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Systematic Analysis of Bond Energies Calculated by the Integrated Molecular Orbital−Molecular Orbital Method

Elena L. Coitiño† and Donald G. Truhlar*

Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431

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This paper tests the ability of the integrated molecular orbital−molecular orbital (IMOMO) method to include the effects of extended basis sets and higher-order electron correlation on bond energies by treating only a capped subsystem of a large molecule at a high level and integrating this with a lower-level calculation on the entire system. First, our results show that improving the basis on the capped subsystem is an excellent way to improve the bond energy without the expense of using a large basis set for the whole system. In a second study, we show that correlated calculations on a capped subsystem with the Hartree−Fock (HF) approximation for the entire system yield results that are within 1 kcal/mol of CCSD(T)/6-31G(d,p) accuracy for a set of molecules involving first-row atoms. For chloroethane, though, the HF level is inadequate for such a treatment, and the calculations have an error of about 3 kcal/mol with respect to a full CCSD(T)/6-31G(d,p) calculation. However, for this case, using even a low level of electron correlation, such as Møller−Plesset second-order perturbation theory (MP2), for the entire system makes it possible to achieve high accuracy. A final set of results show how well we can get an accuracy comparable to MP2/6-31G(d,p) by using only Hartree−Fock calculations for the entire system. Such an integrated strategy, using a double-zeta basis set, is good enough for obtaining MP2/6-31G(d,p) accuracy within 1 kcal/mol for all the molecules investigated except difluoroethane and chloroethane.

1. Introduction

Quantum mechanical electronic structure theory has made great strides in recent years, and it has become possible to calculate bond energies and heats of formation to an accuracy of about 1 kcal/mol even for systems with up to about six non-hydrogen atoms.[1,2] In many cases though one wishes to treat even larger systems. For the calculation of bond dissociation energies, our chemical intuition tells us that we should not need to treat the whole molecule as accurately as the atoms involved in or close to the breaking bond. However, all practical electronic structure methods are based on orbitals, and the incorporation of gradations of accuracy into a quantum mechanical scheme in a systematic and reliable way has proved elusive due to the delocalized nature of optimized electronic orbitals in most practical methods.

Recently, Morokuma and co-workers have proposed a dual-level strategy called the integrated molecular orbital−molecular orbital (IMOMO) method in which one combines high-level and low-level quantum mechanical calculations on a model system (which is a capped subsystem of the original system) with low-level quantum mechanical calculations on the entire original system.[3,4] (The original version of this method, called IMOMM,[5−7] employed classical force fields for the low level.) A special case of the IMOMO method is the class of methods where the high level includes electron correlation, in which case the model system is a "correlated capped small system" or CCSS.[4,8,9] The low level either neglects electron correlation or includes it with a smaller basis set and/or a more affordable, but less reliable, theoretical level. We have tested the CCSS approach for the calculation of bond energies and substituent effects on bond energies, and we found that it can be a powerful tool for achieving the objective of treating different parts of a system at different levels of accuracy.[8,9]

Our previous tests[8,9] involved using many-body perturbation theory (MBPT),[10] the coupled-cluster (CC) method,[11] quadratic configuration intersection (QCI),[12] and spin-projected MBPT[13] as the upper level and semiempirical molecular orbital theory,[14] Hartree−Fock (HF) theory,[15] and density functional theory (DFT)[16] as the low level. The present paper provides a series of further tests of the IMOMO formulation for the calculation of bond energies, and in particular it presents very systematic tests for the case where the upper level is an HF or correlated calculation and the lower level is an HF, MBPT, or spin-projected MBPT calculation. A special aspect not studied previously is the case where HF theory is used for both the upper and lower levels, but with a larger basis set for the former, and the goal is to learn how well the IMOMO method can make up for not using the larger basis set on the entire system.

The present studies of bond energies are of interest in their own right, and in addition the electronic factors that determine bond energies also affect more complicated features of potential energy surfaces such as barrier heights, so tests of the predictive ability of the method for bond energies is a systematic first step toward exploring its usefulness in a more general context as well. In fact, bond breaking is a more dramatic event than bond rearrangement, and so the present test is a difficult and challenging one.

In general, the goal of computational chemistry is to predict or interpret experimental results. In this paper though, we do not compare to experiment because our goal is more methodological. We want to develop and test more efficient ways to carry out a given type of large-scale calculation for a specified system. Experiment is relevant, though, in our choice of methods. For example, we choose to study the CCSD(T) method (see below) because it is known to yield accurate

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† On leave of absence from Laboratorio de Química Teórica y Computacional, Facultad de Ciencias, Universidad de la República, Tristán Narvaja 1674, Montevideo 11200, Uruguay. E-mail: coitino@t1.chem.umn.edu.

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thermochemistry for small molecules.[17] We then ask, how can we make such calculations affordable and carry them out efficiently for larger systems?

2. Calculations

The theory is explained elsewhere.[3,4,8,9] The integrated energy E for the entire system (ES) is given by

$$E(\mathrm{I{:}HL{:}LL,ES}) = E(\mathrm{HL,CSS}) - E(\mathrm{LL,CSS}) + E(\mathrm{LL,ES}) \qquad (1)$$

where CSS denotes the capped small system, HL denotes the high level, and LL denotes the low level. We consider the bond energy for the process

$$\mathrm{H{-}CHXCH_2Y \rightarrow H^{\bullet} + {}^{\bullet}CHXCH_2Y} \qquad (2)$$

where the capped small system is

$$\mathrm{H{-}CH_2X \rightarrow H^{\bullet} + {}^{\bullet}CH_2X} \qquad (3)$$

If we define the equilibrium bond dissociation energies by

$$D_e(\mathrm{ES}) = E(\mathrm{H}) + E(\mathrm{CHXCH_2Y}) - E(\mathrm{CH_2XCH_2Y}) \qquad (4)$$

and

$$D_e(\mathrm{CSS}) = E(\mathrm{H}) + E(\mathrm{CH_2X}) - E(\mathrm{CH_3X}) \qquad (5)$$

then

$$D_e(\mathrm{I{:}HL{:}LL}) = D_e(\mathrm{HL,CSS}) - D_e(\mathrm{LL,CSS}) + D_e(\mathrm{LL,ES}) \qquad (6)$$

Ten pairs of C−H dissociation energies, D_e(ES) and D_e(I:HL:LL), were calculated for a set of six molecules with the following combinations of X and Y substituents: CH_3CH_3, $CH_3CH_2NH_2$, CH_3CH_2OH, CH_3CH_2F, CH_2FCH_2F, and CH_3CH_2Cl. In practice, this represented the evaluation of the energy for 16 full molecular species (each neutral molecule and the radical obtained upon dissociating the H atom) plus the hydrogen atom at each of the theoretical levels described below. Additionally, in calculating the IMOMO D_e(I:HL:LL) energies, it was also required to evaluate D_e(CSS) for five capped small systems (CH_4, CH_3NH_2, CH_3OH, CH_3F, and CH_3Cl) at the different levels of theory selected for the higher and lower levels of the IMOMO calculations reported in this work.

All geometries for all calculations on all species at all levels were calculated by second-order MBPT (within the unrestricted formalism), abbreviated MP2, with the 6-311+G(2df,2pd)[18] basis set. In these calculations, all electrons were correlated, which is sometimes denoted MP2(full). The precise details of the method used to obtain geometries are unimportant. The essential point is that the method we chose yields reasonably accurate geometries so that, in all further calculations, we can concentrate our attention on electronic energies without considering errors in geometries that might occur if geometries were optimized at lower levels.

We performed three series of IMOMO calculations:

I:CL:CL	both high and low level are a correlated level (CL)
I:CL:HF	high level is correlated; low level is Hartree−Fock
I:HF:HF	both high and low level are Hartree−Fock

We considered several correlated levels. For all single-point correlated calculations, only the valence electrons were correlated, and we employed the 6-31G(d,p)[19] basis set. In order of increasing completeness the correlated levels for which we present results are

MP2	second-order MBPT[10]
PMP2	spin-projected MP2[13]
MP3	third-order MBPT[10]
PMP3	spin-projected MP3[13]
CCSD(T)	CCSD with perturbative inclusion of connected triple excitations[11]

At the Hartree−Fock level we considered several basis sets. In order of increasing completeness the basis sets we used are

minimum basis	STO-3G[20]
double-zeta split-valence basis	3-21G[21]
polarized valence double-zeta bases	6-31G(d),[19] 6-31G(d,p),[19] cc-pVDZ[22]
polarized valence triple-zeta basis	cc-pVTZ.[22]

All the calculations were carried out using the GAUSSIAN94 computer package.[23]

3. Results and Discussion

3.1. IHFHF. In the first round of calculations we test whether, at the Hartree−Fock level, it is necessary to use a large basis set on the entire system. Table 1 shows how well we can do. We take our standard of a converged Hartree−Fock calculation as HF/cc-pVTZ where, in the usual way, the overall level is denoted C/B, where C is the electronic structure method or correlation level and B is the one-electron basis set.

First, Table 1 gives the Hartree−Fock bond energy with the most extensive basis set, cc-pVTZ. Then we consider calculations with five smaller basis sets and also calculations in which the smaller basis set is used on the entire system but the larger basis set is used on the capped small system.

The I:HF/cc-pVTZ:HF/STO-3G calculations show that improving the basis on a capped small system is an excellent way to improve the bond energy without the expense of using a large basis set for the whole system. The average unsigned error for the set of 10 dissociation energies considered here is reduced by 1 order of magnitude (from 25.6 to 2.3 kcal/mol) in going from the HF/STO-3G level to the I:HF/cc-pVTZ:HF/STO-3G level. As one uses larger basis sets on the entire system, one sees less *relative* improvement, but the final *absolute* deviation from a large-basis-set calculation on the entire system becomes satisfyingly small. The use of a double-zeta quality basis set, even without polarization functions, is sufficient to obtain IMOMO results that are within 1 kcal/mol of the HF/cc-pVTZ benchmark, and polarized double-zeta basis sets reduce the error to 0.4 kcal/mol or less. Not only are these errors about a factor of 2 smaller than the errors calculated by simply using the low level on the entire system, they are considerably smaller than the mean unsigned error of 2.3 kcal/mol that one obtains by using only the high level on the capped small system. Thus, combining the levels by the IMOMO strategy is better than using either level alone.

Thus, according to what it has been discussed in the previous paragraph, the I:HF:HF approach could be used as a powerful tool to improve the accuracy in Hartree−Fock studies of processes involving bond cleavage and/or bond formation in

TABLE 1: Tests of IHFHF Theory for D_e in kcal/mol

	X:	H	NH_2	H	OH	H	F	H	F	Cl	H	
basis set (B)	Y:	H	H	NH_2	H	OH	H	F	F	H	Cl	av error[a]
D_e at HF/cc-pVTZ level												
		82.9	74.1	81.3	78.1	85.0	82.0	84.8	83.5	81.2	83.2	
|error| in D_e calculated at the HF/cc-pVTZ level on the capped small system												
		2.5	1.0	4.1	1.5	0.4	1.8	0.6	1.3	4.7	2.2	2.0
|error| in D_e calculated at HF/B level (upper entry) and calculated at I:HF/cc-pVTZ:HF/B level (lower entry)												
STO-3G		28.6	27.1	28.1	23.8	26.9	20.5	27.0	19.5	26.8	27.3	25.6
		1.3	3.0	1.8	1.7	3.0	1.3	2.8	2.3	3.3	2.6	2.3
3-21G		1.3	0.3	1.6	1.5	1.8	0.4	1.7	1.1	5.9	0.2	1.6
		0.1	0.9	0.3	0.2	0.5	0.3	0.4	1.0	0.4	1.4	0.6
6-31G(d)		0.9	0.9	0.7	0.7	0.9	0.4	0.8	0.5	0.6	0.7	0.7
		0.3	0.4	0.5	0.4	0.4	0.2	0.4	0.1	0.5	0.5	0.4
6-31G(d,p)		1.6	1.5	1.5	1.5	1.6	1.2	1.6	1.3	1.3	1.5	1.5
		0.2	0.2	0.4	0.3	0.3	0.1	0.3	0.0	0.4	0.4	0.3
cc-pVDZ		0.3	0.3	0.5	0.5	0.1	0.2	0.2	0.0	0.2	0.3	0.3
		0.0	0.1	0.3	0.2	0.2	0.1	0.1	0.3	0.1	0.0	0.1

[a] The last column gives the average unsigned error for the 10 cases.

TABLE 2: Tests of ICLHF and ICLCL for D_e in kcal/mol When the High Level Is CCSD(T)

	X:	H	NH_2	H	OH	H	F	H	F	Cl	H	
low level (L)	Y:	H	H	NH_2	H	OH	H	F	F	H	Cl	av error[a]
D_e calculated by CCDS(T)/6-31G(d,p)												
		106.9	95.4	105.1	99.7	109.2	103.9	108.9	105.7	102.8	106.8	
|error| in D_e calculated at the CCDS(T)/6-31G(d,p) level on the capped small system												
		3.0	1.1	4.8	1.5	0.7	1.7	1.0	0.1	2.0	3.1	1.9
|error| in D_e calculated by level L (upper entry) and calculated by I:CCSD(T)/6-31G(d,p):L (lower entry)												
HF/STO-3G		4.5	5.7	4.2	2.3	2.7	1.4	3.0	2.6	5.2	3.6	3.5
		0.8	2.3	1.2	1.7	2.7	1.4	2.3	2.6	6.0	1.8	2.3
HF/3-21G		22.7	21.0	22.3	20.1	22.5	21.6	22.3	21.1	15.7	23.8	21.3
		0.5	0.9	1.0	0.3	0.8	0.2	0.9	0.7	3.1	0.6	0.9
HF/6-31G(d)		23.1	20.5	23.2	20.8	23.4	21.6	23.2	21.7	21.0	22.9	22.1
		0.2	0.4	0.1	0.4	0.0	0.4	0.1	0.5	3.2	0.4	0.3
HF/6-31G(d,p)		22.4	19.9	22.4	20.2	22.6	20.8	22.5	20.9	20.3	22.2	19.4
		0.2	0.2	0.2	0.2	0.0	0.3	0.2	0.3	3.0	0.5	0.5
MP2/6-31G(d,p)		0.7	0.8	0.6	0.6	0.5	0.8	0.5	0.8	0.3	0.2	0.6
		0.2	0.3	0.3	0.2	0.4	0.2	0.4	0.2	0.1	0.6	0.3
PMP2/6-31G(d,p)		2.0	1.9	1.9	1.8	1.8	1.9	1.8	1.9	1.8	1.7	1.9
		0.1	0.3	0.2	0.3	0.3	0.2	0.3	0.3	0.2	0.4	0.3
MP3/6-31G(d,p)		0.3	0.2	0.3	0.4	0.3	0.3	0.2	0.3	0.2	0.0	0.2
		0.1	0.0	0.1	0.0	0.1	0.1	0.2	0.1	0.1	0.4	0.1
PMP3/6-31G(d,p)		1.1	0.4	1.0	0.3	1.0	0.4	0.9	0.4	0.7	0.9	0.7
		0.0	0.0	0.1	0.0	0.1	0.1	0.2	0.0	0.1	0.2	0.1

[a] The last column gives the average unsigned error for the 10 cases studied.

large systems. The additional computational effort required for calculating the model system using a more extended basis set is relatively small when compared to the cost of performing the calculation for the entire large system with a big basis set. Whereas the results presented here demonstrate the usefulness of the method for bond dissociation (the most violent imaginable disruption of a system), Morokuma *et al*. have previously shown that this kind of approach is also useful for the more subtle effects that come into play in calculating conformational energies in molecules like ethane and butane.[3,4] The computational modeling of binding and bond rearrangement processes taking place in biological systems like the reaction of a substrate at the active site of an enzyme would be, for example, a good application for the I:HF:HF method. Small basis sets like the STO-3G or 3-21G bases are frequently used in this kind of study, in which the complexity of the active site makes correlated levels of theory unaffordable, at least with conventional methods. The next section examines the possibility of including correlation energy more efficiently in large systems.

3.2. ICLHF and ICLCL. The next series of tests is designed to see whether the previous conclusions hold up when the higher level is correlated.

3.2.1. Very Complete High Level. First, we choose a CCSD(T)/6-31G(d,p) calculation as the benchmark high level, because this level has become the *de facto* state of the art for many applications, and we examine a variety of low levels including both HF and CL levels. Table 2 displays the values obtained at the CCSD(T)/6-31G(d,p) level for the set of 10 dissociation energies examined in this work. A second section in the same table collects the absolute error with respect to the CCSD(T)/6-31G(d,p) values for each of the conventional single-level (HF or MBPT) bond energies, as well as for every IMOMO bond energy.

The I:CCSD/6-31G(d,p):HF/B results displayed in Table 2 are in good agreement with what we previously observed in a preliminary analysis of the performance of the I:CL:HF strategies for predicting bond energies and substituent effects.[8,9] In the first of those reports we presented an analysis of the quality of the IMOMO approaches using several high correlated levels (MP4SDQ, CCSD, and QCISD(T)) for the model system combined with a HF/6-31G(d,p) calculation for the entire system.[8] In the second one, we used just one high level, QCISD(T)/cc-pVTZ, but now in conjunction with different lower levels (HF/B, DFT/B, and semiempirical methods).[9]

TABLE 3: Tests of ICLHF for D_e in kcal/mol When the High Level Is MP2

	X:	H	NH_2	H	OH	H	F	H	F	Cl	H	
basis set (B)	Y:	H	H	NH_2	H	OH	H	F	F	H	Cl	av error[a]
D_e calculated by MP2/6-31G(d,p)												
		106.3	94.6	104.5	99.0	108.7	103.1	108.3	104.9	102.5	106.6	
|error| in D_e calculated at the MP2/6-31G(d,p) level on the capped small system												
		2.7	0.8	4.5	1.3	0.3	1.4	0.7	0.4	1.9	2.4	1.6
|error| in D_e calculated at the HF/B level (upper entry) and calculated by I:MP2/6-31G(d,p):HF/B (lower entry)												
HF/STO-3G		5.2	6.5	4.8	2.9	3.2	0.6	3.5	1.8	5.5	3.9	3.8
		1.1	2.6	1.4	1.9	3.1	1.6	2.7	0.3	6.2	2.3	2.3
HF/3-21G		22.1	20.2	30.1	19.4	19.9	20.8	21.8	20.3	15.4	23.5	21.4
		0.3	0.6	0.7	0.0	0.4	0.0	0.6	1.7	3.2	1.2	0.9
HF/6-31G(d)		22.5	19.7	29.6	20.2	22.8	20.8	22.7	20.9	20.7	22.6	22.3
		0.0	0.7	0.1	0.6	0.4	0.6	0.3	1.4	3.3	0.2	0.8
HF/6-31G(d,p)		21.9	19.1	29.0	19.5	20.1	20.0	21.9	20.1	20.0	21.9	21.4
		0.0	0.5	0.0	0.5	0.3	0.4	0.2	1.4	3.2	0.1	0.7

[a] The last column gives the average unsigned error for the 10 cases.

Inspection of the results collected in Table 2 shows that in most of the cases reported here the inclusion of a high level of correlation in the small capped subsystem is enough to lead to a dramatic reduction of the absolute error with respect to only using the HF method.

For the HF/STO-3G calculations it is noticed that the values predicted for the whole system are closer to the CCSD(T)/6-31G(d,p) results than the ones produced using the more extended basis sets considered in this study, a fact that is likely to be caused by the compensation of errors of different sign involved in the minimal basis set calculations. Nevertheless, even though the two levels are very unbalanced in this case, the use of the I:CCSD/6-31G(d,p):HF/STO-3G approach still reduces or maintains the average error for this set of calculations for all the systems containing first-row atoms.

A more balanced approach involves using extended basis sets for the low-level calculation. Rows 6, 8, and 10 of Table 2 show results for this kind of treatment. The mean unsigned error is 0.9 kcal/mol for an unpolarized valence double-zeta basis set, and it is reduced to 0.3−0.5 kcal/mol when polarization functions are added. These errors are not only smaller than the errors (19−21 kcal/mol) in applying the low level to the entire system, they are much smaller than the error of 1.9 kcal/mol that one finds by performing only the high-level calculation on the capped small system. Again, we conclude that the combination of calculations by the IMOMO strategy is better than using either alone.

The error in the I:CCSD(T)/6-31G(d,p):HF/B calculations of the α C−H bond energy in chloroethane is considerably higher than the average error of each HF/B set of calculations (about 3 kcal/mol versus 0.5−0.9 kcal/mol). As we already discussed in a previous communication,[8] this fact is associated with the poor description of the CH_3Cl C−H bond energy given by the HF level. This can be confirmed by the examination of the lower rows in Table 2 where the results obtained in applying the I:CCSD(T)/6-31G(d,p):MBPT/6-31G(d,p) method are displayed. The IMOMO errors for the X = Cl, Y = H case have been reduced here by more than 10 times the magnitude of the I:CL:HF errors.

The last eight rows of Table 2 are relevant to a question that was not touched at all in our previous two papers, namely, the use of the IMOMO scheme to systematically converge a calculation on a large system up to a high level of electron correlation, chosen here as CCSD(T). In this approach we carry out a CCSD(T) calculation on a capped subsystem, and we carry out lower-level *correlated* calculations on the entire system. Then we ask, how high of a correlation level should we use for the entire system to get results in good agreement with using CCSD(T) for the entire system? We examined this question thoroughly and found that convergence with respect to the lower level is quite rapid. Thus, we present results in Table 2 only for second- and third-order MBPT methods as the lower level. Table 2 shows that the use of MP2 calculations for the low level is already sufficient for an average error of only 0.3 kcal/mol. Furthermore, the table shows that the use of MP3 calculations instead of MP2 ones for the entire system lowers the average error from 0.3 to 0.1 kcal/mol. Further increase in the quality of the low-level calculation does not systematically improve the quality of the IMOMO results. Thus, we conclude that it is possible to recover most of the high-level correlation effects using just an MP2 or MP3 calculation for the low level of the integrated approach.

3.2.2. MP2 High Level. A final point which we have focused our attention in this work is the possibility of obtaining results of MP2/6-31G(d,p) quality by using the I:MP2:HF approach. In recent years the MP2/6-31G(d,p) level has become a standard in many applications of quantum mechanical calculations to the analysis of chemical reactions involving medium−size molecular systems. Thus, whether or not we can get MP2 accuracy with only Hartree−Fock calculations for the entire systems is an interesting point to be elucidated. In Table 3 are shown the results obtained in performing a series of I:MP2/6-31G(d,p):HF/B integrated calculations for the 10 cases included in our test suite. The observed trends for this collection of results are similar to the ones already noted in our discussion of the I:CCSD(T)/6-31G(d,p):HF/B results above. The average error with respect to the MP2/6-31G(d,p) results is reduced by a factor of over 20 by I:MP2/6-31G(d,p):HF/B as compared to an uncorrected HF/B calculation when B is a double-zeta or polarized double-zeta basis. For the HF/STO-3G case, the relative reduction in error is smaller for reasons discussed above. Concerning the absolute value of the error for each separate case, with the exception of a few CH bond energies (the aforementioned α dissociation in chloroethane and the CH bond energy in difluoroethane), we can get the same accuracy as MP2/6-31G(d,p) within 1 kcal/mol. Thus, once again the IMOMO strategy used with the I:MP2:HF scheme is successful at the task of providing MP2 quality results at the expense of a lower computational cost than calculating the whole system at the correlated level.

4. Conclusions

In this article we have analyzed in a detailed way the accuracy of different combinations of high and low levels in the framework of an integrated IMOMO scheme for predicting 10 C−H bond energies in a set of six different molecules containing first- and second-row atoms. Our tests involve fixed geometries and are directly relevant to the quality of predicted electronic energies at given geometries. The results collected here can help in deciding on the most appropriate combination of higher and lower levels for predicting bond energies, substituent effects, conformational barriers, etc. Three principal conclusions can be drawn from the information presented in this article:

(1) I:HF:HF strategies can be used successfully to improve the quality of the results in systems where the consideration of correlation effects is not crucial for having an adequate picture of the problem or is unaffordable. In this case, our results show that it is possible to obtain the accuracy of a better converged Hartree–Fock calculation by improving the basis set to be used only in the small capped system.

(2) The use of I:CL:HF approaches (where CL denotes a correlated level) makes it possible to locally include correlation effects in calculations of bond energies and to produce results that are within 1 kcal/mol of the accuracy of the correlated level (CCSD(T) and MP2 in this article) in those cases where the HF level is good enough for describing the small system. For the cases where this condition is not satisfied, the I:CL:HF approach still produces better results than the Hartree–Fock calculation of the entire system, but the absolute error is around 3 kcal/mol.

(3) Finally, the I:CL:CL approach seems to be adequate for recovering the main high-level correlation effects at the cost of including a low level of correlation (MP2) in the small system in calculating bond energies. This is the recommended choice for those cases where correlation effects are crucial in obtaining a fair picture of the bond energy in the small system, and the size of the entire system makes an MP2 calculation on it unaffordable.

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Supporting Information Available: Tables collecting the single-point energies (in hartrees) for the species required to evaluate each bond energy reported here, calculated at the different levels of theory considered in this work (2 pages). Ordering information is given on any current masthead page.

References and Notes

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