mathcal{E}_{\text{MP2}}^{(\infty)}$. Doing this by means of the approach of Ref.\textsuperscript{28} we obtain

$$
\mathcal{E}_{\text{M2}}^{(\infty)} = c_{\text{approx}}^{(\infty)} \frac{\mathcal{E}_{\text{MP2}}^{(3)} 3^\gamma - \mathcal{E}_{\text{MP2}}^{(2)} 2^\gamma}{3^\gamma - 2^\gamma},
$$

where $c_{\text{approx}}^{(\infty)}$ is given by Eq. (5) with $\alpha$ fitted on a training set to reproduce reference values of the $c$ coefficient at the reference CBS limit.
TABLE I: Computed and extrapolated values of the proportionality factors $c^{(n)}$ for the systems of the training set.

| System | $c^{(2)}$ | $c^{(3)}$ | $c^{(\infty)}$ | $c_{M1}^{(\infty)}$ | $c_{M2}^{(\infty)}$ |
|--------|--------|--------|--------|--------|--------|
| He$_2$ | 1.262  | 1.261  | 1.248  | 1.261  | 1.261  |
| Ne$_2$ | 1.185  | 1.236  | 1.273  | 1.274  | 1.253  |
| He-Ne  | 1.229  | 1.266  | 1.274  | 1.294  | 1.279  |
| Ar$_2$ | 0.860  | 0.905  | 0.913  | 0.939  | 0.921  |
| (H$_2$O)$_2$ | 1.048  | 1.031  | 0.937  | 1.019  | 1.026  |
| (H$_2$S)$_2$ | 0.834  | 0.876  | 0.922  | 0.907  | 0.890  |
| (HF)$_2$  | 1.184  | 1.088  | 0.924  | 1.017  | 1.056  |
| (HCl)$_2$ | 0.791  | 0.846  | 0.853  | 0.887  | 0.865  |

TABLE II: Extrapolated correlation interaction energies (kcal/mol) for the systems of the training set computed with different methods. Reference values are CCSD(T)/CBS results. The last line reports the mean absolute error (MAE) and the mean absolute relative error (MARE).

| System | MP2-23 | CCSD(T)-23 | M1 | M2 | Ref |
|--------|--------|------------|----|----|-----|
| He$_2$ | -0.03  | -0.04 -0.04 -0.04 -0.04 |
| Ne$_2$ | -0.09  | -0.11 -0.11 -0.11 -0.11 |
| He-Ne | -0.06  | -0.08 -0.08 -0.08 -0.08 |
| Ar$_2$ | -0.67  | -0.61 -0.63 -0.61 -0.61 |
| (H$_2$O)$_2$ | -1.36  | -1.42 -1.39 -1.38 -1.27 |
| (H$_2$S)$_2$ | -2.21  | -2.04 -2.00 -2.04 -2.04 |
| (HF)$_2$  | -0.92  | -0.86 -0.93 -0.87 -0.85 |
| (HCl)$_2$ | -2.22  | -2.01 -1.97 -2.01 -1.90 |

MAE 0.09 0.04 0.04 0.03
MARE 14.1% 3.7% 3.6% 3.4%

where the value of the coefficient $\gamma = 1.91$ is taken from Ref.20 and $c_{M2}^{(\infty)}$ is given again by Eq. (4) with a proper value of $\alpha$ (see below). In this case only $c_{MP2}^{(3)}$ calculations instead of $c_{MP2}^{(5)}$ are required at most. Thus, the global computational cost of the whole procedure is practically reduced to the calculation of one $\varepsilon_{CCSD(T)}^{(3)}$ (to compute $c^{(3)}$ in Eq. (3)). Of course, in this case to obtain high accuracy it is not possible to use the same $\alpha$ value as for the M1 method (hence, we used the subscripts M1 and M2 to denote the scaling factors in the two methods). On the contrary, it must be determined by fitting to the CBS values of CCSD(T) reference correlation interaction energies, and not CBS limit $c$ values, in order to effectively take into account also the possible inaccuracies in the extrapolated MP2 energy.

III. COMPUTATIONAL DETAILS

All calculations have been performed using the PSI4 code18 and aug-cc-pVnZ basis sets19-22 with $n = D$, T, Q, and 5 (i.e., $n=2,3,4,$ and 5). In all cases frozen core and resolution of identity23 (for both Hartree-Fock and correlated calculations) approximations have been employed. All results include counterpoise correction24. In all calculations, unless otherwise stated, the extrapolation to the CBS limit has been performed using a two-point cubic formula based on aug-cc-pVQZ and aug-cc-pV5Z data25 (the corresponding results are indicated with the label method/CBS). On the other hand, extrapolated results denoted MP2-23 and CCSD(T)-23 have been obtained using the method and parameters reported in Ref.26. A similar notation is used for the scaling coefficients $c^{(n)}$ (see Eq. (3)).

For the parametrization and testing of the methods defined in this work we considered various small non-covalent complexes having different interaction characters. These include He$_2$, Ne$_2$, He-Ne, Ar$_2$, Ne-Ar, CH$_4$-Ne (dispersion interaction; D1), (H$_2$O)$_2$, (HF)$_2$, NH$_3$-H$_2$O, (NH$_3$)$_2$ (hydrogen bond; HB), (H$_2$S)$_2$, (HCl)$_2$, H$_2$S-HCl (dipole-dipole interaction; DD), HCN-CIF, NH$_3$-F$_2$ (charge-transfer interaction; CT), and LiH-HF (dihydrogen interaction; DH). The geometries of the complexes were taken from Refs.17,27-31. Finally, in addition, we considered the systems from the S22×5 test set32.

As reference benchmark data CCSD(T)/CBS results obtained extrapolating from aug-cc-pVQZ and aug-cc-pV5Z calculations or accurate CCSD(T)/CBS results from literature (when indicated). These accurate energies are employed to assess the accuracy of all the methods based on -23 extrapolation, i.e. our own methods as well as MP2-23 and CCSD(T)-23 calculations. Moreover, for completeness, we have considered also SCS(MI)-MP2/CBS33 and MP2.5/CBS34 interaction energies. These methods were in fact developed to “reproduce” CCSD(T) results at a cost close to MP2 calculations. Thus, it is in the same spirit as the ones developed in the present work.

A. Parametrization

To perform the fit required to fix the parameter $\alpha$ in both the M1 and M2 methods, we consider a training set composed of the following non-covalent complexes: He$_2$, Ne$_2$, He-Ne, Ar$_2$ (dispersion complexes), (H$_2$O)$_2$, (HF)$_2$ (hydrogen bond complexes), and (H$_2$S)$_2$, (HCl)$_2$ (dipole-dipole complexes), at equilibrium geometry. The values of $c^{(2)}$, $c^{(3)}$, and $c^{(\infty)}$ for the various systems are reported in Table II. Note that in Table II $c^{(\infty)}$ denotes the “true” CBS limit value of the scaling factor, computed as the ratio of the extrapolated CCSD(T)/CBS and MP2/CBS energies.

Considering method M1, we need to fit Eq. (5) to the
\[ c(\infty) \text{ values. Thus, we minimized the target function} \]
\[ \sigma_{M1}(\alpha) = \sum_i \left( c_{M1}(\alpha)[i] - c(\infty)[i] \right)^2, \tag{8} \]

where the sum runs over all the systems in the training set and the notation \( c_{M1}(\alpha)[i] \) indicates that we consider the \( c(\infty) \) value relative to system \( i \) and computed at a given value of \( \alpha \). Doing so we obtained \( \alpha = 2.1 \) and the \( c_{M1}(\alpha)[i] \) values reported in Table II. The fitted coefficients show a mean absolute error (MAE) of 0.035 and a mean absolute relative error (MARE) of 3.7% with respect to the \( c(\infty) \) ones. The corresponding correlation interaction energies, obtained using the M1 approach, are listed in Table II. They display a good agreement with the reference CCSD(T)/CBS energies having a MAE of 0.06 mHa and a MARE of 3.6%, being similar to CCSD(T)-23 extrapolated energies.

To fit for the M2 method we consider instead, as discussed before, as target values the reference CCSD(T)/CBS correlation interaction energies of Table II hence we minimize
\[ \sigma_{M2}(\alpha) = \sum_i \left( E_{M2}(\alpha)[i] - E_{CCSD(T)/CBS}[i] \right)^2, \tag{9} \]
where \( E_{M2}(\alpha)[i] \) depends on \( \alpha \) through \( c(\infty) \). This yields \( \alpha = 3.4 \) and the scaling factors displayed in the last column of Tab. II. When used in the M2 approach these yield the final M2 energies reported in Tab. III. These energies show by construction a very good agreement with reference values, having a MAE of only 0.05 mHa.

IV. RESULTS

To test the methods developed in the previous sections we applied them to the computation of the interaction energies of several non-covalent complexes. For completeness we considered energies both at the equilibrium distance \( R_0 \) and at elongated distances equal to 1.2\( R_0 \) and 1.5\( R_0 \). The values of the correlation interaction energies, obtained from various methods, are reported in Table III. In addition Fig. 2 reports the absolute error on the correlation interaction energy as obtained from different methods for some complexes, taken as examples, including also shorter (i.e. 0.9\( R_0 \)) and larger (i.e. up to 2.0\( R_0 \)) distances.

Inspection of the table and the figure shows that both the M1 and the M2 methods perform very well for the test set, being competitive with CCSD(T)-23 and MP2.5/CBS, at all distances, and superior to MP2-23 and SCS(MI)-MP2/CBS. In more detail, the M1 method seems to perform slightly better than M2 for hydrogen-bond complexes at equilibrium distance, while M2 gives better results for dispersion complexes and in general at displaced geometries. These differences are however rather small and shall be considered with caution due to the small dimension of the test set. We recall that both methods have a computational cost comparable with CCSD(T)-23 when a single bond distance (e.g. \( R = R_0 \)) is considered and smaller than it when several bond-distances are involved. In particular the M2 method as a computational cost almost comparable to MP2-23 (and SCS(MI)-MP2/CBS), but an accuracy close to CCSD(T)-23. Note however that some the methods considered here are based on extrapolation form triple-zeta quality basis sets at most. Thus, it may happen that they display shortcoming for some systems where this level of basis set is not fully sufficient to describe the correlation effects. This appears to be the case, for example of the HCN-CIF complex which shows a quite larger relative error than other complexes, especially at \( R = 1.5 R_0 \), possibly because of the limitations of the aug-cc-pVTZ basis set to describe correlation in the CIF molecule.

As a further and more extended test we consider in Fig. 3 (see also supporting information), for the methods requiring at most triple-zeta basis set calculations, the absolute errors with respect to accurate values of correlation interaction energies for the complexes of the S22 test set for \( R_0 \), 1.2 \( R_0 \), and 1.5 \( R_0 \). Accurate reference correlation interaction energies have been obtained by subtracting CBS Hartree-Fock values from the benchmark energies of Ref. 32. Statistics for these data are summarized in Table IV. Finally, a comparison of total interaction energy errors with several literature results is also reported in Fig. 4. The plots reported in the figure as well as the data of Table IV confirm the results of Tables II and III showing that the M2 method is competitive with the CCSD(T)-23 approach, as well as with other high level methods (e.g. accurate MP2.5, MP2C, or SCS-CCSD) and can clearly improve over the MP2-23 and...
TABLE III: Computed and extrapolated correlation interaction energies (kcal/mol) for the systems of the test set at different intermolecular distances ($R_0$ denotes equilibrium distance). Reference values are CCSD(T)/CBS results. The label SCS(MI) stands for SCS(MI)-MP2/CBS. In the second column the interaction character for each complex is reported. The last line reports the mean absolute error (MAE) and the mean absolute relative error (MARE).

| System      | Interaction | MP2-23   | SCS(MI)  | MP2.5/CBS | CCSD(T)-23 | M1     | M2     | Ref. |
|-------------|-------------|----------|----------|-----------|------------|--------|--------|------|
| HCN-ClF     | CT          | -3.90    | -2.72    | -3.11     | -2.83      | -2.81  | -2.82  | -2.68|
| NH$_3$F$_2$ | CT          | -2.33    | -1.56    | -2.08     | -2.08      | -2.10  | -2.09  | -2.09|
| LiH-HF      | DH          | -3.60    | -2.65    | -2.85     | -3.06      | -2.97  | -3.03  | -2.87|
| NH$_3$H$_2$O| HB          | -2.17    | -1.72    | -2.09     | -2.08      | -2.06  | -2.10  | -1.96|
| (NH$_3$)$_2$| HB          | -1.70    | -1.27    | -1.64     | -1.66      | -1.60  | -1.61  | -1.57|
| HCl-H$_2$S  | DD          | -3.27    | -2.45    | -2.97     | -2.67      | -2.59  | -2.68  | -2.55|
| CH$_4$-Ne   | DI          | -0.28    | -0.17    | -0.29     | -0.30      | -0.33  | -0.29  | -0.29|
| Ne-Ar       | DI          | -0.29    | -0.08    | -0.29     | -0.24      | -0.24  | -0.24  | -0.24|

MAE 0.41 0.21 0.14 0.09 0.06 0.08
MARE 18.8% 22.7% 7.9% 4.2% 4.0% 3.7%

$R = R_0$

| System      | Interaction | MP2-23   | SCS(MI)  | MP2.5/CBS | CCSD(T)-23 | M1     | M2     | Ref. |
|-------------|-------------|----------|----------|-----------|------------|--------|--------|------|
| HCN-ClF     | CT          | -1.12    | -1.40    | -0.84     | -0.64      | -1.07  | -0.81  | -0.90|
| NH$_3$F$_2$ | CT          | -0.76    | -0.81    | -0.68     | -0.58      | -0.85  | -0.68  | -0.74|
| LiH-HF      | DH          | -1.99    | -2.26    | -1.80     | -1.52      | -1.84  | -1.68  | -1.73|
| NH$_3$H$_2$O| HB          | -1.02    | -1.10    | -0.98     | -0.91      | -1.09  | -0.99  | -0.93|
| (NH$_3$)$_2$| HB          | -0.78    | -0.78    | -0.76     | -0.68      | -0.83  | -0.77  | -0.70|
| HCl-H$_2$S  | DD          | -1.36    | -1.39    | -1.22     | -0.97      | -1.10  | -1.11  | -1.08|
| CH$_4$-Ne   | DI          | -0.07    | -0.14    | -0.07     | -0.06      | -0.10  | -0.08  | -0.09|
| Ne-Ar       | DI          | -0.04    | -0.08    | -0.04     | -0.04      | -0.07  | -0.04  | -0.06|

MAE 0.12 0.21 0.06 0.11 0.09 0.05
MARE 16.2% 30.7% 11.3% 19.1% 14.6% 9.1%

$R = 1.2R_0$

| System      | Interaction | MP2-23   | SCS(MI)  | MP2.5/CBS | CCSD(T)-23 | M1     | M2     | Ref. |
|-------------|-------------|----------|----------|-----------|------------|--------|--------|------|
| HCN-ClF     | CT          | -0.34    | -0.25    | -0.26     | -0.05      | -0.22  | -0.17  | -0.11|
| NH$_3$F$_2$ | CT          | -0.19    | -0.21    | 0.17      | -0.16      | -0.21  | -0.18  | -0.21|
| LiH-HF      | DH          | -0.71    | -1.04    | -0.64     | -0.51      | -0.72  | -0.60  | -0.65|
| NH$_3$H$_2$O| HB          | -0.28    | -0.31    | -0.26     | -0.24      | -0.26  | -0.28  | -0.27|
| (NH$_3$)$_2$| HB          | -0.21    | -0.21    | -0.20     | -0.19      | -0.21  | -0.21  | -0.21|
| HCl-H$_2$S  | DD          | -0.35    | -0.37    | -0.30     | -0.23      | -0.31  | -0.29  | -0.31|
| CH$_4$-Ne   | DI          | -0.01    | -0.02    | -0.01     | -0.01      | -0.02  | -0.01  | -0.02|
| Ne-Ar       | DI          | -0.01    | -0.01    | -0.01     | -0.02      | -0.01  | -0.01  | -0.02|

MAE 0.04 0.08 0.03 0.04 0.03 0.03
MARE 37.5% 33.6% 28.0% 22.9% 16.4% 17.9%

SCS(MI)-MP2/CBS results. We remark that this performance is obtained for all distances by requiring only a single CCSD(T)/aug-cc-pVTZ calculation. Moreover, although no clear systematic trend can be obtained for the accuracy of different methods versus the bonding character type, we remark that the observed behavior of M2 is rather consistent for all the complexes and distances with CCSD(T)-23, being even slightly superior for dispersion complexes. On the contrary, MP2-23 appears rather accurate only for hydrogen bond complexes. Finally, we remark that for $d = R_0$, where more accurate reference data than those in Ref. are available, the results do not change substantially when the best reference values are used. In fact, in this latter case the MAEs (MAREs) of MP2-23, SCS(MI)-MP2/CBS, CCSD(T)-23, and M2 are 1.13 (19.5%), 0.70 (14.5%), 0.28 (6.0%), and 0.31 (6.7%), respectively, in good agreement with the values reported in Table IV.
V. CONCLUSIONS

We have proposed efficient scaling procedures to compute accurate correlation interaction energies of non-covalent complexes. Our methods are based on the observed proportionality between MP2 and CCSD(T) interaction energies as well as on simple basis set extrapolation formulas. In this way correlation interaction energies of CCSD(T)/CBS quality can efficiently be obtained from few MP2 and CCSD(T) calculations using small basis sets. If several bonding distances are of interest, as in PES scanning studies, even a lower computational cost is achieved by exploiting the (almost) constancy of the scaling factors with respect to inter-molecular distance. Thus, the present methods, and in particular the M2 one, represent promising tools for future studies of large non-covalent systems, e.g. in biochemistry.

Nevertheless, future developments can be foreseen starting from the present results, especially to improve further the overall computational efficiency. In this sense, it will be particularly interesting to consider the ex-
tension of the present methodology to scaled-opposite-spin (SOS) MP2 calculations. In fact, the SOS-MP2 method can be implemented with a favorable $O(N^4)$ scaling (as opposed to the $O(N^5)$ of conventional MP2) and also displays a proportionality with accurate correlation results.

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Appendix A: Rationalization of Eq. (4)

Following Refs. we can write

$$E_{\text{CCSD(T)}}^{(n)} = E_{\text{MP2}}^{(\infty)} + Bn^{-\beta} \quad (A1)$$

where $B$, $C$, $\beta$, and $\gamma$ are constants. Taking the ratio of the two equations we find

$$\frac{E_{\text{CCSD(T)}}^{(n)}}{E_{\text{MP2}}^{(n)}} = \frac{E_{\text{CCSD(T)}}^{(\infty)}}{E_{\text{MP2}}^{(\infty)}} + Bn^{-\beta}$$

$$= \frac{E_{\text{CCSD(T)}}^{(\infty)}}{E_{\text{MP2}}^{(\infty)}} + \frac{B}{1 + Cn^{-\gamma}} \quad (A3)$$

with $\tilde{B} = B/E_{\text{MP2}}^{(\infty)}$ and $\tilde{C} = C/E_{\text{MP2}}^{(\infty)}$ (note these are constants with respect to $n$). Now observing that

$$\left| \frac{\tilde{C}n^{-\gamma}}{E_{\text{MP2}}^{(\infty)} - 1} \right| < 1 \quad (A4)$$

we can write

$$e^{(n)} \approx e^{(\infty)} + \tilde{B}n^{-\beta} \left[ 1 - \tilde{C}n^{-\gamma} + O\left(\tilde{C}^2n^{-2\gamma}\right) \right] \approx$$

$$\approx e^{(\infty)} + \tilde{B}n^{-\beta} - e^{(\infty)}\tilde{C}n^{-\gamma} \quad (A5)$$

Finally, considering that $\beta \sim \gamma$ (see Refs.) we can define two new constants $\beta \sim \gamma \sim \alpha$ and $A = B - e^{(\infty)}C$ and obtain

$$e^{(n)} \approx e^{(\infty)} + An^{-\alpha} \quad (A6)$$

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