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Comment on 'Efficient calculation of canonical MP2 energies' [P. Pulay, S. Saebø, K. Wolinski, Chem. Phys. Lett. 344 (2001) 543–552]

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Abstract

Accuracy and efficiency of the resolution of the identity approximation in second-order Møller–Plesset perturbation theory (RI-MP2) are reassessed in the light of the new MP2 code by Pulay et al. It is demonstrated that with the RI approximation considerable computational savings can be achieved, especially for larger basis sets of triple-zeta and higher quality. The error introduced by the RI approximation has to be viewed in comparison with the one-electron basis set error. It is shown that this error is insignificant if optimized auxiliary basis sets are used. © 2002 Published by Elsevier Science B.V.

Code development for correlated methods employing a Møller–Plesset type partitioning of the Hamiltonian [1] is still an active area in contemporary quantum chemistry [2–6]. Recently, in the course of developing a low-order scaling AO-based MP2 code [3], Pulay, Saebø and Wolinski (PSW) have demonstrated, that even for the canonical formulation of MP2 there is potential for improvement [2]. They proposed an integral direct algorithm which due to an improved screening based on localization criteria can very efficiently handle large molecules, which has been demonstrated by calculations with up to 1800 basis functions.

We want to comment on two remarks made by PSW about the RI-MP2 approach, which do not affect the results of their work, but are important to those who use MP2 or similar methods in their research. The first point concerns the accuracy of RI-MP2. At the bottom of page 549 PSW point out that 'RI-MP2 is significantly faster than traditional MP2 but, with the usual fitting basis, total energies are accurate only at the millihartree (10^{-3} E_h) level', while they achieve microhartree accuracy with their screening scheme. For a non-expert reader this could imply that the approach of PSW is more accurate than RI-MP2, which is,

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however, not necessarily the case. The error caused by the resolution of the identity (RI-error) is a smooth and slowly varying function of the geometry. Therefore, a very high global consistency is achieved, because a large fraction of the RI-error cancels out if reaction energies etc. are considered, cf. [6]. Screening errors are a different issue. They may vary abruptly and unsystematically with the geometry and must therefore be kept orders of magnitudes smaller in order to obtain smooth potential energy surfaces and accurate energy differences. In practice, the accuracy of MP2 calculations is governed by the one-electron basis set error while the RI-error is one or two orders of magnitude smaller. This has been demonstrated and discussed in detail in [7,8].

The second point concerns the efficiency. On page 550 PSW compare with previous RI-MP2 calculations carried out by Bernholdt [9] and conclude that their new MP2 code is faster than RI-MP2 (58 h compared to >269 h). The calculations were, however, not comparable (different computer systems, different symmetry exploitation). Thus, it is difficult to draw any conclusions on the efficiency of either code from these timings. As for conventional MP2, the efficiency of RI-MP2 depends much on the implementation. Another important point is the choice of the auxiliary basis for the resolution of the identity. Since it has a strong influence on both the accuracy and the efficiency, the use of atom-optimized auxiliary basis sets is crucial. The size of the auxiliary basis sets can then be kept reasonably small while errors of typically less than 0.1 per cent of the correlation energy are introduced.

To provide a better comparison between conventional MP2 and the RI-MP2 approach, we have recalculated some of the examples given in [2] with the implementations available in TURBOMOLE [10]. We employed the RI-MP2 code reported in [6] and the recent RI-CC2 program [11], which uses a different batching scheme and a modified symmetry treatment. The geometries were kindly made available by Prof. Pulay.

Since we do not have exactly the same computer systems as those used by PSW, we ran our calculations on 1.2 GHz Athlon PCs with 750 MB memory, but without using Athlon specific optimizations or math libraries. To our experience, timings of TURBOMOLE on different PC systems can then be reproduced very well by scaling them with the SPECFP2000 values [12]. For example, the RI-MP2 module was benchmarked on a 750 MHz PIII and a 1.2 GHz Athlon [13]. The ratio found was 0.64 (if the same binaries are used) which compares well with the SPECFP2000 ratio

Table 1
Comparison of timings for conventional MP2 and RI-MP2 codes

Molecule	Calicheamicin fragment[a]		Tetramethoxy-calix[4]arene		C_{60}-fullerene[b]
Symmetry	C_1	C_1	C_{2h}	C_{2h}	$I_h(D_{2h}$[c]$)$
Basis	cc-pVDZ	cc-pVTZ	cc-pVDZ	cc-pVTZ	cc-pVTZ
N	420	924	664	1528	1800
$2n$	124	124	184	184	240
N_x	1567	2429	2464	3876	4860
T_{MP2}	138.2[d]	1690.0	187.5	2357.3	6750.2[d]
T_{RIMP2}	28.0	237.4	36.6	340.5	427.3 (170.9[e])
E_{MP2}	−3.471331[f]	−4.267246	−5.022569	−6.127922[f]	−9.263815[f]
Δ_{RI}	−0.000045	+0.000513	−0.000448	−0.000698	+0.001307

All timings are wall-clock times (in min); T_{MP2} are the scaled timings (see text) from [2]. N denotes the number of basis functions, $2n$ is the number of correlated electrons and N_x is the size of the auxiliary basis set. The RI-error is defined as $\Delta_{RI} = E_{RIMP2} - E_{MP2}$. All energies are given in hartree units (E_h).

[a] The corrected geometry of [15] was taken.

[b] A different geometry was used ($d_{CC}^{5ring} = 145.8$ pm, $d_{CC}^{connect} = 140.7$ pm).

[c] Symmetry used for RI benchmark calculation.

[d] Timing for different geometry, cf. [2].

[e] Timing of new RI code (see text).

[f] Recomputed values (see text).

of 0.67. The same should apply to the code of PSW. We decided to scale the timings of PSW using a factor of 0.68 (ratio 1.2 GHz Athlon/800 MHz PIII) and a factor of 0.83 (C_{60} example; ratio 1.2 GHz Athlon/1 GHz PIII) respectively. The recently optimized [8] auxiliary basis sets for Dunning's correlation consistent series of basis sets [14] were employed. For details on the optimization procedure cf. [7,8]. In all cases, a core memory usage of 512 MB was allowed for.

As examples we chose the calicheamicin fragment, the tetramethoxy-calix[4]arene isomer and buckminsterfullerene (C_{60}), employing the Dunning basis sets of double and triple zeta quality. Moreover, we considered the examples given by PSW which are typically good test cases for low-order scaling methods. The results are summarized in Tables 1 and 2.

For calicheamicin and tetramethoxy-calix[4]arene a very similar picture arises. For the small cc-pVDZ basis set, the wall time elapsed for RI-MP2 is five times shorter than for the conventional calculation. For the larger cc-pVTZ basis, the RI code gains even a factor of 7–8. The RI error is well below 1 mE_h (0.05 per cent of the correlation energy). We recall, that the error in the correlation energy due to an incomplete one-electron basis is much larger: At the double zeta level, typically only 70 per cent of the correlation energy are recovered, at the triple zeta level only as much as 90 per cent; thus e.g., the error for calix[4]arene with cc-pVTZ is still of the order of 600–700 mE_h.

For C_{60} (and the tetramethoxy-calix[4]arene isomer with triple-zeta basis, cf. above) the correlation energies printed in Table 3 of [2] unfortunately seem to be incorrect. We recomputed the values with the conventional MP2 code of TURBOMOLE. The C_{60} calculation was run, however, using a different geometry (see footnote of Table 1), such that for this calculation the computational point group I could be used. For the benchmark RI calculation only D_{2h} was exploited in order to ensure comparability. For C_{60}, with the current implementation of RI-MP2 the calculation runs nearly 16 times faster than it does in the calculation with the fast code of PSW; the expected error in the correlation energy due to basis set incompleteness is about 600 mE_h, whereas the RI error is only 1.3 mE_h. With the RI-CC2 code, the C_{60} calculation is even 40 times faster than the conventional one.

More difficult cases are collected in Table 2. These are molecular systems where the screening procedure of PSW does a good job. For $(glycine)_{10}$ RI-MP2 only gains an acceleration factor of 1.7. The new RI-CC2 code is somewhat better, since it can more efficiently use the mirror plane symmetry. For the water clusters, the computational savings due to RI are rather small as well (1.4 and 1.2), and the increase of the computation time is steep, scaling with $N^{4.7}$ between $(H_2O)_{20}$ and $(H_2O)_{40}$. However, the employed basis sets are very small and not appropriate for applications. For larger basis sets RI-MP2 should be more efficient. The cc-pVDZ auxiliary basis used here, leads to errors of only

Table 2
Timings of typical test cases for low-order scaling codes

Molecule	$(Glycine)_{10}$	$(H_2O)_{20}$	$(H_2O)_{40}$
Symmetry	C_s	C_1	C_1
Basis	6-31G(d, p)	6-31G*	6-31G*
N	734	380	760
$2n$	228	160	320
N_x	2744[a]	1920[a]	3840[a]
T_{MP2}	411.3	44.3	953
T_{RIMP2}	238.1 (137.2[b])	31.3[b]	790[b]
E_{MP2}	−6.202540	−3.796139	−7.616209
Δ_{RI}	+0.000667	−0.000510	−0.001013

See Table 1 for details.
[a] cc-pVDZ optimized auxiliary basis set (used in the CAO basis for $(H_2O)_n$).
[b] Timings of new RI code (see text).

0.02 per cent. The apparently very systematic RI-errors in the correlation energy of the clusters $(H_2O)_{20}$ and $(H_2O)_{40}$ are an example of the globally consistent behaviour of the RI approximation.

In summary, the calculations confirm the previous findings that with optimized auxiliary basis sets the RI-error is typically smaller than 0.1 per cent of the correlation energy and thus is more than two orders of magnitude smaller than the basis set truncation error of a triple-zeta basis. This is the most appropriate basis set for MP2 calculations in the sense of a balanced description, i.e., basis set and many-electron truncation errors are of similar magnitude.

For all examples the RI code is faster than the conventional implementation reported by PSW, in particular for systems with triple zeta basis sets and considerably delocalized electrons. We observe a speed-up by a factor of 7 for such systems, for C_{60} even a factor of 40 is found. For typical test cases for linear scaling algorithms – glycine-chains and water clusters – where orbitals can be well localized, the improved screening criterion of PSW gains considerable savings of cpu time and RI-MP2 is only faster by a factor of 1.2–1.7. For this kind of systems the local MP2 implementations [3,5] have a very early break-even point. For large basis sets and systems with large delocalized fragments RI-MP2 is expected to be more economical in most cases. Thus, RI and local methods are complementary developments.

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