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Assessment of Orbital-Optimized, Spin-Component Scaled Second-Order Many-Body Perturbation Theory for Thermochemistry and Kinetics

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Abstract: An efficient implementation of the orbital-optimized second-order Møller–Plesset perturbation theory (OO-MP2) within the resolution of the identity (RI) approximation is reported. Both conventional MP2 and spin-component scaled (SCS-MP2) variants are considered, and an extensive numerical investigation of the accuracy of these approaches is presented. This work is closely related to earlier work of Lochan, R. C.; Head-Gordon, M. *J. Chem. Phys.* **2007**, *126*. Orbital optimization is achieved by making the Hylleraas functional together with the energy of the reference determinant stationary with respect to variations of the double excitation amplitudes and the molecular orbital rotation parameters. A simple iterative scheme is proposed that usually leads to convergence within 5–15 iterations. The applicability of the method to larger molecules (up to ∼1000–2000 basis functions) is demonstrated. The numerical results show that OO-SCS-MP2 is a major improvement in electronically complicated situations, such as represented by radicals or by transition states where spin contamination often greatly deteriorates the quality of the conventional MP2 and SCS-MP2 methods. The OO-(SCS-)MP2 approach reduces the error by a factor of 3–5 relative to the standard (SCS-)MP2. For closed-shell main group elements, no significant improvement in the accuracy relative to the already excellent SCS-MP2 method is observed. In addition, the problems of all MP2 variants with 3d transition-metal complexes are not solved by orbital optimization. The close relationship of the OO-MP2 method to the approximate second-order coupled cluster method (CC2) is pointed out. Both methods have comparable computational requirements. Thus, the OO-MP2 method emerges as a very useful tool for computational quantum chemistry.

Introduction

Second-order many-body perturbation theory (MBPT2) occupies an important place in quantum chemistry. It is known

to greatly improve upon the results of Hartree–Fock (HF) self-consistent field calculations and is the simplest wave function based ab initio method. With the Møller-Plesset (MP) choice of the zero-order Hamiltonian,[1,2] the method is known as MP2 and has been widely used in computational chemistry. The pertinent features of MP2 are well-known:[3,4]

a. MP2 is size consistent but not variational or even stationary with respect to the wave function parameters.

b. MP2 recovers 80–90% of the basis set correlation energy.

c. MP2 scales as the fifth power of the molecular size, e.g., as $O(N^5)$. It is, therefore, intermediate in computational

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complexity between the HF theory (formally $O(N^4)$, practically $O(N^2)$) and the more rigorous coupled cluster (CC)[5,6] or coupled electron pair (CEPA)[7−9] methods that require at least an iterative $O(N^6)$ process, if only single and double excitations from the HF reference determinant are included (CCSD).

d. MP2 applied to closed-shell organic molecules often yields fairly good structures, but energetics that are slightly worse than with common density functionals.[10]

e. MP2 applied to open-shell molecules or to transition-metal complexes yields distinctly less accurate results.[11]

f. With a HF reference, the first-order MP2 wave function only contains double excitation amplitudes. Hence, MP2 does not incorporate any orbital relaxation in the electron correlation field.

A great deal of effort has been invested into making MP2 computationally affordable for general computational chemistry applications, and consequently, a number of highly efficient MP2 approaches exist. Early on, Almlöf and Saebo demonstrated that MP2 can be done in an integral direct fashion, thus, avoiding the storage of $O(N^4)$ intermediates on disk.[12] Head-Gordon,[13,14] Ahlrichs, and others have reported modifications of the original direct algorithm. The most efficient semidirect algorithm has probably been developed by Pulay and co-workers and does *not* avoid storage of $O(N^4)$ quantities on disk.[15−19] The scaling of their method is still $O(N^5)$, and it completely reproduces the canonical result. Pulay and co-workers have reported very large MP2 calculations with more than 2 000 basis functions on the basis of a parallelized code.[20]

More recently, Ochsenfeld and co-workers have developed a linear scaling integral direct MP2 code.[21,22] Their strategy is based on the Laplace transformation technique introduced originally by Almlöf[23] and discussed in detail by Häser and Almlöf,[24] Häser,[25] and Scuseria.[26] Microhartree accuracy (relative to the canonical result) MP2 calculations with more than 10 000 basis functions have been reported by Ochsenfeld et al.,[27] and a gradient code has also been developed along the same lines.[28]

A number of efficient approximate MP2 treatments are available. One of the first, and still widely used, approximations is the resolution of the identity (RI, equivalently density fitting, DF) technique in which products of orbitals are expanded in an auxiliary basis set.[29] The RI approximation to MP2 (RI-MP2) was first reported by Feyereisen et al.[30] and was based on the results of Vahtras, Feyereisen, and Almlöf, who showed that the RI technique performs best in the Coulomb metric.[31] Häser and Weigend optimized fitting basis sets for RI-MP2 calculation for almost the entire periodic table.[32,33] They are optimally used together with the segmented Gaussian basis sets developed by the Karlsruhe group.[32,34−36] The error introduced by the RI approximation is usually smaller than 0.1 mEh/atom and is very smooth, such that it essentially cancels in chemically relevant energy differences (typical RI errors in energy differences amount to only 0.02 kcal mol^{-1}). The RI technique leads to dramatic speedups of MP2 calculations, in particular, if large basis sets are used, the savings compared to the canonical calculation amount to $1-2$ orders of magnitude. It does,

however, not reduce the formal scaling that remains at the $O(N^5)$ level. Nevertheless, the prefactor for RI-MP2 is so small that, in the range up to at least 2 000 basis functions, the preceding HF calculation still dominates the overall computational effort.

Linear scaling approximate MP2 methods (as opposed to the linear scaling full accuracy MP2 method pursued by Ochsenfeld et al.) have been developed by a number of groups. The most efficient of these have probably been reported by Werner, Schütz and co-workers,[37−41] who used the correlation domain concept of Pulay and Saebo.[42−44] The LMP2 technique has been developed in combination with the standard four index repulsion integrals and together with the DF technique where further dramatic savings are realized.[37,38]

A different approach has been pursued by Friesner and co-workers, who have developed low-order scaling pseudospectral techniques for MP2 calculations that are also characterized by a small error and a low prefactor.[45] We have previously reported a hybrid technique where the HF energy is obtained with a combination of RI and seminumerical integration and the MP2 energy is calculated within the RI framework.[46,47] The technique has been termed RIJCOSX, and it has been shown that it leads to speedups of about a factor of 15 for basis sets of triple-ζ quality compared to standard RI-MP2 calculations.

Overall, it is clear that the development of MP2 has reached a stage where MP2 energies can be obtained faster than the HF energy itself for many chemically interesting systems. Hence, the domain of applicability of MP2 is similar to that of density functional theory (DFT). However, DFT is still more frequently used than MP2, perhaps because it proves to be more robust when applied to electronically difficult situations, such as presented by open-shell systems and by transition-metal complexes. Furthermore, widely used quantum chemistry software packages still use non-RI, disk-based MP2 algorithms so that the calculations remain very time, memory, and disk space consuming.

Given the efficiency of the MP2 technique it seems natural to look for extensions that improve the accuracy of the MP2 method while not worsening the computational scaling. Perhaps the most successful of these techniques has been the spin-component scaled MP2 method (SCS-MP2) previously proposed by one of us.[48−50] SCS-MP2 has proven to be a robust, efficient, and accurate technique when applied to closed-shell main group systems. However, it has also shown some deficiencies in the calculation of activation and reaction energies involving open-shell molecules.[9,51] A modification of the SCS-MP2 idea that reduces the scaling behavior to $O(N^4)$ has been proposed by Head-Gordon and co-workers and has been termed SOS-MP2.[52−54]

A second successful extension of MP2 has been the proposals of double-hybrid DFT (DHDF),[55−57] and third-order spin-component scaled perturbation theory.[58] The DHDFs have quickly gained popularity in the computational chemistry community and, to some extent, combine the best features of DFT and MP2 in terms of robustness, efficiency, and accuracy.[59] Because neither (SCS-)MP2 nor DHDF methods are variational or even stationary, the formulation

of analytic gradients is more involved,[59] and hence, structure optimizations on the basis of these methods are more expensive than with conventional DFT.

One notorious problem with MP2 has been its inability to calculate response properties since it 'inherits' the poor pole structure of the HF method. This has been the motivation for the introduction of second-order polarization propagator approaches (SOPPA) that are broadly consistent with MP2 ground states.[60,61] Another workaround has been the development of a second-order CC method that has been termed CC2 by its developers.[62] Response properties of the CC2 method are readily formulated within the standard CC hierarchy.[63] CC2 has the same scaling as MP2 but requires an iterative process. It is, hence, more expensive than MP2 itself. The accuracy of CC2 for ground-state energies and for structures appears to be similar (or slightly worse) to that of MP2.[64,65] Thus, its main strength is the calculation of response properties, such as excitation energies.[66–69] Efficient techniques based on the RI approximation have been developed by Hättig and co-workers and are available in the TurboMole program.[66,67,70] In addition, spin-component scaling with emphasis on excited-state calculations has been investigated in the CC2 framework as well.[65] More recently, Schütz and co-workers have reported local CC2 methods and have combined them with DF and Laplace techniques.[71,72]

In the present work, we investigate another modification of the MP2 technique that, in our opinion, suggests itself: the orbital-optimized MP2 technique (OO-MP2). Thus, one bases the calculation on the well-known Hylleraas functional[73] which is made stationary with respect to both amplitude variations and orbital rotations. Hence, a fully stationary energy, which simplifies the calculation of first-order properties is obtained. Closely related ideas have previously been pursued by Adamowicz and Bartlett,[74–79] Head-Gordon and co-workers[52,80] and Kollmar.[81] In ref 52, orbital optimization as been applied to the opposite-spin scaled MP2 method (dubbed O2), and encouraging results for atomization energies and vibrational frequencies of open-shell systems have been reported. Noteworthy is the substantial reduction of spin contamination for small molecules by the OO procedure. It was also pointed out that OO-MP2 is not bounded from below, and hence, in worst case the energy could 'run away' to infinity. However, importantly, the recent analysis of Head-Gordon and co-workers shows that with orbital optimization methods, the stability of MP2-type procedures is greatly enhanced by turning a first derivative discontinuity problem into a second derivative discontinuity problem.[80] Hence, in or close to symmetry-breaking situations orbital optimization will be essential.

In this paper, we perform additional detailed benchmark studies of the orbital optimization technique and pursue the original (and generally more accurate) spin-component scaling technique as opposed to opposite-spin scaling that has been pursued in ref 52. An efficient RI-based implementation of the OO-RI-MP2 and OO-RI-SCS-MP2 techniques into the ORCA program package is reported, and both approaches are characterized through detailed benchmark calculations. The relationship between OO-MP2 and CC2 will be pointed out in the discussion.

The evaluation will focus on those cases where MP2 itself (and also to some extent SCS-MP2) are more difficult to apply. Thus, special attention will be devoted to open-shell systems where spin contamination in the UHF reference often significantly deteriorates the quality of the subsequent MP2 correction.[9,82]

A suitable test set is provided by the radical stabilization energies (RSE, see also ref 83) of organic systems. Two sets of radicals will be investigated. The first set has been proposed in an extensive study by Zipse,[84] who thoroughly investigated trends in RSE for different types of substituents. The second set of test cases is taken from the investigation of Hemelsoet et al.[85] They reported that dissociation energies for C–H bonds in methyl groups connected to aromatic hydrocarbons are particularly strongly affected by spin contamination. All kinds of open-shell transition states represent cases where significant spin contamination may occur. As benchmark for transition states, the hydrogen transfer barrier heights of the HTBH38 set from Zhao et al. have been selected.[86]

In order to judge whether the orbital optimization approach also provides an improvement over the well-established SCS-MP2 method for closed shell systems, a restricted set of such systems has also been included in the study. The test set includes some prototypical main group reactions that have already been investigated in the original parametrization of the SCS-MP2 method.[49] Further, ligand binding energies of some transition-metal complexes will be studied. For these systems, it is commonly claimed that second-order perturbation methods are insufficient, and higher-order correlation methods are required in order to reach quantitative accuracy.[87]

1. Theory

Throughout this paper, indices i,j,k refer to occupied orbitals in the reference determinant, a,b,c refer to virtual orbitals, and p,q,r refer to general orbitals from either set, while P and Q denote auxiliary basis functions. The MP2 energy can be regarded as being stationary with respect to the MP2 amplitudes, since they can be considered as having been optimized through the minimization of the Hylleraas functional:[88]

$$E_{MP2} = \min_{\mathbf{t}} \{ 2\langle \Psi_1 | \hat{H} | \Psi_0 \rangle + \langle \Psi_1 | \hat{H}_0 - E_0 | \Psi_1 \rangle \} \quad (1)$$

$\hat{H}_0$ is the zero-order Hamiltonian, as proposed by Møller and Plesset, Ψ_0 is the reference determinant, Ψ_1 is the first-order wave function, and $E_1 = E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$ is the reference energy. The quantities $\mathbf{t}$ collectively denote the MP2 amplitudes.

The fundamental idea of the OO-MP2 method is to not only minimize the MP2 energy with respect to the MP2 amplitudes but also to minimize the total energy with respect to changes in the orbitals. Since the MP2 energy is not variational with respect to the MO coefficients, no orbital relaxation due to the correlation field is taken into account. If the reference determinant is poor, then the low-order perturbative correction becomes unreliable. This may be alleviated to a large extent by choosing better orbitals in the

reference determinant. Numerical evidence for the correctness of this assumption will be presented below.

In order to allow for orbital relaxation, the Hylleraas functional can be regarded as a functional of the wave function amplitudes **t** and the orbital rotation parameters **R** that will be defined below. Through a suitable parametrization, it becomes unnecessary to ensure orbital orthonormality through Lagrange multipliers. The functional that we minimize reads:

$$\mathscr{A}\{\mathbf{t}, \mathbf{R}\} = E_0[\mathbf{R}] + 2\langle\Psi_1|\hat{H}|\Psi_0\rangle + \langle\Psi_1|\hat{H}_0 - E_0[\mathbf{R}]|\Psi_1\rangle \tag{2}$$

Ψ_0 is the reference determinant. However, it does no longer correspond to the HF determinant. Hence, the reference energy $E_0[\mathbf{R}] = \langle\Psi_0[\mathbf{R}]|\hat{H}|\Psi_0[\mathbf{R}]\rangle$ also changes during the variational process and is no longer stationary with respect to the HF MO coefficients. Obviously, $E_0[\mathbf{R}] \geq E_{\text{HF}}$ since the HF determinant is, by construction, the single determinant with the lowest expectation value of the full Hamiltonian.

The reference energy is given as

$$E_0[\mathbf{R}] = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \tag{3}$$

The first-order wave function excluding single excitations is

$$|\Psi_1\rangle = \frac{1}{4}\sum_{ijab} t_{ab}^{ij}|\Psi_{ij}^{ab}\rangle \tag{4}$$

A conceptually important point is that Brillouin's theorem[89] is no longer obeyed since the Fock matrix will contain off-diagonal blocks. Under these circumstances, the first-order wave function would contain contributions from single excitations. Since the orbital optimization brings in all important effects of the singles, we prefer to leave them out of the treatment. Any attempt to the contrary will destroy the convergence properties. We have, nevertheless, contemplated to include the single excitations perturbatively:

$$E_{\text{singles}}^{(2)} = -\sum_{ia} \frac{|F_{ia}|^2}{\varepsilon_a - \varepsilon_i} \tag{5}$$

The perturbative nature of this correction would destroy the stationary nature of the total energy and is, hence, not desirable. Furthermore, results with inclusion of single excitation contributions represent no improvement to the results reported below. They will, therefore, not be documented below and, henceforth, be omitted from the OO-MP2 method by default.

The explicit form of the OO-MP2 Hylleraas functional employing the RI approximation (OO-RI-MP2) becomes

$$\mathscr{L}_{\text{oo}}[\mathbf{t},\mathbf{R}] = \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle + \sum_{iaP}(ia|P)\Gamma_{ia}'^P +$$
$$\sum_{ij}D_{ij}F_{ij} + \sum_{ab}D_{ab}F_{ab} \tag{6}$$

with

$$\Gamma_{ia}'^P = \sum_Q V_{PQ}^{-1}\sum_{jb}(Q|jb)t_{ab}^{ij} \tag{7}$$

$$(ia|P) = \int\int \psi_i(\mathbf{r}_1)\psi_a(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\eta_P(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{8}$$

$$(P|Q) = V_{PQ} = \int\int \eta_P(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\eta_Q(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{9}$$

Here, $\{\psi\}$ is the set of orthonormal molecular orbitals and $\{\eta\}$ denotes the auxiliary basis set. F_{pq} denotes a Fock matrix element:

$$F_{pq} = \langle p|\hat{h}|q\rangle + \sum_k \langle pk||qk\rangle \tag{10}$$

and it is insisted that the orbitals diagonalize the occupied and virtual subspaces, respectively:

$$\begin{aligned}F_{ij} &= \delta_{ij}F_{ii} = \delta_{ij}\varepsilon_i \\ F_{ab} &= \delta_{ab}F_{aa} = \delta_{ab}\varepsilon_a\end{aligned} \tag{11}$$

The MP2 like density blocks are

$$\begin{aligned}D_{ij} &= -\frac{1}{2}\sum_{kab}t_{ab}^{ik}t_{ab}^{jk} \\ D_{ab} &= \frac{1}{2}\sum_{ijc}t_{ac}^{ij}t_{bc}^{ij}\end{aligned} \tag{12}$$

where the MP2 amplitudes in the case of a block diagonal Fock matrix are obtained through the condition $(\partial\mathscr{L}_{\text{OO}})/(\partial t_{ab}^{ij}) = 0$:

$$t_{ab}^{ij} = -\frac{\langle ij||ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{13}$$

The orbital changes are parametrized by an anti-Hermitian matrix **R** and an exponential Ansatz:

$$\begin{aligned}\mathbf{c}^{\text{new}} &= \mathbf{c}^{\text{old}}\exp(\mathbf{R}) \\ \mathbf{R} &= \begin{pmatrix} 0 & \mathbf{R}_{ia} \\ -\mathbf{R}_{ia} & 0 \end{pmatrix}\end{aligned} \tag{14}$$

The orbitals changes to second order are

$$\begin{aligned}\exp(\mathbf{R})|i\rangle &= |i\rangle + \sum_a R_{ai}|a\rangle - \frac{1}{2}\sum_{jb}R_{bi}R_{bj}|j\rangle + \dots \\ \exp(\mathbf{R})|a\rangle &= |a\rangle - \sum_i R_{ai}|i\rangle - \frac{1}{2}\sum_{jb}R_{aj}R_{bj}|b\rangle + \dots\end{aligned} \tag{15}$$

Through this Ansatz it is ensured that the orbitals remain orthonormal and that no Lagrangian multipliers need to be introduced. The first-order expansion of the Fock operator due to the orbital rotations is

$$F_{pq}[\mathbf{R}] = F_{pq}[0] + R_{pq}^{(1)} + \sum_r R_{rp}F_{rq}[0] + R_{rq}F_{pr}[0] \tag{16}$$

$$R_{pq}^{(1)} = \sum_{kc}R_{ck}\{\langle pc||qk\rangle + \langle pk||qc\rangle\} \tag{17}$$

The first-order energy change becomes ($h_{pq} \equiv \langle p|\hat{h}|q\rangle$, $g_{pqrs} \equiv \langle pq||rs\rangle$):

$$
\begin{aligned}
\mathscr{L}_{OO}[\mathbf{t}, \mathbf{R}] &= \sum_{ic} R_{ci}(h_{ci} + h_{ic}) + \frac{1}{2}\sum_{ijc} R_{ci}(g_{cjij} + g_{ijcj}) + \\
&\quad R_{cj}(g_{icij} + g_{ijic}) \\
&+ 2\sum_{iacP} R_{ci}(ac|P)\Gamma_{ia}'^{P} - 2\sum_{ikaP} R_{ak}(ik|P)\Gamma_{ia}'^{P} \\
&- 2\sum_{ij} D_{ij}\left(R_{ij}^{(1)} + \sum_{c}(R_{ci}F_{cj} + R_{cj}F_{ic})\right) \\
&+ 2\sum_{ab} D_{ab}\left(R_{ab}^{(1)} - \sum_{c}(R_{ak}F_{kb} + R_{bk}F_{ak})\right)
\end{aligned}
\tag{18}
$$

The condition for the energy functional to be stationary, with respect to the orbital rotations, $(\partial\mathscr{L}_{OO}[\mathbf{t},\mathbf{R}]/\partial R_{ai} = 0)$ yields the expression for the orbital gradient and, hence, the expression for the OO-RI-MP2 Lagrangian.

$$
\begin{aligned}
\frac{\partial\mathscr{L}_{OO}[\mathbf{t}, \mathbf{R}]}{\partial R_{ai}} &\equiv g_{ai} = 2F_{ai} + 2\sum_{j} D_{ij}F_{aj} - \\
&\quad 2\sum_{b} D_{ab}F_{ib} + R^{(1)}(\mathbf{D})_{ai} \\
&+ 2\sum_{cP}(ac|P)\Gamma_{ia}'^{P} - 2\sum_{kP}(ik|P)\Gamma_{ia}'^{P}
\end{aligned}
\tag{19}
$$

The goal of the orbital optimization process is to bring this gradient to zero. There are obviously many ways to achieve this. In our experience, the following simple procedure is essentially satisfactory. We first build a matrix $\mathbf{B}$ in the current MO basis with the following structure:

$$
\begin{aligned}
\mathbf{B}_{ij} &= \delta_{ij}F_{ii} \\
\mathbf{B}_{ab} &= \delta_{ab}(F_{aa} + \Delta) \\
\mathbf{B}_{ai} &= \mathbf{B}_{ia} = g_{ai}
\end{aligned}
\tag{20}
$$

where Δ is a level shift parameter. The occupied/occupied and virtual/virtual blocks of this matrix are arbitrary, but their definition has a bearing on the convergence properties of the method. The orbital energies of the block diagonalized Fock matrix appear to be a logical choice. If the gradient is zero, then the $\mathbf{B}$ matrix is diagonal. Hence, one obtains an improved set of orbitals by diagonalizing $\mathbf{B}$. In order to accelerate convergence, a standard DIIS scheme is used.[90,91] However, in order to carry out the DIIS extrapolation of the $\mathbf{B}$-matrix, it is essential that a common basis is used that does not change from iteration to iteration. Since the $\mathbf{B}$ matrix itself is defined in the molecular orbitals of the current iteration, we choose as a common set of orthonormal orbitals the MOs of the HF calculation. The extrapolation is carried out in this basis, and the extrapolated $\mathbf{B}$ matrix is transformed back to the current set of MOs prior to diagonalization. Obviously, the same strategy can be used for orbital optimization in any method for which an orbital gradient is available.

For well-behaved cases this simple scheme converges in 5−10 iterations. Transition metals and more complicated molecules may require up to 20 iterations and level shifting in order to achieve convergence.

It has been argued by Rice et al.[92] and by Scuseria and Schaefer,[93] that one would obtain a Newton−Raphson-like scheme by regarding g_{ai} as an electronic perturbation

and solve a set of coupled-perturbed HF equations in order to obtain new orbital rotation parameters. We have implemented this scheme and found it to be not competitive with the simple DIIS scheme. Each orbital update requires the expensive solution of the CPHF equations. Yet, the convergence is no better or worse than that of the DIIS scheme. This makes sense, the method is not a true Newton−Raphson procedure, because the SCF Hessian is used in place of the much more elaborate OO-MP2 electronic Hessian. The true Newton−Raphson method requires the exact second derivatives of the total energy with respect to the orbital rotation parameters. The CPHF method simply contains the second derivative of the energy of the reference determinant with respect to these rotations and, hence, misses substantial contributions that come from the dynamic correlation part. Since the Hessian is not the exact one, quadratic convergence does not occur. In fact, convergence is at best linear, and the scheme is overall too expensive for large-scale applications.

To illustrate this point, the performance of the (quasi) Newton−Raphson procedure is compared to the DIIS scheme for the glycine molecule in the TZVPP basis and the TZVPP/C auxbasis (411 basis functions, 986 auxiliary basis functions). The time for the DIIS extrapolation is negligible compared to the total time of the iterative OO-MP2 procedure. By contrast, the Newton−Raphson procedure amounts to about 20% of the total OO-MP2 calculation time. Whereas the DIIS extrapolation takes about 1 s per OO-MP2 cycle, the solution of the CPSCF equations takes about 680 s per cycle (10 cycles for energy convergence to 10^{-7} E_h are required in both schemes).

We note, in passing, that upon convergence the sum of the matrix $\mathbf{D}$ and the density of the reference determinant $P_{\mu\nu} = \sum_{i}c_{\mu i}c_{\nu i}$ form the true one-particle density matrix of the OO-MP2 approach that can be used for property or gradient calculations. This will be investigated in detail elsewhere.

2. Implementation and Timings

The OO-RI-MP2 and OO-RI-SCS-MP2 methods have been implemented in closed-shell and spin-unrestricted versions into a development version of the ORCA program package. The implementation is based on the previously reported parallelized gradient code for RI-MP2 and DHDF methods.[59] Since the details have been documented in the previous publication, we only briefly discuss the timings for a medium-sized test case, the cocaine molecule with the TZVP basis set (43 atoms, 544 basis functions, 1 025 auxiliary functions).

The RHF calculation takes 105 min and converges in 15 cycles to an accuracy of 10^{-9} E_h (single CPU of a MacPro 3.1; operating system OS X 10.5, 2 quad-core Intel XEON 3.0 GHZ CPUs that have 12 MB level 2 cache). The RI-MP2 calculation takes only 2 min. The effort for the OO-RI-MP2 method is obviously higher. In addition to its iterative nature, the necessary terms for the orbital gradient must be calculated, which involves the calculation of the response operator (eq 17), the unrelaxed density (eq 12), and
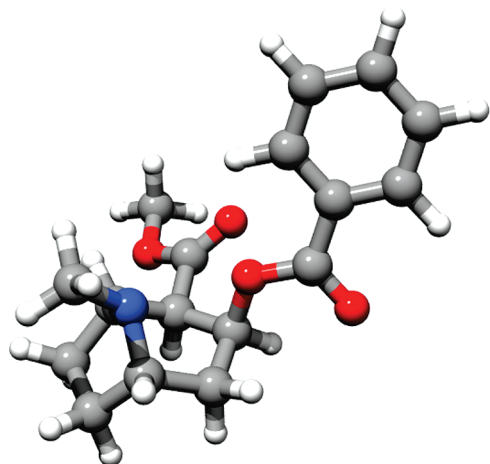
Figure 1. Structure of the cocaine molecule used in the benchmark calculations (43 atoms, 976 basis functions with TZVPP, 976 and 1025 auxiliary functions).

the two external/internal contributions (eq 19), all of which are expensive.

In this example, there are 16 orbital iterations required to converge the energy to about 10^{-9} E_h, which takes 12.2 h. No single term is dominating the calculation time. The construction of the Fock (13%) and response (16%) operators as well as the calculation of the $(ia|jb)$ integrals (15%), the virtual part of the Lagrangian (15%), the internal part of the density (13%) and the calculation of the three-index, two particle density (15%) all take about the same amount of time. The remaining time goes, in about equal parts, to the three-index integral transformation, the virtual part of the density as well as the internal part of the Lagrangian.

Thus, the effort for the total calculation is substantially higher than that for a RI-MP2 calculation (by a factor typically 8−12), but the calculations are feasible even for larger molecules. As will be explained in a different context, the computational effort can be significantly reduced by additional approximations.

In order to illustrate that the effort for a RI-OO-MP2 calculation is still substantially lower than that of a CCSD calculation, we have compared the timings for the tyrosine molecule with the TZVP basis set (313 basis functions). We emphasize that the ORCA CCSD program has state of the art performance such that the comparison is fair. The time required to complete the OO-RI-MP2 calculation is 5 353 s, while the CCSD calculation takes 66 299 s. This shows that the effort for orbital-optimized MP2 calculations is intermediate between that of CCSD and that of MP2 (RI-MP2: 1 016 s including SCF). Also, the computational scaling for MP2 (with or without orbital optimization) is $O(N^5)$ while CCSD is well-known to scale as $O(N^6)$.

3. Calculations

3.1. Computational Details. Unless otherwise noted, all geometries were optimized without constraints at the B3LYP[94−97]/TZVP[35] level using the TurboMole program suite (Version 5.9).[98,99] For the larger systems in the RSE set, an empirical dispersion correction[100−102] was added (B3LYP-D). The transition-metal complexes were optimized

using RI-BP86[95,103]/TZVP together with matching auxiliary basis sets[104] and TurboMole multigrid 'm4'.[105] Single point energies were computed at each given level of theory at the optimized geometries. The exception are the systems from the HTBH38 test set that were taken in an unchanged way from the literature.[86] B2PLYP-D[106,107] BDEs for the poly-cyclic aromatic hydrocarbons were also calculated with the TurboMole program. In these calculations, the TZVPP basis was used together with matching auxiliary basis sets and RI approximation for the Coulomb-exchange part[108] as well as for the second-order perturbation part.

OO-MP2 and OO-SCS-MP2 calculations were carried out with a development version of the ORCA program system.[109] As explained above, the RI approximation was used throughout together with the auxiliary basis sets of Weigend et al.[108] Reaction energies, barrier heights, and RSE are based on the QZVP basis set.[34] All other calculations employed the TZVPP basis set.

Ligand dissociation energies for the carbonyl systems were computed with the RICC program developed in Münster, Germany, at the SCS-MP3[58]/TZVPP level of theory (or equivalently also with the ORCA program).

Reference data for the RSE were calculated at the CCSD(T) level together with the standard two-point basis set extrapolation scheme of Helgaker, Klopper, and co-work-ers.[110,111] For the extrapolation the Dunning basis sets, cc-pVDZ and cc-pVTZ are applied.[112−114] These calculations were carried out using MOLPRO 2006.[115]

All open-shell species were treated in the spin-unrestricted formalism.

3.2. Reaction Energies. In order to assess the perfor-mance of OO-SCS-MP2 for thermochemical applications, a set of reactions constructed from the molecules of the G2 set was investigated.[4] In our opinion, this data are more relevant for chemical applications than atomization energies, as discussed in detail in ref 49. The present test set is a subset of the one that has been used to parametrize SCS-MP2. Only transition states and protonation reactions have been omitted but will be discussed below. Furthermore, reactions involving ozone are omitted as well due to the multireference character of O_3.

It is evident from the results in Table 1 that OO-MP2 is not an improvement over MP2 itself. The mean average deviations of both methods are almost identical, but for OO-MP2, the error range is even larger than that of MP2. Interestingly, the errors of MP2 and OO-MP2 are almost always of opposite signs. Hence, it appears that OO-MP2 is overcorrecting the MP2 results. Turning now to the spin-component scaled results, Table 1 demonstrates that OO-SCS-MP2 improves upon the already excellent results of SCS-MP2. The mean absolute deviation (MAD) drops from 2.5 to 2.2 kcal mol^{-1}. However, at the same time, the error range increases. It was hypothesized that this problem might be alleviated by reoptimization of the two SCS-MP2 scaling parameters. Thus, the calculations were repeated for the entire test set for a collection of systematically varied scaling parameters. The statistical results of this investigation are collected in Table 2. It is apparent that the achievable improvements through reoptimization of the SCS-MP2

Table 1. Reaction Energies for Closed-Shell Molecules[a]

	reaction	ref[b]	deviation			
			SCS-MP2[c]	OO-SCS-MP2[c]	MP2	OO-MP2
1	$F_2 + H_2 \rightarrow 2\ HF$	−132.9	−5.9	−2.6	−10.0	7.8
2	$F_2O + H_2 \rightarrow F_2 + H_2O$	−67.5	−4.5	−1.3	−4.9	1.1
3	$H_2O_2 + H_2 \rightarrow 2\ H_2O$	−85.9	−3.9	−2.2	−5.8	4.9
4	$CO + H_2 \rightarrow CH_2O$	−3.9	−1.3	−0.7	−1.6	2.1
5	$CO + 3\ H_2 \rightarrow CH_4 + H_2O$	−62.3	−2.3	0.1	−4.1	3.7
6	$N_2 + 3\ H_2 \rightarrow 2\ NH_3$	−36.7	0.0	2.2	−2.1	2.0
7	$^1CH_2 + H_2 \rightarrow CH_4$	−128.2	−3.9	−3.9	−7.6	9.4
8	$N_2O + H_2 \rightarrow N_2 + H_2O$	−80.2	0.2	6.1	3.5	−11.3
9	$HNO_2 + 3\ H_2 \rightarrow 2\ H_2O + NH_3$	−119.8	−6.8	1.0	−10.5	2.7
10	$C_2H_2 + H_2 \rightarrow C_2H_4$	−48.8	1.4	2.1	1.6	−1.8
11	$CH_2{=}CO + 2\ H_2 \rightarrow CH_2O + CH_4$	−42.9	0.2	1.9	1.7	−3.6
12	$BH_3 + 3\ HF \rightarrow BF_3 + 3\ H_2$	−94.0	2.9	1.5	0.9	0.2
13	benzene $+ 3\ H_2 \rightarrow$ cyclohexane	−69.4	2.7	2.3	4.1	−3.1
14	$HCO{-}OH \rightarrow CO_2 + H_2$	1.2	−1.5	−3.0	−1.6	2.8
15	$CO + H_2O \rightarrow CO_2 + H_2$	−6.7	−1.8	−4.3	−3.5	7.2
16	$C_2H_2 + HF \rightarrow CH_2{-}\ CHF$	−26.9	2.7	2.6	3.2	−2.6
17	$HCN + H_2O \rightarrow CO + NH_3$	−12.7	2.7	2.4	3.5	−3.6
18	$HCN + H_2O \rightarrow HCO{-}NH_2$	−21.0	1.3	0.6	0.3	1.9
19	$HCONH_2 + H_2O \rightarrow HCOOH + NH_3$	0.4	1.0	0.6	1.3	−1.0
20	$HCN + NH_3 \rightarrow N_2 + CH_4$	−38.3	0.4	0.4	1.5	−1.9
21	$CO + CH_4 \rightarrow CH_3{-}CHO$	4.2	−1.2	−1.0	−2.4	3.6
22	$N_2 + F_2 \rightarrow N_2F_2$	17.6	3.8	3.6	0.6	1.5
23	$BH_3 + 2\ F_2 \rightarrow BF + 3\ HF$	−246.1	−6.4	−0.9	−15.2	10.8
24	$2\ BH_3 \rightarrow B_2H_6$	−43.0	1.4	1.0	−1.8	4.5
25	$2\ ^1CH_2 \rightarrow C_2H_4$	−198.4	−7.5	−8.3	−14.3	1 8.1
26	$CH_3{-}O{-}NO \rightarrow CH_3{-}NO_2$	−3.1	−3.4	−2.1	−5.5	3.3
27	$CH_2{=}C \rightarrow C_2H_2$	−44.6	−5.9	−5.8	−8.2	8.5
28	allene $\rightarrow$ propyne	−1.5	−2.7	−2.6	−3.2	3.1
29	Cyclopropene $\rightarrow$ propyne	−23.9	−0.2	−0.7	0.1	0.1
30	oxirane $\rightarrow CH_3CHO$	−26.8	0.9	0.2	1.6	−0.9
31	vinyl alcohol $\rightarrow CH_3CHO$	−10.1	−0.1	−0.6	−1.0	1.5
32	cyclobutene $\rightarrow$ 1,3- butadiene	−11.6	1.3	0.9	2.3	−2.2
33	$C_2H_4 + {}^1CH_2 \rightarrow C_3H_6$	−106.5	−5.9	−5.6	−11.6	1 3.8
34	$C_2H_2 + C_2H_4 \rightarrow$ cyclobutene	−31.5	−0.5	0.4	−2.8	3.3
35	*cis*-1,3 butadiene $+ C_2H_4 \rightarrow$ cyclohexene	−44.4	6.7	6.4	2.5	−1.5
36	$3\ C_2H_2 \rightarrow$ benzene	−151.1	0.2	2.5	−7.3	7.7
37	$^3CH_2 \rightarrow {}^1CH_2$	9.9	−1.7	−1.2	4.5	−5.0
38	$2\ NH_3 \rightarrow (NH_3)_2$	−3.1	0.5	0.4	−0.1	0.2
39	$2\ H_2O \rightarrow (H_2O)_2$	−5.2	0.5	0.4	0.1	0.2
40	$2\ HF \rightarrow (HF)_2$	−4.7	1.5	1.4	0.1	0.1
	MD		−0.9	−0.1	−2.3	−2.2
	MAD		2.5	2.2	4.0	4.1
	$\Delta_{min\text{-}max}$		14.2	14.7	19.7	29.4

[a] Given are the reference values (ref) and the deviations (E(method) − E(reference)) for SCS-MP2 and OO-SCS-MP2. The mean deviation (MD), the mean absolute deviation (MAD), and the error range ($\Delta_{min\text{-}max}$ = maximum deviation − minimum deviation) are also listed. All energies are in kcal mol^{-1}. [b] QCISD(T) with QZVP basis for heavy atoms (TZVP for H) on B3LYP/TZVP geometries taken from ref 49. [c] With QZVP basis set on B3LYP/TZVP geometries.

Table 2. Statistical MD and MAD (in parentheses) Values for the Reaction Set for Different Combinations of Same Spin (c_{ss}) and Opposite Spin (c_{os}) Scaling Parameters in OO-SCS-MP2[a]

c_{ss}	c_{os}		
	1.15	1.20	1.25
0.30	0.0 (2.0)	0.0 (2.1)	0.0 (2.3)
0.35	−0.2 (2.1)	−0.2 (2.2)	−0.1 (2.3)
0.40	−0.3 (2.1)	−0.3 (2.3)	−0.3 (2.4)

[a] All values in kcal mol^{-1}.

parameters are marginal. Thus, we prefer to keep the method as simple as possible and to keep the original SCS-MP2 scaling parameters also for OO-SCS-MP2. All remaining calculations have been performed in this way.

3.3. Transition-Metal Complexes. As a more challenging test, the performance of OO-SCS-MP2 is tested for a selection of organometallic transition-metal complexes. In transition-metal carbonyls, the metal−ligand bonds are still strong but are nevertheless difficult to describe with high accuracy by wave-function methods. Experience indicates that at least third-order perturbation contributions must be accounted for in order to correctly treat these bonds.[87] Hence, they provide a particularly challenging test set for OO-SCS-MP2.

Our results obtained with the SCS-MP3,[58] SCS-MP2 and OO-SCS-MP2 methods in conjunction with the TZVPP basis set are shown in Table 3. The CCSD(T) data serve as the reference in this case. They are extremely well reproduced by SCS-MP3, that is, in essentially quantitative agreement. The otherwise very successful LPNO-NCPF/1 method, on

Table 3. Ligand Dissociation Energies D_e (in kcal mol^{-1}) Based on BP86/TZVPP Geometries[a]

	D_e						
dissociation reaction	CCSD(T)	LPNO-NCPF/1	SCS-MP3	OO-SCS-MP2	SCS-MP2	OO-MP2	MP2
$[Cr(CO)_6] \rightarrow [Cr(CO)_5] + CO$	42.0	34.9	41.6	44.1	50.3	59.2	46.8
$[Cr(CO)_5(C_2H_4)] \rightarrow [Cr(CO)_5] + C_2H_4$	30.2	23.9	28.1	39.6	36.3	46.0	46.8
$[Cr(CO)_5(CS)] \rightarrow [Cr(CO)_5] + CS$	74.4	65.6	76.4	89.8	89.7	100.9	107.9
$[Ni(CO)_4] \rightarrow [Ni(CO)_3] + CO$	29.4[b]	22.9	22.1	61.2	43.9	55.6	89.1

[a] For the single point energies the TZVPP basis set was also applied. [b] The T1 diagnostic is 0.031 for both $Ni(CO)_3$ and $Ni(CO)_4$.

Table 4. Barrier Heights for Hydrogen Transfer Reactions[a]

	reaction	lit[b]	deviation			
			SCS-MP2[c]	OO-SCS-MP2[c]	MP2	OO-MP2
1	$H + HCl \rightarrow TS1$	5.7	3.7	2.5	5.1	5.7
2	$H_2 + Cl \rightarrow TS1$	8.7	1.8	0.9	−0.1	−2.1
3	$OH + H_2 \rightarrow TS2$	5.1	4.9	1.1	2.3	−2.9
4	$H_2O + H \rightarrow TS2$	21.2	8.0	4.3	10.1	7.7
5	$CH_3 + H_2 \rightarrow TS3$	12.1	2.2	1.0	0.8	−1.0
6	$CH_4 + H \rightarrow TS3$	15.3	4.0	2.6	4.4	5.0
7	$OH + CH4 \rightarrow TS4$	6.7	4.4	−0.4	1.2	−4.8
8	$H_2O + CH_3 \rightarrow TS4$	19.6	5.6	1.3	5.4	−0.2
9/10	$H + H_2 \rightarrow TS5$	9.6	3.7	2.9	3.5	4.5
11	$OH + NH_3 \rightarrow TS6$	3.2	7.3	−0.3	3.7	−5.7
12	$H_2O + NH_2 \rightarrow TS6$	12.7	8.3	1.1	6.0	−3.1
13	$HCl + CH_3 \rightarrow TS7$	1.7	2.3	0.8	1.1	−1.0
14	$Cl + CH_4 \rightarrow TS7$	7.9	2.2	0.7	−0.5	−2.8
15	$OH + C_2H_6 \rightarrow TS8$	3.4	5.4	0.2	2.4	−4.6
15	$H_2O + C_2H_5 \rightarrow TS8$	19.9	6.0	1.5	6.0	0.0
16	$F + H_2 \rightarrow TS9$	1.8	4.6	1.7	3.1	−1.2
17	$HF + H \rightarrow TS9$	33.4	7.5	5.1	11.7	10.5
18	$O + CH_4 \rightarrow TS10$	13.7	5.8	1.9	3.8	−0.4
19	$OH + CH_3 \rightarrow TS10$	8.1	5.5	2.3	4.0	0.4
20	$H + PH_3 \rightarrow TS11$	3.12	2.8	2.0	2.5	3.4
21	$H_2 + PH_2 \rightarrow TS11$	23.2	3.3	3.0	1.4	0.5
22	$H + OH \rightarrow TS12$	10.7	6.8	3.5	6.9	5.4
23	$H_2 + O \rightarrow TS12$	13.1	5.2	1.5	3.0	−1.4
24	$H + H_2S \rightarrow TS13$	3.5	3.5	2.5	3.2	4.0
25	$H_2 + HS \rightarrow TS13$	17.3	2.1	1.4	−0.6	−2.2
26	$O + HCl \rightarrow TS14$	9.8	8.7	2.6	6.1	−1.8
27	$OH + Cl \rightarrow TS14$	10.4	8.3	3.0	4.7	−2.8
28	$NH_2 + CH_3 \rightarrow TS15$	8.0	5.1	2.4	3.1	0.0
29	$NH + CH_4 \rightarrow TS15$	22.4	3.3	0.4	1.9	−1.4
30	$NH_2 + C_2H_5 \rightarrow TS16$	7.5	6.2	3.6	4.1	1.0
31	$NH + C_2H_6 \rightarrow TS16$	18.3	5.2	1.9	3.4	−0.3
32	$C_2H_6 + NH_2 \rightarrow TS17$	10.3	4.4	1.2	1.4	−2.8
33	$C_2H_5 + NH_3 \rightarrow TS170$	17.4	4.1	1.2	2.7	−0.8
34	$NH_2 + CH_4 \rightarrow TS18$	14.5	2.7	−0.2	−0.2	−3.8
35	$NH_3 + CH_3 \rightarrow TS18$	17.8	3.1	0.3	1.8	−1.6
37/38	*s-trans cis*-$C_5H_8 \rightarrow TS19$	38.4	1.5	1.4	−2.8	−5.2
	MD		4.6	1.7	3.1	−0.2
	MAD		4.6	1.8	3.5	2.9
	$\Delta_{\text{min-max}}$		6.9	5.5	14.5	16.2

[a] Given are the reference values from the literature and the deviations ($\Delta E^{\ddagger}$(method) − $\Delta E^{\ddagger}$(reference)) for SCS-MP2 and OO-SCS-MP2. The mean deviation (MD), the mean absolute deviation (MAD), and the error range ($\Delta_{\text{min-max}}$) are listed at the bottom. All energies in kcal mol^{-1}. [b] Best estimates from experiment and theory taken from ref 49. [c] With QZVP basis set on geometries taken from ref 49.

the other hand, systematically underestimates all binding energies by 6−9 kcal/mol. Turning to the SCS-MP2 and OO-SCS-MP2 data, it is evident from the data in Table 3 that orbital optimization is not able to improve the description of the complex electronic situation in these transition-metal carbonyl complexes. Given the success of the SCS-MP3 method, the most likely explanation is that it is necessary to correctly account for electron pair−pair couplings that are invariably neglected in any MBPT2 variant. Hence, the results of OO-SCS-MP2 and SCS-MP2 are of about the same quality and both show significant deviations from the reference values, in particular for $Ni(CO)_4$. Comparison to the nonscaled MP2

and OO-MP2 shows that spin-component scaling brings in a substantial improvement, which is, however, not enough to render the results chemically accurate. The smallness of the test set does not allow for a statistical evaluation.

3.4. Barrier Heights. In the next step of the evaluation, barrier heights from the HTBH38 benchmark set are considered. As has recently been pointed out by Zheng et al.,[116] reaction barriers are particularly challenging for MP2 methods. Our results are collected in Table 4. Note that, for two of the reactions, reactant and product are identical (entries 9, 10 and 37, 38). They are listed only once but are considered individually for the statistical evaluations in order

to maintain consistency with the previous evaluations for this benchmark test.[49]

It becomes evident from the data in Table 4 that OO-SCS-MP2 provides particularly accurate results for these barriers. The MAD from the reference values decreases from 4.6 to only 1.7 kcal mol^{-1} in comparison with SCS-MP2. Interestingly, the comparison of MP2 and OO-MP2 reveals that the improvement by orbital optimization alone is rather moderate. Hence, it is the combination of orbital optimization and spin-component scaling that renders the method accurate. The results for OO-SCS-MP2 are almost as good as those delivered by the previously evaluated CEPA methods that are computationally much more demanding[9] (unless efficient approximations are employed).[117] In fact, the MAD of 1.7 kcal/mol for OO-SCS-MP2 is of the same size as what is obtained with the best current (and highly parametrized) density functionals and is much better than B3LYP, which provides an MAD of about 4 kcal/mol^{-1} for this benchmark.[118] Interestingly, OO-SCS-MP2 and SCS-MP2 themselves tend to overestimate barrier heights, especially when one of the reactants is a hydrogen atom, while the corresponding back reaction barriers are described better.

3.5. Radical Stabilization Energies. We now turn to the systems that the OO-SCS-MP2 method was mainly designed for. These are the reactions of radical species. In the evaluation reactions of the general homodesmotic type:

$$R-H + CH_3\cdot \rightarrow R\cdot + CH_4 \qquad (21)$$
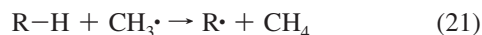
are considered. If the reaction is exothermic, the rest R stabilizes the radical better than a methyl group. For our investigation, we took the set of R groups, as previously proposed in the study of Zipse.[84] However, we believe that it is desirable to obtain more rigorous reference values than those provided by the earlier restricted open-shell MP2 (ROMP2) calculations.[84] Therefore, we have turned to CCSD(T) calculations in combination with basis set extrapolation. For simplicity and since we only compare theoretical data among each other, ZPVE and thermal effects were not considered. The new reference data together with the results of OO-SCS-MP2 and SCS-MP2 calculations are collected in Table 5.

As in the case of reaction barriers, it is observed that OO-SCS-MP2 drastically improves upon the results of SCS-MP2. The MAD value drops by about a factor of 3 from 4.7 to 1.5 kcal mol^{-1}, and at the same time, the error range is reduced from 43.4 kcal mol^{-1} (SCS-MP2) to only 16.3 kcal mol^{-1} (OO-SCS-MP2), again a factor of 3. In addition, in this case OO-MP2 also improves substantially upon MP2. It is, in fact, the most accurate method for this test set.

For judging the effect of spin contamination, the $\langle S^2 \rangle$ values for the UHF reference are also listed in Table 5. Clearly, if the reference suffers from spin contamination, then the SCS-MP2 results are strongly biased. OO-SCS-MP2, on the other hand, decreases this effect to a remarkable extent. This is in agreement with the results of ref 52. Unfortunately, we have not yet implemented the calculation of the $\langle S^2 \rangle$ value on the basis of OO-SCS-MP2, which would allow us to judge the precise extent of residual spin contamination. Nevertheless, the behavior of SCS-MP2 versus OO-SCS-MP2 is visualized in Figure 2.

3.6. Bond Dissociation Energies in Polycyclic Aromatic Hydrocarbons. Encouraged by the performance of OO-SCS-MP2 for the RSE test set, we have turned to study bond dissociation energies in polcyclic hydrocarbons as another challenging application of the method. Here, it is demonstrated that OO-SCS-MP2 can be applied to larger systems in conjunction with sufficiently saturated basis sets.

In the test reactions, the C–H bond in a methyl group is broken which leads to a benzyl type radical (Figure 3). The design of the test set goes back to an investigation of Hemelsoet et al.,[85] who reported that these systems significantly suffer from spin contamination.

The results of our computations are collected in Table 6. In agreement with the results of Hemelsoet et al.,[85] very large deviations from the expected $\langle S^2 \rangle$ value of 0.75 are found. This leads to such a large bias for the SCS-MP2 results that these are rendered essentially useless. Again, however, OO-SCS-MP2 yields greatly improved the results. However, they cannot be directly compared to the results of ref 85 because, in the previous study, vibrational and thermal corrections were added, and a basis set of only double-ζ quality was used. Since this puts some doubt on the accuracy of the results in ref 85, we also computed B2-PLYP-D values for these reactions. These should also be much less influenced by spin contamination because the Kohn–Sham determinant is usually much less prone to symmetry breaking and spin contamination than that of the UHF wave function. Hence, the results are considered to be more reliable. Indeed, the corresponding $\langle S^2 \rangle$ values in Table 6 deviate less strongly from 0.75 but still indicate significant problems with the reference.

On an absolute scale both methods, OO-SCS-MP2 and B2-PLYP-D, differ by about 5 kcal mol^{-1}, but the trends are the same. There is a slight increase in BDE of 1 kcal mol^{-1} from **5−13** to **5−14**, then a larger increase of 10 kcal mol^{-1} to **5−1**, and the bond in **5−2** is less stable by about 2 kcal mol^{-1}. The step from **10−14** to **10−1** leads to an increase of about 6 kcal mol^{-1} in BDE, and there is almost no difference between **10−1** and **10−12**. Both methods are in qualitative agreement with the findings of Hemelsoet et al. We note, in passing, that their B2-PLYP results do *not* show the same trend. The reason for this discrepancy is not clear.

4. Discussion

In this work, the orbital-optimized MP2 method has been developed into a useful tool for computational quantum chemistry. The motivation for the work is to improve upon the results of the second-order many-body perturbation theory through incorporation of orbital relaxation effects to all orders, while maintaining acceptable computational efficiency. This goal is clearly reached by the OO-MP2 method that, as we have demonstrated here, can be applied in reasonable turnaround times to molecules of significant size. The effort for a OO-RI-MP2 calculation is nevertheless substantially higher than that of a RI-MP2 (RI-SCS-MP2) calculation due to its iterative nature and to the extra terms required to obtain the orbital gradient. The ratio for a reasonably large calculation has been found to be 8−12 in

Table 5. Reference Radical Stabilization Energies Together with the Deviations (RSE(method) − RSE(reference)) for SCS-MP2 and OO-SCS-MP2 are given in kcal mol⁻¹ [a]

| substituent	ref[b]	deviation				
		SCS-MP2[c]	OO-SCSMP2[c]	MP2	OO-MP2	$<S^2>$[d]
·CH₂−C₆H₅	−15.2	22.9	0.7	24.4	0.5	1.335
CH₂=C·−CN	1.9	30.1	0.8	27.3	−1.1	1.385
·CF=CH₂	6.8	7.8	0.5	6.0	−0.7	0.934
·CH₂−CCl₃	7.4	4.2	1.5	7.1	4.6	0.825
·CH₂−CF₂−CH₃	0.1	0.5	0.1	0.5	−0.1	0.762
·CH₂−CF₃	1.4	0.5	0.1	0.5	−0.1	0.762
·CH₂−CH₂−Cl	−3.2	1.4	0.4	1.4	0.2	0.774
·CH₂−CH₂−F	−1.3	0.4	−0.1	0.3	−0.3	0.763
·CH₂−CH₂−OH	−1.8	0.6	0.2	0.4	−0.1	0.764
·CH₂−CH=CH₂	−17.5	6.9	1.0	6.0	0.1	0.951
·CH₂−CHO	−10.0	9.7	0.7	9.6	0.2	0.927
·CH₂−CN	−8.6	11.6	0.7	10.9	0.0	0.938
·CH₂−CO−CH₃	−8.7	8.5	0.6	8.4	0.2	0.909
·CH₂−CO-NH₂	−6.3	1.9	−0.1	1.8	−0.3	0.793
·CH₂−CO−NH−CH₃	−6.3	4.0	−0.2	1.6	−0.5	0.786
·CH₂−CO−O−CH₃	−6.6	2.5	0.0	2.4	−0.3	0.802
·CH₂−CO−OH	−6.4	2.7	0.1	2.6	−0.1	0.807
·CH₂−CH(−CH₂)₂	−3.0	0.6	0.1	0.5	−0.1	0.763
·CH₂−F	−3.9	1.0	0.2	0.3	−0.8	0.762
·CH₂−NH₂	−12.0	0.8	−0.4	0.1	−1.4	0.763
·CH₂−NH₃⁺	4.7	0.6	0.3	0.2	−0.1	0.763
·CH₂−NH−CH₃	−12.6	0.9	−0.5	0.3	−1.5	0.764
·CH₂−NH−CHO	−11.1	1.7	0.2	1.0	−0.7	0.777
·CH₂−NH−OH	−8.6	1.8	−0.4	0.9	−1.7	0.772
·CH₂−N(−CH₃)₂	−12.8	1.2	−0.5	0.6	−1.3	0.764
·CH₂−NO₂	−3.3	2.3	0.1	1.6	−0.7	0.787
·CH₂−O−CF₃	−3.9	1.4	0.4	0.7	−0.4	0.764
·CH₂−O−CH₃	−2.7	0.9	0.1	0.4	−0.5	0.763
·CH₂−O−CHO	−5.9	1.3	0.4	0.6	−0.6	0.765
·CH₂−CO−O−CH₃	−6.2	1.5	0.3	0.7	−0.8	0.766
·CH₂−OH	−4.2	0.9	0.2	0.2	−0.6	0.762
·CH₂−PH₃⁺	0.7	0.2	0.1	0.5	0.3	0.762
·CH₂−S−CH₃	−10.8	1.4	−0.7	0.7	−1.8	0.773
·CH₂−S−CHO	−8.4	1.6	−0.5	1.0	−1.7	0.776
·CH₂−SH₂⁺	2.7	0.5	0.0	0.2	−0.4	0.765
·CH₂−SH	−9.4	1.1	−0.6	0.5	−1.6	0.772
·CH₂−SO−O−CH₃	0.0	0.9	−0.4	0.9	−0.9	0.763
·CH₂−SO−CH₃	−2.9	1.2	−0.3	1.0	−1.0	0.771
NH₂−CH·−CN	−22.5	10.3	−0.4	8.8	−2.3	0.908
NH₂−CH·−CO−NH₂	−24.1	1.2	−1.0	0.0	−2.7	0.776
NH₂−CH·−CO−OH	−25.4	1.4	−1.0	0.0	−2.8	0.779
·CH₂−C≡CH	−13.1	10.7	0.9	9.5	0.1	0.960
·C(−CH₃)₃	−6.4	1.5	0.6	1.3	0.1	0.767
·CH₂−C(−CH₃)₃	−2.3	0.8	0.3	0.8	0.2	0.763
MD		3.8	0.1	3.3	−0.5	
MAD		3.8	0.4	3.3	0.8	
Δ₍min-max₎		29.9	2.5	27.2	7.4	

[a] The $<S^2>$ values are taken from the unrestricted Hartree−Fock calculation. The mean deviation (MD), the mean absolute deviation (MAD), and the error range (Δ₍min-max₎) are listed at the bottom. [b] CCSD(T)/CBS(D→T). [c] QZVP basis set on B3LYP/TZVP geometries. [d] The theoretical value is always 3/4.

this work. As will be developed in detail elsewhere, this ratio improves in analytic gradient calculations where all of these terms also have to be calculated for RI-MP2.

The results of an extensive numerical evaluation of the OO-MP2 and OO-SCS-MP2 methods indicate that they do drastically improve the accuracy (and stability) of the parent nonorbital-optimized methods in electronically difficult situations. The errors typically decrease by a factor of 3 to 5. This is particularly evident for open-shell species and transition states and less so for transition-metal complexes. For standard main group closed-shell species, the results of orbital-optimized and conventional MP2 methods is, however, comparable, and it is questionable whether the extra effort for the orbital optimization is well invested. The

consistent improvement offered by spin-component scaling in the conventional MP2 method persists in the OO-MP2 approach, and it was found in this work that very little, if anything, can be gained through reoptimization of the SCS-MP2 same-spin and opposite-spin scaling parameters.

Thus, there is a well-defined domain of applicability for OO-(SCS)-MP2 that is intermediate between the conventional MP2 and the more rigorous coupled-cluster approaches. The cost for OO-(SCS)-MP2 is also intermediate between these extremes. In many cases, the much better orbitals delivered by the OO-(SCS)-MP2 method may also be advantageous for coupled cluster investigations, in particular for open-shell transition-metal complexes. This subject will be investigated elsewhere.
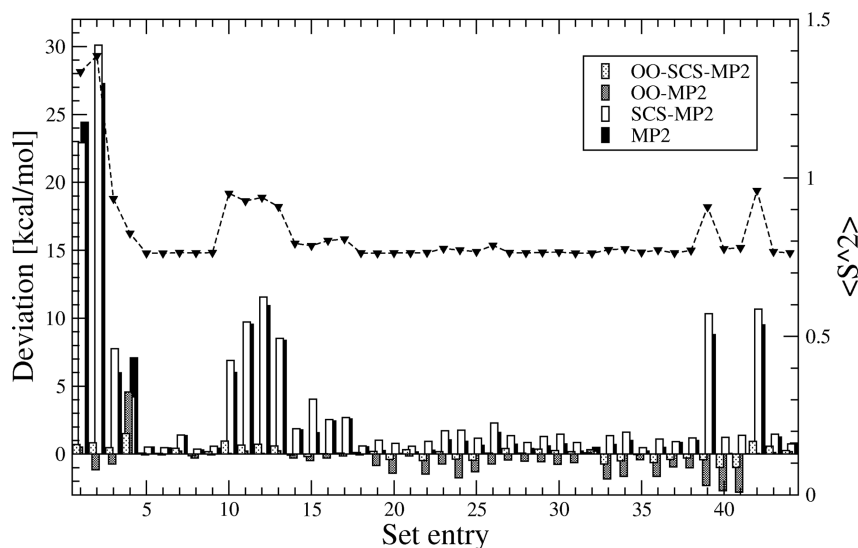
Figure 2. Errors of the methods under investigation for the RSE set (RSE(theory) - RSE(reference)). In order to demonstrate the relation of the error with spin contamination, the $\langle S^2 \rangle$ value for each UHF reference is plotted on top.
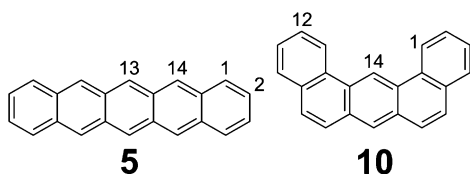
Figure 3. Polycyclic aromatic hydrocarbons. Methylated positions, where bond dissociations in the methyl group are considered, are indicated by numbers.

Methodologically, the OO-MP2 method is closely related to the CC2 coupled cluster variant. The CC2 doubles amplitude equations correspond to the conventional MP2 residual, eq 22[72] (but with integrals that are 'dressed' with t_1 amplitudes). In order to emphasize the similarities between the OO-MP2 and CC2 methods, one may write the CC2 singles residual and the OO-MP2 orbital gradient in the following forms:

CC2-singles residual:

$$\sigma_a^i = \tilde{F}'_{ai} + \frac{1}{2}\sum_{lcd}\tau_{cd}^{il}\overline{\langle al||cd\rangle} - \frac{1}{2}\sum_{kld}\tau_{ad}^{kl}\overline{\langle kl||id\rangle} \quad (22)$$

$$\tau_{cd}^{il} = t_{cd}^{il} + t_c^i t_d^l \quad (23)$$

$$\overline{\langle al||cd\rangle} = \langle al||cd\rangle - \sum_k \langle kl||cd\rangle t_a^k \quad (24)$$

$$\overline{\langle kl||id\rangle} = \langle kl||id\rangle + \sum_c \langle kl||cd\rangle t_c^i \quad (25)$$

OO-MP2 orbital gradient:

$$R_{ai} = \hat{F}_{ai} + \sum_{ldc} t_{cd}^{il}\langle al||cd\rangle - \sum_{kld} t_{ad}^{kl}\langle kl||id\rangle \quad (26)$$

Thus, in both approaches, an effective one-particle Fock matrix enters the quantity to be brought to zero together with three internal and three external integrals contracted in an

Table 6. Bond Dissociation Energies for the C–H bond of the Methyl Group of Polycyclic Aromatic Hydrocarbons Based on Single Point Energies with the TZVPP Basis on B3LYP-D/TZVP Geometries[a]

	BDE			BDE	
system	SCS-MP2	OO-SCS-MP2	$\langle S^2\rangle$[b]	B2PLYP-D	$\langle S^2\rangle$[b]
5–13	183.0	85.4	3.509	90.8	0.896
5–14	180.8	86.4	3.469	91.9	1.361
5–1	189.7	95.7	3.689	103.8	0.757
5–2	187.5	94.1	3.656	102.0	0.850
10–14	187.5	90.4	3.303	94.4	1.112
10–1	115.6	97.3	1.483	99.4	1.046
10–12	194.6	97.2	3.377	98.9	0.757

[a] The $\langle S^2\rangle$ from the unrestricted Hartree–Fock and DFT calculation is also given. Energies in kcal mol⁻¹. [b] The theoretical value is always 3/4.

identical way with double excitation amplitudes. The difference is that in CC2 one uses a fixed set of SCF orbitals and obtains integrals and amplitudes that are dressed in a nonlinear way with t_1 amplitudes. In the OO-MP2 technique, one has orbitals that change in each iteration, but one may well think of the changes as a "dressing" of the SCF orbitals with orbital rotation parameters. In CC2, one needs to do a "dressing transformation" in each iteration, while in OO-MP2 a new integral transformation is required. The dressing of the integrals and amplitudes in CC2 is, in fact, relaxing the orbitals. In a Brückner sense, one could even absorb the t_1 amplitudes into the orbitals in each iteration. The similarity transformed integrals that are usually used in CC2 implementations expose this feature rather clearly. If the t_1 operator, $\hat{t}_1 = \sum_{ia} t_a^i a_a^+ a_i$, would now be replaced by the full orbital rotation operator, $\hat{\kappa} = \sum_{ai}\kappa_{ai}(a_a^+ a_i - a_i^+ a_a)$, then one would fully relax to orbital-optimized CC2 that must resemble OO-MP2. A highly interesting discussion of orbital-optimized coupled cluster theory has been given by Köhn and Olsen.[119]

The effective Fock matrices are given by

CC2:

$$\tilde{F}'_{ai} = F_{ai} - \sum_{kc}(F_{kc}\tau_{ca}^{ik} + t_c^k\langle ak||ic\rangle) + \sum_c F_{ac}t_c^i -$$

$$\sum_k F_{ik}t_a^k + \frac{1}{2}\sum_{kcd}t_c^kt_d^i\langle ak||cd\rangle - \frac{1}{2}\sum_{klc}t_a^lt_c^k\langle lk||ic\rangle \quad (27)$$

OO-MP2:

$$\hat{F}_{ai} = F_{ai} + \sum_j D_{ij}F_{aj} - \sum_b D_{ab}F_{ib} + \sum_{cd} D_{cd}\langle ca||di\rangle +$$

$$\sum_{kl} D_{kl}\langle ka||li\rangle \quad (28)$$

again, similar terms can be recognized. The computational effort for both methods must, for optimal implementations, be rather similar. However, the stationary properties of the OO-MP2 method make it more efficient for the calculation of first-order and perhaps also of response properties. This subject will be investigated elsewhere. From this point of view, one may regard OO-MP2 as an improved or, at least, modified second-order coupled-cluster-type theory.

In conclusion, this work evaluates a wave function based second-order ab initio method that complements existing approaches such as MP2, SCS-MP2, B2PLYP, or CC2.

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