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Benzenium−Ethene Complex: A Fundamental Problem for Standard Second-Order Møller−Plesset Theory

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Recently, Kolboe and Svelle pointed out that second-order Møller−Plesset perturbation theory (MP2) incorrectly predicts a barrierless reaction of the benzenium-ethene complex to the ethyl-1H-benzene cation in contrast to other considered quantum chemical methods [*J. Phys. Chem. A* 2008, *112*, 6399]. In a subsequent Letter in this Journal, van Mourik related this behavior to the basis set superposition error [*J. Phys. Chem. A* 2008, *112*, 11017]. Here we can show that this is not the case but that the failure is due to an intrinsic (overcorrelation) problem of MP2. Improved perturbation methods (SCS-MP2 and B2PLYP double-hybrid functionals) provide correct results.

Noncovalently bound organic systems and in particular positively charged π-systems play an important role in many biological structures. In their theoretical investigation of the benzenium−ethene model system, Kolboe and Svelle first considered a molecule−ion complex (see Figure 1a) that should be stable in the gas phase.[1] Interestingly, all of the applied quantum chemical methods (B3LYP, CCSD, and QCISD) confirmed this except for second-order Møller−Plesset theory (MP2) with a larger atomic orbital basis sets, which leads in structure optimizations apparently without any barrier to the corresponding ethyl-1*H*-benzene cation (see Figure 1c).

This is particularly surprising because in general one expects MP2 to be more reliable than common DFT methods when applied to systems where noncovalent interactions play a major role. Furthermore, in the benzenium−ethene ion complex, self-interaction (delocalization) error related problems in DFT[2] can be expected. Also because MP2 is still a widely used standard method in ab initio quantum chemistry, the findings of Kolboe and Svelle raised some wider interest for this problem. In a subsequent study, van Mourik reexamined the system and performed a counterpoise (CP)[3] corrected optimization at the MP2/6-311++G(d,p) level of theory.[4] In this treatment a stable benzenium−ethene complex could be found and she related the MP2 failure observed by Kolboe and Svelle to the basis set superposition error (BSSE) for which the CP correction is an approximate cure.

In this context it has to be noted that the CP method typically overcorrects and so artificially destabilizes the complex[5] compared to the reactands, especially when used with unbalanced basis sets. On the other hand MP2 is well-known to overrate electron correlation effects in unsaturated systems and complexes[6] that leads often to overbinding. So it might be the case that there is nevertheless an inherent MP2 problem that is just covered in van Mourik's treatment by finite basis set effects together with an overcorrection of the CP procedure.

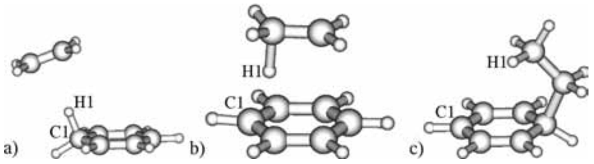

Figure 1. Start geometry based on $C_6H_7 \cdot C_2H_4$ complex optimized with CCSD/6-311++G(d,p) as provided by Kolboe and Svelle[1] (a), transition state-like structure (b), and the ethyl-1*H*-benzene product (c).

While this study was carried out, two theoretical papers on the subject appeard. Kolboe et al. readdressed the failure of MP2 and related it to an overcorrection of the energies for geometries along the reaction path form the complex to the ethyl-1*H*-benzene.[7] The authors do not concider CP corrections and also used basis sets of only triple-ζ-quality. Sancho-García[8] has carried out a thorough investigation of the binding energy of the complex as well as the reaction energy to ethyl-1*H*-benzene with various sophisticated wave function and DFT methods. His conclusions are supported by our calculations, in particular regarding the fact that other perturbation methods are in better agreement with the high-level coupled-cluster results than MP2 is. Neither the potential energy surface is scanned nor the CP correction has been considered, which are major points of our study.

Because the system is small enough to apply very large AO basis sets close to the limit, we have done a series of calculations for the benzenium−ethene ion complex and the ethyl-1*H*-benzene cation to get a definite answer to the MP2 problem. We will compare results of MP2 to those of other methods for different points on the potential energy surface, present complete basis set (CBS) results, and structure optimization with and without CP correction with two basis sets of different size, so that the BSSE should play a systematically varying role. Finally, a partitioning of the MP2 correlation energy is discussed to better understand the physics of the problem.

All calculations have been run with a modified version of TURBOMOLE.[9−14] Besides MP2 and Hartree−Fock (HF), the

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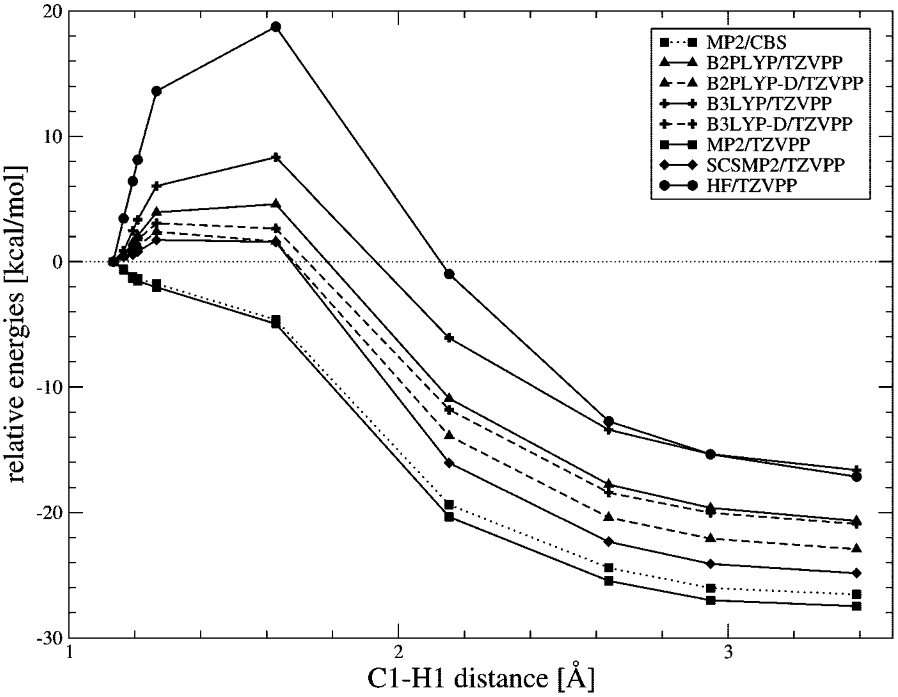

Figure 2. Single point relative energies (starting complex geometry taken as zero) for different methods on some points of the $C_6H_7{\cdot}C_2H_4$ hypersurface. As reaction coordinate, the C1−H1 distance is taken (see Figure 1).

hybrid density functional B3LYP[15,16] and the double-hybrid functional B2PLYP,[17,18] both with and without an empirical correction for dispersion effects,[19] and the SCS-MP2 method, which is known to compensate some of MP2's short comings,[6] are applied. For single point energies and the correlation contribution partitioning, the TZVPP basis set[20] is used. The CBS results have been obtained with aug-cc-pVXZ (X = Q, 5) basis sets[21,22] together with a standard two-point extrapolation scheme.[23−26] The CP corrected geometry optimizations were done with the cc-pVDZ and cc-pVQZ basis sets.[21] When not mentioned otherwise, the density fitting (RI) procedure is employed in all calculation steps and the results are not corrected for BSSE. Corresponding auxiliary basis sets have been taken form the TURBOMOLE basis set library.[13] For single point energies all electrons have been correlated while the frozen-core approximation was applied in the CP including geometry optimizations to speed up the calculations.

Single Point Energies along the Reaction Pathway. In Figure 2 the relative energies from the different methods calculated for ten points on the $C_6H_7{\cdot}C_2H_4$ potential energy surface are shown. The geometries have been taken from an MP2/aug-cc-pVTZ optimization run that started from the complex geometry provided in the Supporting Information of ref 1 and ended with the ethyl-1*H*-benzene cation. We take them as representatives for the "true" reaction coordinate, which unfortunately could not be located. We think that the precise choice of these structures does not affect our qualitative conclusions regarding the performance of MP2 compared to other methods. As a measure of the structural change, the C1−H1 distance (see Figure 1) is taken (reaction coordinate).

Clearly all methods except MP2 show a barrier when going from the complex to ethyl-1*H*-benzene. We note in passing that the B3LYP barrier is too high because of the neglect of long-range correlation effects necessary for a description of dispersion interactions. This can be seen from the influence of the dispersion correction ("-D" appended) and the HF result, which does not include electron correlation at all and so yields an even higher barrier than B3LYP. The outcome for SCS-MP2 and B2PLYP(-D) is especially interesting because these methods also (at least in part) account for electron correlation in an MP2-like manner and may suffer from the mentioned problems, too. Nevertheless, a barrier is correctly found in agreement with the results of Sancho-García.[8] And, most importantly, the curves for MP2/TZVPP and MP2/CBS are very similar and do not show any barrier, which is in agreement with the conclusions of Kolboe and Svelle. Because at least the MP2/CBS(aug-cc-pVQZ→aug-cc-pV5Z) results should be virtually free of BSSE, this is in contradiction to the conclusions by van Mourik.

Geometry Optimizations. In light of the above results we wanted to find out in which cases the CP corrected MP2 geometry optimization might erroneously lead to a stable complex. Therefore we performed optimizations at MP2/cc-pVDZ and MP2/cc-pVQZ levels of theory, respectively. This was done with and without CP correction, using a script provided by TURBOMOLE for this purpose. Our idea was that for the large basis, which seems to be not too far away from the CBS, only slight differences should be observeable when used with or without CP correction. This might not be the case for the smaller double-ζ basis. Again we started from the CCSD/6-311++G(d,p) structure.

And indeed on the MP2/cc-pVDZ level of theory the results differ. Without CP correction, the optimization leads directly to the product whereas otherwise a stable noncovalently bound complex is found. When turning to the larger quadruple-ζ basis set, things change qualitatively. Now both optimizations only give the ethyl-1*H*-benzene as a local minimum.

These results, which partly duplicate those of van Mourik, seem to indicate that the wrong general conclusion in ref 4 regarding the behavior of MP2 is a result of the CP procedure in conjuction with a too small and unbalanced AO basis set (6-311++G(d,p)). At this level, the overestimation of the correlation energy by MP2 is counterbalanced by the insufficient AO basis, an effect that is further amplified by the overshooting of the CP procedure.

Analysis of Correlation Contributions. For a better understanding we finally partition the MP2 correlation energy into

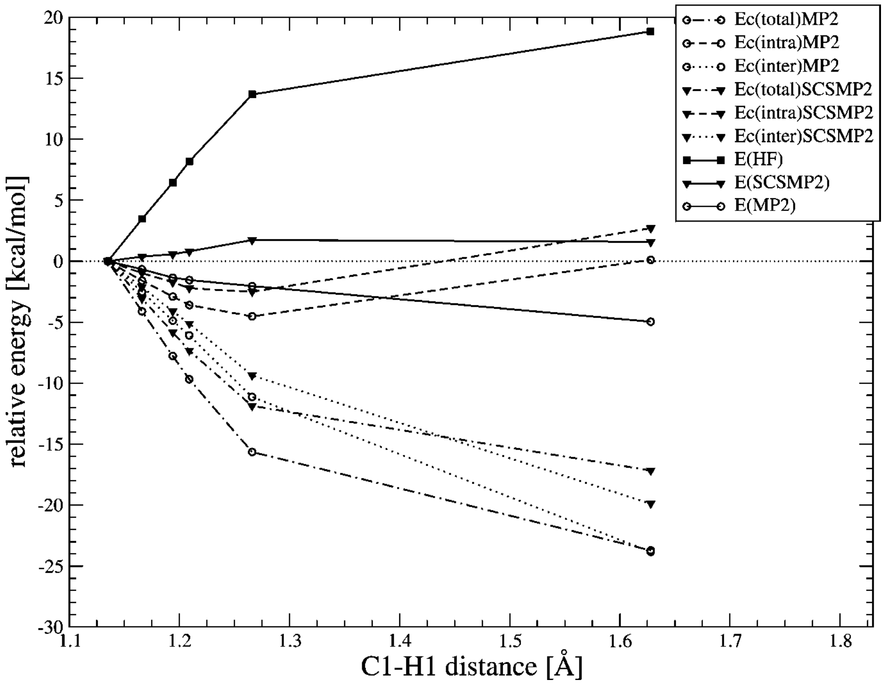

Figure 3. Inter- and intrafragment electron correlation contributions relative to the initial complex geometry at the MP2/TZVPP and SCS-MP2/TZVPP levels for the same first six points of the reaction as in Figure 2. E_c(total) is the total relative correlation energy, E_c(intra) and E_c(inter), respectively, their intrafragment and interfragment contribution and E is the total relative energy.

intra- and interfragment contributions. This is done by localization of the molecular orbitals, assigning each to one of the fragments, and determining which electron pair correlations occur within a fragment or between separated parts of the complex (for more details and an application of this analysis technique, see ref 27). We take the same points on the PES and compare here with SCS-MP2, which yields a qualitatively correct result (see Figure 3). Because the separation into fragments becomes problematic when the formation of the new σ-bond occurs only the first six steps on the path from $C_6H_7 \cdot C_2H_4$ to ethyl-1*H*-benzene are considered.

When the electron densities of both fragments approach each other, the interfragment correlation energy decreases, which compensates the larger Pauli repulsion. The intrafragment part changes less during the process. For both components and all points, MP2 overestimates the correlation effect relative to SCS-MP2. Furthermore, the error increases along the PES toward the product. In the case of MP2, the increase of the HF energy is thus overcompensated so that no reaction barrier can be found. MP2 is known to yield often too large correlation corrections and this can be related to the equal treatment of same- and opposite-spin electron pairs because the former are already correlated at first-order (which is HF).[28] SCS-MP2 has been parametrized to correct this and indeed cures the problem in this reaction entirely.

In summary we can conclude that the MP2 failure to describe the $C_6H_7 \cdot C_2H_4$ complex as a local minimum is a method-specific, basis set independent problem and can also not in general be attributed to BSSE. Both MP2/CBS results for some significant points on the PES and optimizations with a large quadruple-ζ basis with and without CP correction provide the same picture. The MP2 problem could be traced back to its typical overestimation of electron correlation in delocalized systems. When using small- to medium-sized basis sets, the overcorrection is less pronounced; together with the CP correction a seemingly right result is obtained for the wrong reasons. In general, the CP correction seems to be more useful for smaller than for larger basis sets where its overcorrection may be of the same size as the BSSE itself.

Because of the enormous increase in computation time for a CP corrected optimization, we recommend employment of large and balanced AO basis sets (probably with basis set extrapolations and no CP corrections), and the SCS-MP2 method or double-hybrid density functionals in similar cases. Simple dispersion corrected semilocal density functionals may not be sufficient when charged, delocalized π-systems are considered.

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