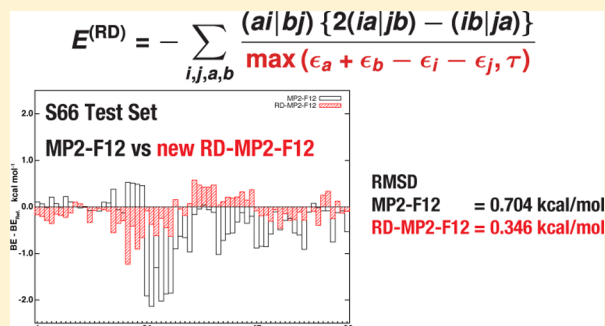


Interaction Energy of Large Molecules from Restrained Denominator MP2-F12

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S Supporting Information

ABSTRACT: A new one-parameter correction scheme to second-order Møller–Plesset many-body perturbation theory (MP2) has been proposed to correctly evaluate intermolecular interaction energies of large π – π dispersion interaction systems as well as hydrogen-bonded and σ – σ dispersion interaction ones. The scheme restrains the denominator of the MP2 correlation energy expression based on the observation that larger corrections to MP2 are required as the orbital energy gaps become small as in large π – π stacking systems. The root-mean-square-deviation of the restrained denominator MP2 with F12 correction (RD-MP2-F12) on the S66 set of 0.346 kcal/mol is less than half of that of MP2-F12. The interaction energies of RD-MP2 are similar to those of dispersion corrected density functional theory for a series of polyaromatic hydrocarbon dimers. For the C₆₀-fullerene dimer, however, the RD-MP2-F12 result somewhat deviates from the experimental estimate, indicating that an explicit inclusion of higher order correlation is required for the system.



1. INTRODUCTION

Accurate calculation of large molecular systems based on electronic structure theory is still one of the major challenges in quantum chemistry. Such calculations are indispensable to investigate complicated electronic and molecular structures of metalloenzymes, organic electronic devices, metal clusters, and so on. To this end, we have to care about both the accuracy of theory itself and the quality of the basis sets employed in the calculations. The former is guaranteed by using so-called post Hartree–Fock (HF) theory such as many-body perturbation, coupled-cluster (CC), and various multireference methods.¹ In addition, quantum Monte Carlo methods are also becoming popular in recent years.^{2–5} For the basis set convergence, the explicitly correlated F12 theory has been developed to combine with the correlated methods.^{6–10} F12 with augmented triple- ζ quality of basis sets provides reaction enthalpies almost equivalent to those in the complete basis set (CBS) limit.

Although the computational scheme to achieve highly accurate quantum chemical calculations is available in principle, application of these theories to large systems including more than a hundred atoms is not easy because of computational cost and memory requirement. One way to transcend the limitation is to employ massively parallel computing architectures with thousands of central processing units (CPUs). We have implemented second-order Møller–Plesset perturbation theory (MP2) based on numerical quadratures¹¹ and MP2-F12¹² for massively parallel computers mainly to investigate the intermolecular interactions of large molecules, which can be one of the most important factors to determine the performances of organic electronic

devices. It is, however, well-known that MP2 tends to overestimate the dispersion interaction of conjugated molecules. Several correction schemes to improve the accuracy have been proposed such as the spin component scaled (SCS) method of Grimme,¹³ scaled opposite spin (SOS) method of Jung et al.,¹⁴ and their relatives.¹⁵ SCS works well for the evaluation of interaction energies of small π – π dispersion interaction systems (e.g., benzene dimer), while σ – σ dispersion interactions are frequently overcorrected.^{17,18} For the latter, the conventional MP2 generally presents results closer to the CC singles and doubles with perturbational triples (CCSD(T)). In addition, the SCS correction seems weak in the magnitude for larger π – π interaction systems such as coronene dimer.^{19,20} In this study, we investigate the interaction energies of several sizes of π – π interacting molecules with a new correction scheme based on the above observations.

This paper is organized as follows: the new correction scheme is introduced in the next section. After explaining the computational details in the third section, the results by the new correction scheme are presented on the S66 test set,¹⁸ several polyaromatic hydrocarbon (PAH) dimers, and fullerene dimers in the fourth section, followed by the conclusion.

2. THEORY

The conventional MP2 method overestimates the binding energies of π – π dispersion interaction, while reasonable results are

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obtained for hydrogen-bonded and σ – σ dispersion interaction systems.^{16–19} SCS-MP2 basically exhibits an opposite trend (i.e., the method is accurate for small π – π interaction systems), while the dispersion interactions are underestimated for hydrogen-bonded and aliphatic systems.¹⁸ In addition, the precision of the SCS correction is not obvious for larger π – π interaction systems. In fact, Jankowski and Pulay¹⁹ reported significant difference between the SCS-MP2 and CCSD(T) binding energies for the coronene dimer (23.45 and 17.67 kcal/mol with the double- ζ quality of basis set, respectively). The system dependency of the SCS applicability indicates the necessity of a nonuniform correction to individualize correlation components.

The above features might be ameliorated by exploiting the orbital energy differences between the occupied and virtual orbitals. As the size of π system increases, the orbital energy gap becomes smaller. The MP2 energy artificially diverges toward the metallic limit due to the energy denominator in the perturbation energy expression, while the real dynamic correlation should be finite.²¹ This gives rise to the overestimation of π – π dispersion interaction. The simplest way to avoid the denominator problem is to introduce the restraints on the orbital energy differences,

$$E_{\text{corr.}}^{\text{RD-MP2}} = - \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \frac{(aibj)[2(aibj) - (ajbi)]}{\max(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j, \tau)} \quad (1)$$

where the standard notations for two-electron integrals and occupied/virtual orbitals are employed. In this particular work, we use the threshold $\tau = 65$ eV, which is empirically determined in such a way that the absolute deviations from the CCSD(T) binding energies are minimized for the π – π benzene and σ – σ pentane dimers. Hereafter, we call this scheme the restrained denominator MP2 (RD-MP2). The analytic energy gradient of RD-MP2 can be discontinuous when the expression includes a denominator exactly equal to τ . This shortcoming can be side-stepped by introducing a smoothing function in the restraints, which will not be discussed in the present study. For explicit electron correlation, the standard F12 correction for MP2 can be applied to RD-MP2 without modification because the slow basis set convergence is originating from high angular momentum excitations with orbital energy differences much larger than τ . The F12 corrections of the same- and opposite-spin contributions are scaled separately for SCS-MP2-F12.

Recently, Shepherd and co-workers investigated the correlation energies of the MP2, random phase approximation, and CCSD methods for the homogeneous electron gas,^{22,23} changing the band gap with fixed number of plane waves. It is demonstrated that the correlation energy of the MP2 method diverges in the thermodynamic limit while CCSD is convergent to a constant energy (Figure 2b of ref 22). The crossover between the MP2 and CCSD correlation behaviors is around 35 eV. Twice that of this gap, $2E_{\text{gap}} = 70$ eV, corresponds to the restraint parameter in RD-MP2 suggested from homogeneous electron gas, which is quite close to $\tau = 65$ eV, empirically determined in this work. It is noted that the same authors proposed the use of a range-separation in Brueckner coupled cluster theory,²³ which is beyond the scope of this paper.

3. DETAILS OF COMPUTATION AND IMPLEMENTATION

Interaction energies of the S66 test set molecules and PAH dimers are calculated with MP2-F12,^{24,25} SCS-MP2,¹³ and B3LYP-D3(BJ),²⁶ where BJ stands for the Becke–Johnson

damping factor.^{27–29} In the evaluation of the interaction energy of fullerene dimer, HF, B3LYP,^{30–33} scaled opposite spin MP2 (SOS-MP2),¹⁴ S2-MP2³⁴ (using a redefined unperturbed Hamiltonian including \hat{S}^2 operator for the scaling parameters), SCS-MP2-vdW³⁵ (parameters are optimized for van der Waals interaction of ethylene dimer), second-order Feenberg scaling MP2 (FE2-MP2),³⁶ SOS- π -MP2³⁷ (SOS parametrized for stacked π -complexes), SCS for molecular interaction (SCS(MI)-MP2),³⁸ and SCS for nucleobases (SCSN-MP2)³⁹ are also examined.

Dunning's aug-cc-pVTZ basis set⁴⁰ is employed in most of molecular orbital calculations, while aug-cc-pVDZ is used for the C₆₀ fullerene dimer in order to save the computation time. We confirmed that there is no significant difference in the interaction energy of the fullerene dimer between the aug-cc-pVDZ and aug-cc-pVTZ basis sets if the counterpoise corrections⁴¹ are applied properly for the basis set superposition error (BSSE), as summarized in Supporting Information. DFT and DFT-D calculations are performed with 6-311G(d,p)⁴² and 6-31G(d)^{43,44} for PAHs and fullerene dimer, respectively.

HF and MP2-F12 calculations are performed with the development version of the GELLAN⁴⁵ program on the K computer at the RIKEN Advanced Institute for Computational Science in Kobe, Japan. The DFT calculations are performed with Gaussian 09⁴⁶ on Xeon workstation. The dispersion corrections are separately estimated using the DFT-D3 program^{26,47} by Grimme et al. The Euler–Maclaurin and Lebedev schemes⁴⁸ are employed for the radial and angular parts of the numerical integration in MP2-F12. We use the medium fine (MFine) grid consisting of 2830 and 4558 points per one hydrogen and carbon atoms, respectively, for PAH and C₆₀. The accuracy of the grid is given in Supporting Information. In the calculation of the S66 test sets, we employ the ultra fine (UFine) grid with 23842 and 9340 points for second row and hydrogen atoms, respectively.

The massively parallel implementation of MP2-F12 basically resembles the numerical MP2 reported by us previously.¹¹ Grid-based molecular orbital (MO) amplitudes, two- and three-center integrals are calculated by distributing the quadrature points. Then, the message passing interface (MPI) processes switch to deal with partial pair functions over the occupied orbitals in terms of objects with full information on quadrature indices. The necessary redistribution is performed by Allgather and SendRecv functions. Various F12 objects are efficiently calculated by DGEMM for the summation over quadrature points from the redistributed MO amplitudes and integrals in each MPI process. Although the above scheme includes slightly complicated SendRecv, the communication is not a serious problem on a computer with efficient internode connection. The details of the algorithms will be reported elsewhere.¹²

The geometries of PAH monomers (benzene, naphthalene, anthracene, pyrene, coronene, and ovalene) are optimized at ω B97X-D⁴⁹/6-31G(d), and the interaction energies are calculated fixing the monomer geometries. The C₆₀ fullerene has two bond lengths, r_{HH} and r_{PH} , where HH and PH stand for the bond connecting two hexagons and that between the pentagon and hexagon, respectively. These lengths are manually optimized at the MP2-F12/aug-cc-pVTZ (1s core frozen). The results of MP2/DZP (1.412, 1.451 Å) and MP2/TZP (1.406, 1.446 Å)⁵⁰ are not saturated at the second and third decimal places, respectively, compared to the present MP2-F12 result in the near CBS limit, $r_{\text{HH}} = 1.402$ and $r_{\text{PH}} = 1.441$ Å, slightly deviating from the experimental estimates, $r_{\text{HH}} = 1.38(2)$ and $r_{\text{PH}} = 1.454(12)$ Å.⁵¹ The geometries of the molecules in the

Table 1. RMSD of the Listed Methods with Respect to the CCSD(T)/CBS Calculations on the S66 Test Set

method	RMSD (kcal/mol)	ref.
MP2-F12 ^a	0.704	this work
RD-MP2-F12 ^a	0.346	this work
MP2/CBS	0.69	18
SCS-MP2/CBS	0.87	18
SCS(MI)-MP2/CBS	0.38	18

^aThe aug-cc-pVTZ basis set is used.

S66 test set are taken from the Supporting Information of ref 18.

4. RESULTS AND DISCUSSION

4.1. S66 Test Set. We first investigate the performance of RD-MP2-F12 on the S66 test set, which is designed to measure the performance for interaction energies including hydrogen-bonded, π - π and σ - σ dispersion, and their mixtures. The root-mean-square deviations (RMSD) of this study and representative results from ref 18 are summarized in Table 1. As reported by Hobza et al., MP2/CBS and MP2-F12/aug-cc-pVTZ give

reasonable results for the hydrogen-bonded and σ - σ dispersion interaction systems, while the π - π dispersion interactions are significantly overestimated with large RMSD about 0.7 kcal/mol. The RMSD of SCS-MP2 is larger than that of conventional MP2 due to the increased errors for hydrogen-bonded and σ - σ dispersion interaction systems. RD-MP2-F12 performs overall satisfactorily notwithstanding the fact that the restraint threshold τ is optimized only for the benzene and pentane dimers. The RMSD of RD-MP2-F12 is slightly smaller than the SCS(MI) one, in which the parameters are specially optimized for the intermolecular interaction on the S22 test set. More detailed results for the individual interaction energies are provided in Supporting Information.

4.2. Polyaromatic Hydrocarbon Dimers. Next, we discuss the results for PAHs. All intermolecular interaction energies are calculated in the sandwich conformations in D_{2h} point group symmetry. Figure 1 shows the interaction energies as functions of the distance R between the two planes of PAHs. For the benzene dimer (Figure 1a), all results except MP2-F12 are consistent with the CCSD(T) reference.⁵² The same trends are observed for the naphthalene dimer (Figure 1b) albeit the SCS-MP2-F12 result becomes somewhat more attractive

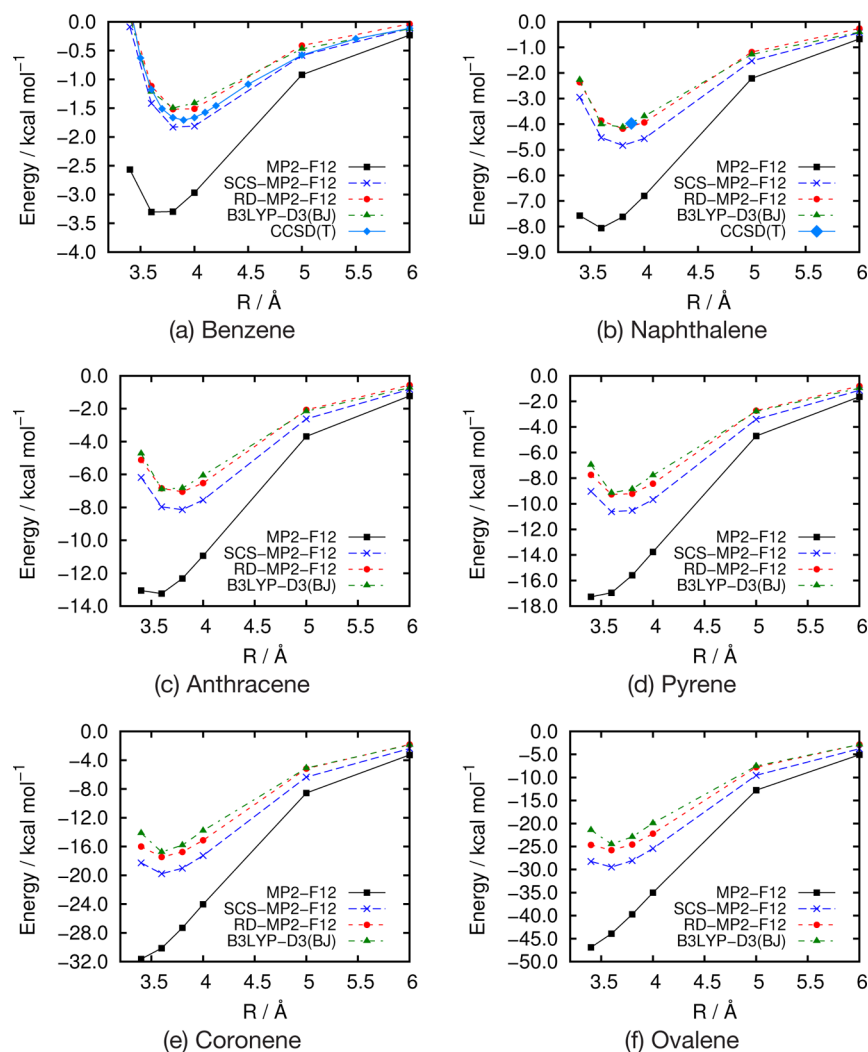


Figure 1. Intermolecular interaction energies of (a) benzene, (b) naphthalene, (c) anthracene, (d) pyrene, (e) coronene, and (f) ovalene dimers of D_{2h} conformation in kcal/mol calculated by the MP2-F12, SCS-MP2-F12, RD-MP2-F12, and B3LYP-D3(BJ) methods. The CCSD(T) results available for benzene⁵² and naphthalene¹⁹ dimers.

compared to the others. Comparisons with the CCSD(T) curves along with the result of Janowski and Pulay¹⁹ indicate that B3LYP-D3(BJ) is quite reliable for the binding energies of PAHs. This is also supported by the results obtained for the fullerene dimer as shown later.

As the π system becomes larger, the deviation of SCS-MP2-F12 from RD-MP2-F12 and B3LYP-D3(BJ) increases as shown in Figures 1c–f. RD-MP2-F12 resembles the intermolecular interaction energies of B3LYP-D3(BJ) in all cases. The deviations of SCS-MP2-F12 and RD-MP2-F12 from the B3LYP-D3(BJ) result at $R = 3.6$ Å are about 5 and 1 kcal/mol, respectively. It is indicated that RD-MP2 is capable of predicting reasonable interaction energies for the large PAHs.

4.3. C_{60} Fullerene Dimer. Finally, we discuss the applicability of RD-MP2-F12 to the C_{60} fullerene dimer in the P–P conformation, in which pentagons are facing each other as shown in Figure 2. It is noted that this is one of the most stable

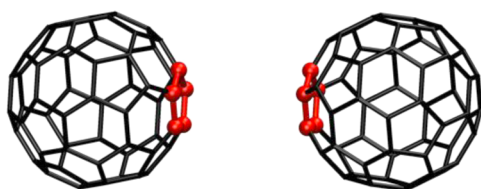
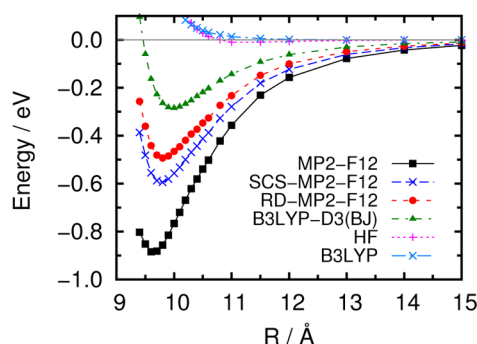


Figure 2. P–P conformations in the calculation of intermolecular interaction energy of fullerene dimer. The nearest carbon atoms are indicated by red-colored ball-and-stick.

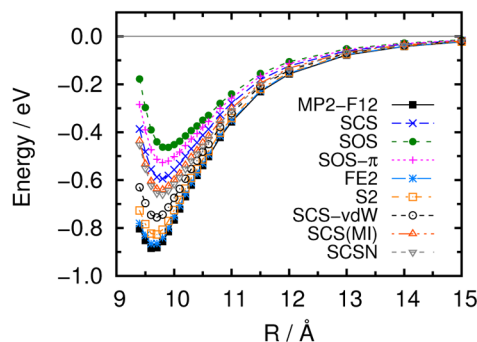
conformers of the C_{60} dimer.⁵³ Although the direct measurement of the intermolecular interaction of the fullerene dimer has not been reported to our best knowledge, the equilibrium distance between the centroid of fullerenes and binding energy are experimentally estimated to be around 9.93 Å and 0.28 eV, respectively, from the lattice constant of the fcc crystal⁵⁴ and heat of sublimation of fullerite.⁵⁵

The results from DFT and MP2 methods are depicted in Figure 3a. The HF and B3LYP methods do not show attractive potential energy curves. Contrarily, the binding energy of MP2-F12, ca. 0.9 eV, is a significant overestimate in comparison with the value estimated from the experimental measurements, 0.28 eV. Although SCS-MP2-F12 (blue cross in Figure 3a) improves the result of MP2-F12, the binding energy is still twice as large as the experimental value. The calculated binding energy and equilibrium distance from B3LYP-D3(BJ) are 0.28 eV and 10.0 Å, respectively, in agreement with experiment. Although RD-MP2-F12 outperforms the other second-order correction methods, it is not sufficient to fill the gap from experiment for the fullerene dimer system.

We note that none of the correction schemes presents a reasonable potential energy curve for the fullerene dimer as shown in Figure 3b. Even SOS-MP2-F12 (green filled circle) with the smallest binding energy, 0.48 eV, still overestimates the experimental value. The small gaps between the occupied and virtual orbitals are likely to cause the difficulty in the accurate calculation of fullerene by the MP2-based methods. The HOMO–LUMO gap of fullerene calculated at RHF/cc-pVDZ is 6.88 eV. This value is significantly smaller than those of benzene (12.84 eV) and naphthalene (10.32 eV), for which the RD scheme works well. Although the ovalene has as small gap of 7.15 eV as fullerene, the deviation of the RD-MP2 interaction energy of the ovalene dimer from B3LYP-D3 is much smaller than that for the fullerene dimer. In fullerene, due to the



(a) HF, Selected MP2, and B3LYP-D3(BJ) methods



(b) Various corrected MP2 methods

Figure 3. Intermolecular interaction energies of fullerene dimer in the P–P conformation calculated by various methods denoted in the figures. The “-MP2-F12” is omitted from the graph legend of the (b) for the sake of the clarity. For the B3LYP and B3LYP-D3(BJ) methods, 6-31G(d) basis set were employed and aug-cc-pVDZ was employed for the others.

degenerated HOMOs and LUMOs, there exists several orbital pairs having the small gap and it is reasonably considered that this gives rise to the instability of the MP2-based methods. In fact, Jiménez-Hoyos et al. reported that the broken symmetry solution is more stable than the RHF in fullerene and polyradical character is theoretically predicted.⁵⁶ For fullerene, further investigation will be needed by the calculation including higher order correlation effects or a multireference method.

5. CONCLUSIONS

The restrained denominator (RD) correction scheme to the second-order Møller–Plesset many-body perturbation theory (MP2) has been proposed. In RD-MP2, the denominator of the MP2 correlation energy expression is replaced with a constant when the absolute value of the denominator is smaller than the constant threshold. The restraint parameter was empirically determined such that the RD-MP2 method by minimizing the error in the binding energies of benzene dimer and pentane dimer from the CCSD(T) references. The RMSD of RD-MP2-F12 on the S66 test set was slightly smaller than that of the SCS(MI) method, whose parameters were specially optimized for the intermolecular interaction on the S22 test set. The RD-MP2 method also presents reasonable binding energies for the series of polyaromatic hydrocarbons dimers from benzene to ovalene compared to the B3LYP-D3(BJ) method. For the fullerene dimer, however, any second-order correction schemes involving RD-MP2 gave large deviations from the experimental and the B3LYP-D3(BJ) results indicating that explicit inclusion of higher order correlation effects is inevitable for the system.

■ ASSOCIATED CONTENT

■ Supporting Information

All the interaction energies of the S66 test set, the Cartesian coordinates of the polyaromatic hydrocarbons and C₆₀ monomers, and the basis set and grid size dependences of the interaction energy of fullerene dimer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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