Theor Chem Acc (1997) 97:331–340

Theoretical
Chemistry Accounts

RI-MP2: first derivatives and global consistency

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Received: 17 December 1996 / Accepted: 27 March 1997

Abstract. The evaluation of RI-MP2 first derivatives with respect to nuclear coordinates or with respect to an external electric field is described. The prefix RI indicates the use of an approximate resolution of identity in the Hilbert space of interacting charge distributions (Coulomb metric), i.e., the use of an auxiliary basis set to approximate charge distributions. The RI technique is applied to first derivatives of the MP2 correlation energy expression while the (restricted) Hartree-Fock reference is treated in the usual way. Computational savings by a factor of 10 over conventional approaches are demonstrated in an application to porphyrin. It is shown that the RI approximation to MP2 derivatives does not entail any significant loss in accuracy. Finally, the relative energetic stabilities of a representative sample of closed-shell molecules built from first and second row elements have been investigated by the RI-MP2 approach, and thus it is tested whether such properties that refer to potential energy hypersurfaces in a more global way can be described with similar consistency to the more locally defined derivatives.

Key words: Gradients – Perturbation theory of electronic structure – MP2 – Electron correlation – Coulomb interaction

1 Introduction

The calculation of electronic interaction matrix elements is one of the most demanding steps in ab initio approaches that use atom-centered functions as one-electron basis sets. This is particularly true of Møller-Plesset perturbation theory (MP2), also known as second-order many-body perturbation theory MBPT(2) [1–4]. With the advent of computationally less demanding and sometimes more reliable density functional approaches, MP2 theory has lost some of its appeal as the most economic ab initio approach to describe electronic correlations [5–8]. Undimished, however, is the significance of MP2 theory as a starting point for more accurate approaches (like CCSD(T)) [9–11], in applications where density functional approaches must fail (e.g., if van der Waals interactions are non-negligible), in calculations of chemical shift tensors [12, 13], and as an ingredient in high-accuracy density functional approaches [14, 15]. Improving the efficiency of MP2 calculations thus is a rewarding research goal.

Almlöf et al. contributed to the latter objective in many ways: by the development of integral-direct MP2 codes [16] that can utilize any finite molecular point group [17], by suggesting novel ways as to how canonical molecular orbitals (MOs) in the MP2 energy expression may be replaced non-iteratively by local quantities [18, 19], and by using auxiliary basis sets to short-cut the evaluation of two-electron interactions [20, 21]. The use of the Coulomb metric in conjunction with auxiliary basis sets for the approximate description of two-electron interactions can be traced to Whitten [22] and to Dunlap et al. [23]. Recently this technique has been applied to the calculation of MP2 energies (termed RI-MP2 energies) [24, 25], including an implementation on parallel computers [26].

In this work the calculation of MP2 derivatives [27] in the RI approximation is described, and computational savings by one order-of-magnitude as compared to conventional (semi-) direct [28] MP2 derivative calculations are demonstrated. To test the accuracy of the RI approximation we probe properties like equilibrium structures and dipole moments that refer to a single molecular configuration, and – as a test of global consistency – we investigate the relative energetic stabilities of a representative sample of closed-shell molecules built from first- and second-row elements.

2 Theory

For a given closed-shell restricted Hartree-Fock (RHF) reference wave function the MP2 correlation energy can be written as

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$$E_{MP2} = \sum_{ijab} t_{ij}^{ab}(ia|jb) \ , \tag{1}$$

where the *t*-amplitudes obey the following equation

$$\sum_k (t_{ik}^{ab}\varepsilon_{kj} + \varepsilon_{ik}t_{kj}^{ab}) - \sum_c (t_{ij}^{ac}\varepsilon_{cb} + \varepsilon_{ac}t_{ij}^{cb}) \\ = 2(ia|jb) - (ib|ja) \ . \tag{2}$$

The labels a, b, c refer to virtual MOs, while i, j, k refer to "active" occupied valence MOs; without loss of generality we exclude "frozen" core orbitals from the correlation treatment. Besides the separation into frozen core and active valence MOs we do not assume canonicity of the (real-valued) RHF MOs. $(ia|jb)$ is the energy of the electrostatic interaction between the transition densities $i(\underline{r})a(\underline{r})$ and $j(\underline{r})b(\underline{r})$.

Using the RI approximation in the Coulomb metric

$$(ia|jb) \approx (ia|jb)_{\mathrm{RI}} := \sum_P B_{ia}^P B_{jb}^P \tag{3}$$

with

$$B_{ia}^P = \sum_Q (ia|Q) V_{QP}^{-1/2} \ . \tag{4}$$

Here P, Q label auxiliary basis functions. Equation (3) is obtained upon expanding the transition densities of the type $i(\underline{r})a(\underline{r})$ into this auxiliary basis; $V_{QP}^{-1/2}$ is an element of the inverse square root of the (positive definite) metric matrix

$$V_{QP} = (Q|P) = \int d^3\underline{r}_1 \int d^3\underline{r}_2 \ \ Q(\underline{r}_1)P(\underline{r}_2)/r_{12} \ . \tag{5}$$

Let ξ be a perturbation parameter. Assuming that the perturbation can be dealt with in the RHF formalism with real MOs, those MOs $i(\underline{r},\xi), a(\underline{r},\xi)$ and corresponding lagrangians (orbital energies in the case of canonical MOs) $\varepsilon_{ij}(\xi), \varepsilon_{ab}(\xi)$ will become functions of ξ[29]. ξ might refer to a distortion of the molecular structure or to an external electric field.

The derivative of the RI-MP2 *t*-amplitudes [cf.Eq. (2)] at $\xi = 0$ (unperturbed system) becomes

$$\frac{d}{d\xi}t_{ij}^{ab}\bigg|_{\xi=0} = t_{ij}^{ab^\xi} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \\ \times \left\{ 2(ia|jb)_{\mathrm{RI}}^\xi - (ib|ja)_{\mathrm{RI}}^\xi + \sum_c t_{ij}^{ac}\varepsilon_{cb}^\xi + \varepsilon_{ac}^\xi t_{ij}^{cb} \right. \\ \left. - \sum_k t_{ik}^{ab}\varepsilon_{kj}^\xi + \varepsilon_{ik}^\xi t_{kj}^{ab} \right\} \tag{6}$$

where we assumed canonical unperturbed MOs, i.e.

$$\varepsilon_{ab}(\xi = 0) = \varepsilon_a \delta_{ab} \tag{7}$$

$$\varepsilon_{ij}(\xi = 0) = \varepsilon_i \delta_{ij} \tag{8}$$

and where

$$(ia|jb)_{\mathrm{RI}}^\xi = \sum_{PQ} \left\{ (ia|P)^\xi V_{PQ}^{-1}(Q|jb) + (ia|P)V_{PQ}^{-1}(Q|jb)^\xi \right\} \\ - \sum_{RSPQ} (ia|R)V_{RP}^{-1}V_{PQ}^\xi V_{QS}^{-1}(S|jb) \ . \tag{9}$$

Differentiation of the RI-MP2 correlation energy expression with respect to ξ yields [cf. Eqs. (1, 2, 6–8)]

$$\frac{1}{2}E_{MP2}^\xi = \sum_{ijab} t_{ij}^{ab}(ia|jb)_{\mathrm{RI}}^\xi + \sum_{ab} P_{ab}\varepsilon_{ab}^\xi + \sum_{ij} P_{ij}\varepsilon_{ij}^\xi \tag{10}$$

with the symmetric "relaxed densities"

$$P_{ab} = \sum_{ijc} t_{ij}^{ac} \frac{(ib|jc)_{\mathrm{RI}}}{\varepsilon_i + \varepsilon_j - \varepsilon_b - \varepsilon_c} \tag{11}$$

$$P_{ij} = -\sum_{abk} t_{ik}^{ab} \frac{(ja|kb)_{\mathrm{RI}}}{\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b} \ . \tag{12}$$

Inserting Eq. (9) into Eq. (10) leads to

$$\frac{1}{2}E_{MP2}^\xi = 2\sum_{iaP} \Gamma_{ia}^P (P|ia)^\xi - \sum_{PQ} \gamma_{PQ} V_{PQ}^\xi + \sum_{ab} P_{ab}\varepsilon_{ab}^\xi \\ + \sum_{ij} P_{ij}\varepsilon_{ij}^\xi \tag{13}$$

where

$$\Gamma_{ia}^P = \sum_{jbQ} t_{ij}^{ab} B_{jb}^Q V_{QP}^{-1/2} \tag{14}$$

$$\gamma_{PQ} = \sum_{iaR} \Gamma_{ia}^P B_{ia}^R V_{RQ}^{-1/2} \tag{15}$$

$$(P|ia)^\xi = \sum_{\mu\nu} (P|\mu\nu)^\xi c_{\nu i} c_{\mu a} + \sum_q (P|qa) U_{qi}^\xi \\ + \sum_q (P|iq) U_{qa}^\xi \ . \tag{16}$$

Here ν, μ label functions that belong to the expansion basis for the MOs, and $c_{\nu i}$ and $c_{\mu a}$ are corresponding expansion coefficients (commonly referred to as LCAO-MO coefficients).

$$c_{\nu i}^\xi = \sum_q c_{\nu q} U_{qi}^\xi \tag{17}$$

$$c_{\mu a}^\xi = \sum_q c_{\mu q} U_{\mu a}^\xi \tag{18}$$

describe the first-order response of the LCAO-MO coefficients to the perturbation ξ; here and in the following the labels p, q, r, s refer to generic MOs, i.e. active or frozen occupied orbitals as well as virtual orbitals.

By insertion of

$$\Gamma_{\nu\mu}^P = \sum_{ia} c_{\nu i} \Gamma_{ia}^P c_{\mu a} \tag{19}$$

and of Eq. (16) into Eq. (13) one gets

$$\frac{1}{2}E^{\xi}_{MP2} = 2\sum_{\nu\mu P}\Gamma^{P}_{\nu\mu}(P|\nu\mu)^{\xi} - \sum_{PQ}\gamma_{PQ}V^{\xi}_{PQ} + \sum_{iq}L_{iq}U^{\xi}_{qi} + \sum_{aq}L''_{aq}U^{\xi}_{qa} + \sum_{ab}P_{ab}\varepsilon^{\xi}_{ab} + \sum_{ij}P_{ij}\varepsilon^{\xi}_{ij} \tag{20}$$

where

$$L_{iq} = 2\sum_{aP}\Gamma^{P}_{ia}(P|qa) \tag{21}$$

$$L''_{aq} = 2\sum_{iP}\Gamma^{P}_{ia}(P|iq) \ . \tag{22}$$

Unitary invariance of the RHF wave function has that U^{ξ}_{ij} and U^{ξ}_{ab} may be chosen in any convenient way as long as the condition of orthogonality is fulfilled:

$$U^{\xi}_{pq} + S^{(\xi)}_{pq} + U^{\xi}_{qp} = 0 \tag{23}$$

where

$$S^{(\xi)}_{pq} = \sum_{\nu\mu} c_{\nu p}S^{\xi}_{\nu\mu}c_{\mu q} \ . \tag{24}$$

Thus U^{ξ}_{ij} and U^{ξ}_{ab} may be chosen

1. either canonically, such that

$$\varepsilon^{\xi}_{ij} = \varepsilon^{\xi}_{ii}\delta_{ij} \,, \quad \varepsilon^{\xi}_{ab} = \varepsilon^{\xi}_{aa}\delta_{ab} \,, \tag{25}$$

2. or symmetrically, i.e.

$$U^{\xi}_{ij} = -\frac{1}{2}S^{(\xi)}_{ij} \,, \quad U^{\xi}_{ab} = -\frac{1}{2}S^{(\xi)}_{ab} \,, \tag{26}$$

3. or, for example, semi-canonically as a mixture of 1 and 2 [30].

Up to this point all equations for E^{ξ}_{MP2} are valid for any choice of U^{ξ}_{ij} and U^{ξ}_{ab}. As is well-known, the canonical choice suffers from numerical instability, but has the advantage that only diagonal elements of P_{ab} and P_{ij} need to be calculated. The symmetric choice is numerically stable, but it requires the calculation of all P_{ab} and P_{ij}. It has been suggested that canonical perturbed orbitals be used unless $\varepsilon_a \approx \varepsilon_b$ or $\varepsilon_i \approx \varepsilon_j$ [30]. In this way it is possible to combine the advantages of the canonical and of the symmetric choice. In our preliminary implementation we start from the conceptually simple symmetric choice. As a consequence

$$\varepsilon^{\xi}_{ij} = F^{(\xi)}_{ij} - \frac{\varepsilon_i + \varepsilon_j}{2}S^{(\xi)}_{ij} + \sum_{lc}A_{ijlc}U^{\xi}_{cl} - \frac{1}{2}\sum_{lm}A_{ijlm}S^{(\xi)}_{ml} \tag{27}$$

$$\varepsilon^{\xi}_{ab} = F^{(\xi)}_{ab} - \frac{\varepsilon_a + \varepsilon_b}{2}S^{(\xi)}_{ab} + \sum_{lc}A_{ablc}U^{\xi}_{cl} - \frac{1}{2}\sum_{lm}A_{ablm}S^{(\xi)}_{ml} \ . \tag{28}$$

Here l, m represent general occupied orbitals (including the frozen core), $F^{(\xi)}_{pq}$ is an element from a Fock matrix that has been built from derivative integrals, i.e.,

$$F^{(\xi)}_{pq} = \sum_{\nu\mu} c_{\nu p}c_{\mu q}\left[h^{\xi}_{\nu\mu} + \sum_{\kappa\lambda l}\{2(\nu\mu|\kappa\lambda) - (\nu\lambda|\kappa\mu)\}^{\xi}c_{\kappa l}c_{\lambda l}\right] , \tag{29}$$

and

$$A_{pqrs} = 4(pq|rs) - (ps|rq) - (pr|sq) \ . \tag{30}$$

To be consistent with the RHF wave function, to which the RI approximation is *not* applied in this work, Eqs. (29, 30) contain conventional electron repulsion integrals.
Let f denote any frozen core orbital. We then define

$$\tilde{\pi}_{pq} = P_{ab} \oplus P_{ij} \oplus \frac{L_{if}}{\varepsilon_i - \varepsilon_f} \tag{31}$$

where the symbol $\oplus$ is to indicate that some (smaller) matrices – their index ranges are implied by the index symbol convention – are patched (added) onto a compound matrix. Inserting Eqs. (26–28) into Eq. (20), observing the condition $\varepsilon^{\xi}_{if} = 0$, noting the definition $L_{fa} = 0$, and solving the Z-vector equation [31]

$$L''_{al} - L_{la} - \sum_{pq}A_{alpq}\tilde{\pi}_{pq} = (\varepsilon_a - \varepsilon_l)P_{al} + \sum_{bm}A_{albm}P_{bm} \ , \tag{32}$$

we finally obtain [32]:

$$\frac{1}{2}E^{\xi}_{MP2} = 2\sum_{\nu\mu P}\Gamma^{P}_{\nu\mu}(P|\nu\mu)^{\xi} - \sum_{PQ}\gamma_{PQ}V^{\xi}_{PQ} + \sum_{pq}\left\{\pi_{pq}F^{(\xi)}_{pq} - W_{pq}S^{(\xi)}_{pq}\right\} \tag{33}$$

with

$$\pi_{pq} = \tilde{\pi}_{pq} \oplus P_{al} \tag{34}$$

$$W_{pq} = \frac{1}{2}\left\{(\varepsilon_p + \varepsilon_q)\pi_{pq} \oplus \sum_{rs}A_{lqrs}\pi_{rs} \oplus L_{iq} \oplus L''_{aq}\right\} \ . \tag{35}$$

3 Implementation and performance

In modern, integral driven (semi-direct) MP2 derivative programs the four-center integrals $(\mu\nu|\kappa\lambda)$, once calculated, are successively transformed to the MO basis [33, 34]. The operation count for these transformations scales with nN^4 (N = number of basis functions, n = number of occupied active orbitales i). Mass storage requirements scale with nN^3, unless the integrals $(\mu\nu|\kappa\lambda)$ are re-evaluated many times.

RI-MP2 derivatives require the transformation and mass storage of three-index quantities only (Fig. 1). The integral-driven transformation of $(\nu\mu|P)$ to B^{Q}_{ip} gives rise to nN^2N_x and nNN_x^2 matrix multiply operations where the number of auxiliary basis functions N_x is typically smaller than $3N$. A repeated evaluation of $(\nu\mu|P)$ in the (three-center) integral-driven transformation algorithm has a negligible effect on computation times but reduces the main memory storage requirements to $\sim N^2$. Once

```
1. Form $V_{PQ}^{-1/2}$                                                    2.1
2. Loop $I$ ($I$ is a subset of active occupied orbitals)
       calculate for all $P$: $(\nu\mu|P)$
       form $B_{ip}^{Q} \leftarrow c_{\nu i}c_{\mu p}(\nu\mu|P)V_{PQ}^{-1/2}$   $(i\in I)$      35.8
       store $B_{ip}^{Q}$ on disc
   end of loop $I$
3. Loop $I$ (subset of active occupied orbitals)
     Loop $J$ (subset of active occupied orbitals)
       form   $(ia|jb) \leftarrow B_{ia}^{Q}B_{jb}^{Q}$   $(i\in I,\ j\in J)$                  71.8
              $t_{ij}^{ab} \leftarrow \{2(ia|jb)-(ib|ja)\}/(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)$   2.9
              $Y_{ia}^{P} \leftarrow t_{ij}^{ab}B_{jb}^{P}$                                  72.8
              $P_{bc} \leftarrow t_{ij}^{ab}(ia|jc)/(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_c)$   13.5
       records labeled $(A,J)$ containing sets of pairs $((ia|jb),(ib|ja))$, $b\le a$, are stored on disc   6.1 (76.9)
     end of loop $J$
     Loop $A$ (subsets of virtual orbital pairs $(a,b)$ with $b\le a$)
       read records $(A,J)$ for all $J$
       form $t_{ij}^{ab}$ and $t_{ij}^{ba}$, $i\in I$, $(a,b)\in A$.             7.5(20.4)
       $P_{jk} \leftarrow \frac{1}{(1+\delta_{ab})}\{t_{ij}^{ab}(ia|kb)+t_{ij}^{ba}(ib|ka)\}/(\varepsilon_i+\varepsilon_k-\varepsilon_a-\varepsilon_b)$
     end of loop $A$
     $L_{ap}'' \leftarrow Y_{ia}^{P}B_{ip}^{P}$                                      1.8
     $\Gamma_{ia}^{P} \leftarrow Y_{ia}^{Q}V_{QP}^{-1/2}$
     $\tilde{\gamma}_{PQ} \leftarrow \Gamma_{ia}^{P}B_{ia}^{Q}$                       11.5
     $\Gamma_{i\nu}^{P} \leftarrow \Gamma_{ia}^{P}c_{\nu a}$
     store $\tilde{\gamma}_{PQ}$ and $\Gamma_{i\nu}^{P}$ on disc
   end of loop $I$
4. $\gamma_{PQ} = \tilde{\gamma}_{PR}V_{RQ}^{-1/2}$                            0.3
   $E_{MP2}^{\xi} \leftarrow \gamma_{PQ}V_{QP}^{\xi}$
5. Loop $\Xi$ (subsets of basis functions $\nu$)
     $E_{MP2}^{\xi} \leftarrow \Gamma_{i\nu}^{P}c_{\mu i}(\mu\nu|P)^{\xi}$   $(\nu\in\Xi)$     19.0
     $L_{ip} \leftarrow (\nu\mu|P)\Gamma_{i\nu}^{P}c_{\mu p}$
   end of loop $\Xi$
6. Assemble $\tilde{\pi}_{pq} \leftarrow P_{ab}\oplus P_{ij}\oplus L_{if}/(\varepsilon_i-\varepsilon_f)$ and $A_{lpqr}\tilde{\pi}_{qr}$   34.4
   solve $(\varepsilon_a-\varepsilon_l)P_{al}+A_{albm}P_{bm} = L_{al}''-L_{la}-A_{lapq}\tilde{\pi}_{pq}$   181.5
   $\pi_{pq} \leftarrow \tilde{\pi}_{pq}\oplus P_{al}$
   $W_{pq} = \frac{(\varepsilon_p+\varepsilon_q)}{2}\pi_{pq}\oplus\frac{1}{2}A_{lqrs}\pi_{rs}\oplus\frac{1}{2}L_{iq}\oplus\frac{1}{2}L_{aq}''$
7. $E_{MP2}^{\xi} \leftarrow 2(\pi_{pq}+\delta_{ip}\delta_{iq})h_{pq}^{(\xi)}-2(W_{pq}+\delta_{ip}\delta_{iq}\varepsilon_i)S_{pq}^{(\xi)}$   1.1
   $E_{MP2}^{\xi} \leftarrow (2\pi_{pq}+\delta_{ip}\delta_{iq})(F_{pq}^{(\xi)}-h_{pq}^{(\xi)})$                 108.3
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Fig. 1. Algorithm for RHF/RI-MP2 first derivatives with cpu (wall) times (minutes) for porphyrin

calculated, nNN_x matrix elements B_{ip}^{Q} are successively written to mass storage; this is the only I/O operation thus far.

The computational bottlenecks in RI-MP2 energy or derivative calculations are the $n^2N^2N_x$ matrix multiply operations needed to form $(ia|jb)_{\mathrm{RI}}$ and Y_{ia}^{P} (Fig. 1). The construction of P_{bc} and P_{jk} scale only with $n^2N^3/2$ and $n^3N^2/2$ operations, respectively. To keep with $\sim N^2$ main memory storage requirements, the calculation of P_{jk} implies an intermediate storage of $\sim nN^2$ integrals $(ia|jb)_{\mathrm{RI}}$ on mass storage (for fixed i).

The final two steps (6 and 7 in Fig. 1) of the implementation are organized as in more conventional MP2 derivative programs. Here all calculations proceed integral-driven in the AO basis, so *no* further integral transformations are needed. The derivatives obtained are a sum from the RHF and RI-MP2 contributions.

To judge the performance of this RI-MP2 derivatives algorithm we use a distorted (non-symmetric and non-planar) porphyrin molecule as a reference. Porphyrin has been chosen, since its MP2/SVP equilibrium structure is known and shows large deviations from the (bond alternant) RHF equilibrium structure [35], so that we had an opportunity to verify the accuracy of the RI-MP2 approach in structure optimizations of large molecules (Section 5). Currently it is still difficult to calculate (non-RI-) MP2 derivatives for molecules much larger than porphyrin. As numerical characteristics of the calculations we mention 38 atoms, $N = 406$ basis functions (SVP basis sets [36]), $n = 57$ valence orbitals out of 81 occupied orbitals, and $N_x = 1036$ auxiliary basis functions (their choice is outlined in Sect. 4). Timings for the individual steps of an RI-MP2 derivatives calculation (first derivatives of the energy with respect to atomic positions in porphyrin; frozen core approximation applied) are detailed in the right margin of Fig. 1. They refer to an IBM RS6000 3CT workstation computer. While forming $(ia|jb)_{\mathrm{RI}}$ and Y_{ia}^{P} scales proportional to $n^2N^2N_x$, it takes *less* time than solving the Z-vector equation, and will become the dominant step only as molecules double in size.

Table 1. Comparison of computation times and mass storage requirements for RHF, RHF derivatives[a], MP2 derivatives[a], and RI-MP2 derivatives[a] calculations applied to a distorted (non-symmetric and non-planar) porphyrin molecule[b]

Method	cpu time [h]	Wall time [h]	Mass storage [MB]
RHF (11 iterations)	3.0	3.0	900[c]
RHF derivatives	1.0	1.0	0
MP2 derivatives	133.8	145.9	2800
RI-MP2 derivatives	13.0	16.2	972
RI-MP2 derivatives with frozen core	9.5	11.4	684[c,d]

[a] First derivatives with respect to all atomic coordinates

[b] The calculations were performed on an IBM 3CT workstation computer with 128 MB of main memory

[c] Partial storage of four-index integrals in the (semi-direct) RHF part or in the Z-vector equations solver is user-defined and was set at 900 MB

[d] Mass storage used in RI part

The construction of P_{ab} and P_{ij} would be unnecessary if canonical orbitals were used in the RI-MP2 scheme. This would save 20 min of computation time. In addition the I/O of t-amplitudes (1.5 h) could be eliminated. Thus it will be worthwhile to consider the semi-canonical approach suggested by Lee et al. [30].

A comparison of computation times for RHF, MP2 and RI-MP2 calculations of porphyrin is presented in Table 1. The semi-direct MP2 derivatives calculation (carried out with the TURBOMOLE MPGRAD program [34] is seen to take about 10 times more computation time than the RI-MP2 derivatives calculation.

Table 2. Auxiliary basis sets for hydrogen and carbon

Hydrogen	
Exponent	Contraction coefficient
3 *s*	
34.061341	0.60251978E-02
5.1235746	0.45021094E-01
1.1646626	0.20189726
1 *s*	
0.32723041	1.0000000
1 *s*	
0.10307241	1.0000000
1 *p*	
0.46000000	1.0000000
1 *p*	
1.3800000	1.0000000
1 *d*	
0.96000000	1.0000000
Carbon	
6 *s*	
13575.349682	0.22245814352E-03
2035.2333680	0.17232738252E-02
463.22562359	0.89255715314E-02
131.20019598	0.35727984502E-01
42.853015891	0.11076259931
15.584185766	0.24295627626
1 *s*	
6.2067138508	1.0000000000
1 *s*	
2.5764896527	1.0000000000
1 *s*	
0.57696339419	1.0000000000
1 *s*	
0.22972831358	1.0000000000
1 *s*	
0.95164440028E-01	1.0000000000
3 *p*	
34.697232244	0.53333657805E-02
7.9582622826	0.35864109092E-01
2.3780826883	0.14215873329
1 *p*	
0.81433208183	1.0000000000
1 *p*	
0.28887547253	1.0000000000
1 *p*	
0.10056823671	1.0000000000
1 *d*	
1.3800000000	1.0000000000
1 *d*	
0.46000000000	1.0000000000
1 *f*	
0.96000000000	1.0000000000

Table 3. Total energies (in E_h) of selected molecules calculated by RHF, MP2 and RI-MP2 methods at RHF/SVP equilibrium geometries. The frozen core approximation has been used. ΔRI refers to the difference RI-MP2 versus MP2

Molecule	RHF	MP2	RI-MP2	ΔRI
Hydrocarbons:				
H_2	−1.128929	−1.155253	−1.155189	+0.000064
CH_4	−40.169178	−40.330456	−40.330310	+0.000146
$H_3C{-}CH_3$	−79.175012	−79.477040	−79.476798	+0.000242
$H_2C{=}CH_2$	−77.977993	−78.251866	−78.251743	+0.000123
$HC{\equiv}CH$	−76.762550	−77.016954	−77.017287	−0.000333
$HC{\equiv}C{-}C{\equiv}CH$	−152.384051	−152.877552	−152.878330	−0.000778
C_6H_6 (benzene)	−230.536045	−231.315356	−231.315248	+0.000108
C_4H_4 (tetrahedran)	−153.493570	−154.019862	−154.020245	−0.000383
Oxygen compounds:				
H_2O	−75.961338	−76.161538	−76.162673	−0.001135
H_2O_2	−150.652982	−151.031639	−151.033618	−0.001979
CO	−112.647161	−112.930603	−112.932151	−0.001548
CH_2O	−113.779774	−114.092963	−114.094188	−0.001225
CH_3OH	−114.954862	−115.290622	−115.291632	−0.001012
CO_2	−187.487402	−187.962363	−187.965562	−0.003199
H_2CO_3	−263.453358	−264.120668	−264.124639	−0.003971
CH_2O_2 (formic acid)	−188.221448	−188.762162	−188.764599	−0.002437
Fluorine compounds:				
F_2	−198.511773	−198.893683	−198.895146	−0.001463
HF	−99.932832	−100.131559	−100.132485	−0.000926
CF_4	−435.297117	−436.151748	−436.155594	−0.003846
OF_2	−273.223635	−273.786802	−273.789106	−0.002304
Nitrogen compounds:				
N_2	−108.854222	−109.156661	−109.157870	−0.001209
N_4 (tetraazatetrahedran)	−217.340996	−217.997791	−217.999806	−0.002015
$HN{=}NH$	−109.899572	−110.225415	−110.226076	−0.000661
$H_2N{-}NH_2$	−111.093594	−111.441226	−111.441860	−0.000634
NH_3	−56.148885	−56.334849	−56.3351732	−0.000324
HCN	−92.801389	−93.082404	−93.0831912	−0.000787
HNC	−92.785819	−93.055324	−93.0559813	−0.000657
$H_2C{=}NH$	−93.960042	−94.259576	−94.2599184	−0.000342
C_2H_3N (3-aza-cyclopropene)	−131.677759	−132.104878	−132.105420	−0.000542
HNO	−129.684025	−130.024675	−130.026076	−0.001401
HNO_2	−204.458315	−205.004882	−205.007984	−0.003102
HNO_3	−279.226824	−279.952871	−279.957225	−0.004354
NF_3	−352.248472	−352.965401	−352.968257	−0.002856
$H_3N \cdot HF$ (hydrogen-bridged)	−156.101826	−156.489867	−156.491172	−0.001305
Boron compounds:				
BH_3	−26.370472	−26.462847	−26.462521	+0.000325
B_2H_6	−52.778687	−52.994654	−52.994291	+0.000363
B_4H_4	−100.852507	−101.218426	−101.218353	+0.000073
$H_3B \cdot CO$	−139.033139	−139.433662	−139.435078	−0.001415
$H_3B \cdot NH_3$	−82.560173	−82.857322	−82.857421	−0.000099
$B_3N_3H_6$ (borazol)	−240.982338	−241.717261	−241.718301	−0.001040
BF_3	−322.936365	−323.564194	−323.567125	−0.002931
Beryllium compounds:				
Be	−14.553727	−14.575757	−14.575349	+0.000408
Be_4	−58.282495	−58.422923	−58.422686	+0.000237
BeH_2	−15.753542	−15.796833	−15.796543	+0.000290
Be_2H_4	−31.539787	−31.636342	−31.635906	+0.000436
$Be(CH_3)_2$	−93.797033	−94.123604	−94.123287	+0.000317
Be_2F_4	−427.039661	−427.854352	−427.858536	−0.004184
$(H_2O)_2BeF_2$	−365.483018	−366.295118	−366.299543	−0.004425
Lithium compounds:				
Li_2	−14.854395	−14.866183	−14.866093	+0.000090
Li_8	−59.450431	−59.543303	−59.542873	+0.000430
LiH	−7.974003	−7.993467	−7.993398	+0.000070
Li_4H_4	−32.118487	−32.207438	−32.207228	+0.000210
$(LiCH_3)_4$	−188.132335	−188.800554	−188.800466	−0.000088
Li_2O	−89.663589	−89.872399	−89.873809	−0.001410
LiF	−106.838566	−107.036351	−107.037447	−0.001096
Li_3N	−76.617091	−76.839095	−76.839551	−0.000456
$LiBH_4$	−34.428502	−34.563434	−34.563244	+0.000190

Table 3. (Contd.)

Molecule	RHF	MP2	RI-MP2	ΔRI
Phosphorus compounds:				
P_2	−681.246442	−681.467035	−681.466815	+0.000220
P_4	−1362.544493	−1362.996038	−1362.995752	+0.000285
PH_3	−342.363919	−342.496400	−342.496026	+0.000374
P_2H_4	−683.578552	−683.824131	−683.823443	+0.000688
P_2H_2	−682.394096	−682.627357	−682.626880	+0.000477
HCP	−378.986140	−379.230779	−379.230907	−0.000128
H_3PO_4	−641.692934	−642.540450	−642.545801	−0.005351
PF_3	−638.784332	−639.448289	−639.451253	−0.002964
PF_5	−837.535511	−838.580601	−838.585650	−0.005049
PLi_3	−362.943376	−363.084586	−363.084149	+0.000437
Sulfur compounds:				
$S_2,\ldots(2\pi_u)^4(5\sigma_u)^2$, $^1\Sigma_g$	−794.435090	−794.829014	−794.828031	+0.000983
S_5 (ring)	−1986.981399	−1987.616276	−1987.614945	+0.001331
H_2S	−398.567167	−398.709425	−398.709137	+0.000288
H_2S_2	−795.965958	−796.229098	−796.228504	+0.000594
CS_2	−832.636733	−833.024841	−833.025201	−0.000360
H_2SO_4	−697.676579	−698.552043	−698.557713	−0.005670
thiophene	−551.067765	−551.723451	−551.723438	+0.000013
SF_2	−596.035191	−596.532853	−596.534520	−0.001667
SF_4	−794.691037	−795.587732	−795.591678	−0.003947
SF_6	−993.377706	−994.653449	−994.659422	−0.005974
Li_2S	−412.334480	−412.464584	−412.463865	+0.000719
BeS	−411.977505	−412.130743	−412.130591	+0.000152
Chlorine compounds:				
Cl_2	−918.659062	−918.926261	−918.925446	+0.000816
HCl	−459.938294	−460.083238	−460.083029	+0.000209
CCl_4	−1875.200101	−1875.882146	−1875.882165	−0.000020
ClF	−558.606635	−558.930542	−558.931106	−0.000563
ClF_3	−757.093699	−757.831263	−757.833919	−0.002656
LiCl	−466.867465	−467.003084	−467.002645	+0.000439
Li_4Cl_4	−1867.744545	−1868.307881	−1868.307308	+0.000573
Larger systems:				
porphyrin (D_{2h})	−982.522818	−985.787068	−985.789467	−0.002399
porphyrin (C_{2v})	−982.528399	−985.755793	−985.758098	−0.002304

4 Global consistency of the RI approximation to MP2 energies

The applicability of approximate MP2 methods hinges on the question whether the approximation can systematically be refined to any degree of accuracy, and whether it reproduces – at substantially reduced computation costs – derivatives of the energy as well as properties that connect distant regions of a potential hypersurface. In this section we probe the last point (global consistency) by comparing relative energetic stabilities of a representative sample of closed-shell molecules built from first- and second-row elements calculated at the RHF, MP2 and RI-MP2 levels of theory. We used RHF equilibrium structures, TURBOMOLE SVP basis sets [36], and the frozen core approximation in all MP2 treatments. The auxiliary basis sets were constructed from TURBOMOLE TZV basis sets [37, 38]: the most diffuse *s*- and *p*-shells contained in any contraction were decontracted, and three sets of polarization functions were added (usually 2*d*1*f*). Table 2 shows the auxiliary basis sets employed for hydrogen and carbon as examples. These auxiliary basis sets have *not* been optimized to represent charge distributions. Total energies obtained in this way for the aforementioned sample of molecules are given in Table 3.

The absolute errors due to the RI approximation to MP2 energies are seen to be largest for some electron-rich compounds with perfluorinated compounds being the worst cases, e.g., 6 mE_h in the case of SF_6. In most applications errors are smaller than 1 mE_h, and may be positive as well as negative.

Calculated reaction energies regarding compounds from Table 3 are given in Table 4. One observes a substantial error cancellation, with most errors being smaller than 1 kJ/mol (when compared to corresponding MP2 results). Perfluorination reactions are an exception: errors top 9 kJ/mol for $P_4 + 6F_2 \rightarrow 4PF_3$, but this is still small when compared to reaction energies of several thousand kJ/mol. We have preliminary indications that these errors can be reduced even further, if auxiliary basis sets specifically designed for the approximation of charge distributions are employed.

The seemingly large RI error of 6 kJ/mol for the reaction $5\,S_2 \rightarrow 2\,S_5$ (Table 4) is due to the excited nature of the $^1\sum_g$ closed-shell electronic state of the S_2 molecule. This error is small in view of an MP2 correlation energy contribution of 1837 kJ/mol to this reaction.

Systems as large as porphyrin can be described consistently with the same accuracy as the smaller molecules: an RI error of 8 kJ/mol for the fragmentation reaction of porphyrin into hydrocarbons and HCN

Table 4. Reaction energies in kJ/mol calculated from data in Table 3. Δ*RI* refers to differences between RI-MP2 and MP2 energies. The last column (ΔMP2) shows correlation energy contributions according to the MP2 approximation

Reaction	RHF	MP2	RI-MP2	ΔRI	ΔMP2
$HCCCCH + H_2 \rightarrow 2HCCH$	−31.8	−2.9	−2.8	+0.1	+28.9
$C_2H_2 + H_2 \rightarrow C_2H_4$	−227.1	−209.1	−208.1	+1.0	+18.0
$C_2H_4 + H_2 \rightarrow C_2H_6$	−178.8	−183.6	−183.4	+0.2	−4.8
$C_2H_6 + H_2 \rightarrow 2CH_4$	−90.4	−75.1	−75.2	−0.1	+15.3
$3C_2H_2 \rightarrow C_6H_6$	−652.2	−694.4	−691.5	+2.9	−42.2
$3C_4H_4 \rightarrow 2C_6H_6$	−1552.7	−1499.5	−1495.9	+3.6	+53.2
$H_2O_2 + H_2 \rightarrow 2H_2O$	−369.6	−357.6	−358.5	−0.9	+12.0
$CO + H_2 \rightarrow CH_2O$	−9.7	−18.7	−18.0	+0.7	−9.0
$CH_2O + H_2 \rightarrow H_3COH$	−121.2	−111.3	−110.9	+0.4	+9.9
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−122.7	−121.1	−121.2	−0.1	+1.6
$CO + H_2O \rightarrow CO_2 + H_2$	−20.6	−66.9	−68.1	−1.2	−46.3
$CO_2 + H_2O \rightarrow H_2CO_3$	−12.1	+8.5	+9.5	+1.0	+20.6
$CH_2O_2 \rightarrow CO + H_2O$	−1016.2	−866.4	−867.0	−0.6	+149.8
$F_2 + H_2 \rightarrow 2HF$	−590.6	−562.3	−563.5	−1.2	+28.3
$4F_2 + CH_4 \rightarrow CF_4 + 4HF$	−2132.4	−2029.0	−2033.8	−4.8	+103.4
$OF_2 + 2H_2 \rightarrow 2HF + H_2O$	−907.1	−859.5	−861.6	−2.1	+47.6
$N_4 \rightarrow 2N_2$	−964.7	−828.4	−829.5	−1.1	+136.3
$N_2 + H_2 \rightarrow N_2H_2$	+219.4	+227.1	+228.4	+1.3	+7.7
$N_2H_2 + H_2 \rightarrow N_2H_4$	−170.9	−159.0	−159.1	−0.1	+11.9
$N_2H_4 + H_2 \rightarrow 2NH_3$	−197.6	−192.2	−192.4	−0.2	+5.4
$HCN + H_2 \rightarrow H_2CNH$	−78.0	−57.5	−56.5	+1.0	+20.5
$HNC \rightarrow HCN$	−40.9	−71.1	−71.4	−0.3	−30.2
$2C_2H_3N \rightarrow N_2 + C_2H_2 + C_2H_4$	−628.1	−566.4	−567.3	−0.9	+61.7
$2HNO + H_2 \rightarrow N_2 + 2H_2O$	−734.9	−722.4	−724.3	−1.9	+12.5
$2HNO_2 + 3H_2 \rightarrow N_2 + 4H_2O$	−1040.1	−859.3	−858.6	+0.7	+180.8
$2HONO_2 + 5H_2 \rightarrow N_2 + 6H_2O$	−1375.6	−1165.4	−1164.4	+1.0	+210.2
$N_2 + 3F_2 \rightarrow 2NF_3$	−282.0	−244.4	−244.7	−0.3	+37.6
$NH_3 + HF \rightarrow H_3NHF$	−52.8	−61.6	−61.7	−0.1	−8.8
porphyrin $\rightarrow 4HCN + 3C_4H_2 + 2C_2H_2$	+1671.2	+2085.3	+2077.4	−7.9	+414.1
$2BH_3 \rightarrow B_2H_6$	−99.1	−181.1	−181.8	−0.7	−82.0
$BH_3 + NH_3 \rightarrow H_3BNH_3$	−107.2	−156.5	−156.8	−0.3	−49.3
$BH_3 + CO \rightarrow H_3BCO$	−40.7	−105.6	−106.1	−0.5	−64.9
$B_4H_4 + 4H_2 \rightarrow 2B_2H_6$	−496.6	−393.5	−392.4	+0.9	+103.1
$B_3N_3H_6 + 6H_2 \rightarrow 3H_3BNH_3$	+197.9	+201.7	+202.6	+0.9	+3.8
$B_2H_6 + 6F_2 \rightarrow 2BF_3 + 6HF$	−4254.4	−4098.4	−4106.3	−7.8	+156.0
$4Be \rightarrow Be_4$	−177.4	−314.8	−318.4	−0.4	−137.4
$Be + H_2 \rightarrow BeH_2$	−186.1	−172.8	−173.3	−0.5	+13.3
$2BeH_2 \rightarrow Be_2H_4$	−85.9	−112.0	−112.4	−0.4	−26.1
$Be + C_2H_6 \rightarrow Be(CH_3)_2$	−179.3	−185.9	−186.8	−0.9	−6.6
$2Be + 2F_2 \rightarrow Be_2F_4$	−2385.7	−2403.6	−2409.0	−5.4	−17.9
$Be_2H_4 + 4HF \rightarrow Be_2F_4 + 4H_2$	−746.3	−821.2	−823.0	−1.8	−74.9
$Be_2F_4 + 4H_2O \rightarrow 2BeF_2(H_2O)_2$	−212.7	−235.6	−235.9	−0.3	−22.9
$4Li_2 \rightarrow Li_8$	−86.3	−206.3	−206.1	+0.2	−120.0
$Li_2 + H_2 \rightarrow 2LiH$	+92.7	+90.6	+90.5	−0.1	−2.1
$4LiH \rightarrow Li_4H_4$	−584.1	−613.2	−613.4	−0.2	−29.1
$LiH + BH_3 \rightarrow LiBH_4$	−220.6	−281.2	−281.8	−0.6	−60.6
$2Li_2 + 2C_2H_6 \rightarrow (LiCH_3)_4$	−160.7	−259.8	−261.4	−1.6	−99.1
$3Li_2 + 2NH_3 \rightarrow 2Li_3N + 3H_2$	+630.1	+326.3	+325.4	−0.9	−303.8
$Li_2 + H_2O \rightarrow Li_2O + H_2$	+61.0	+0.2	−0.6	−0.8	−60.8
$Li_2 + F_2 \rightarrow 2LiF$	−816.4	−821.4	−823.5	−2.1	−5.0
$2P_2 \rightarrow P_4$	−135.5	−162.7	−163.1	−0.4	−27.2
$P_2 + H_2 \rightarrow P_2H_2$	−49.2	−13.3	−12.8	+0.5	+35.9
$P_2H_2 + H_2 \rightarrow P_2H_4$	−145.8	−109.0	−108.6	+0.4	+36.8
$P_2H_4 + H_2 \rightarrow 2PH_3$	−53.4	−35.2	−35.2	−0.0	+18.2
$P_4 + 6H_2 \rightarrow 4PH_3$	−361.3	−152.4	−150.2	+2.2	+208.9
$P_2 + HCCH \rightarrow 2HCP$	+96.4	+58.9	+58.5	−0.4	−37.5
$PH_3 + 4H_2O \rightarrow H_3PO_4 + 4H_2$	+1.6	−49.6	−52.1	−2.5	−51.2
$P_4 + 6F_2 \rightarrow 4PF_3$	−3996.5	−3767.6	−3776.5	−8.8	+228.9
$PF_3 + F_2 \rightarrow PF_5$	−628.6	−626.5	−628.2	−1.7	+2.1
$3Li_2 + P_2 \rightarrow 2PLi_3$	−202.5	−272.0	−271.0	+1.0	−69.5
$5S_2 \rightarrow 2S_5$	−4692.5	−2855.1	−2861.0	−6.4	+1837.4
$S_5 + 5H_2 \rightarrow 5H_2S$	−550.8	−405.9	−406.4	−0.5	+144.9
$S_5 + 5H_2S \rightarrow 5H_2S_2$	−33.0	+47.0	+47.5	+0.5	+80.0
$CH_4 + S_2 \rightarrow CS_2 + 4H_2$	−6690.0	−6527.7	−6531.1	−3.4	+162.2

Table 4. (Contd.)

Reaction	RHF	MP2	RI-MP2	ΔRI	ΔMP2
$H_2S+4H_2O \rightarrow H_2SO_4+4H_2$	+578.2	+479.2	+476.1	−3.1	−99.0
$S_2+4HCCH \rightarrow$ 2 thiophene	−1707.1	−1444.2	−1443.2	+1.0	+263.0
$S_2+2F_2 \rightarrow 2SF_2$	−1606.1	−1179.7	−1183.3	−3.6	+426.4
$SF_2+F_2 \rightarrow SF_4$	−378.2	−423.2	−425.3	−2.1	−45.0
$SF_4+F_2 \rightarrow SF_6$	−459.2	−451.7	−453.1	−1.6	+7.5
$Li_2+H_2S \rightarrow Li_2S+H_2$	−109.9	−116.1	−115.1	+1.0	−6.2
$Be+H_2S \rightarrow BeS+H_2$	+38.0	−2.1	−3.4	−1.3	−40.1
$Cl_2+H_2 \rightarrow 2HCl$	−232.6	−223.1	−224.3	−1.2	+9.5
$CH_4+4Cl_2 \rightarrow CCl_4+4HCl$	−388.2	−471.5	−478.2	−6.7	−83.3
$Cl_2+F_2 \rightarrow 2ClF$	−111.4	−108.0	−109.3	−1.3	−3.4
$ClF+F_2 \rightarrow ClF_3$	+64.9	−18.5	−20.1	−1.6	−82.4
$Li_2+Cl_2 \rightarrow 2LiCl$	−581.5	−561.1	−561.2	−0.1	+20.4
$4LiCl \rightarrow Li_4Cl_4$	−721.1	−776.0	−779.0	−3.0	−54.9

Table 5. Equilibrium structures and dipole moments (μ) calculated by the RHF, MP2 and RI-MP2 methods

Molecule			RHF	MP2	RI-MP2
CO					
	$d_{\text{c-o}}$	[a.u.]	2.0916	2.1542	2.1554
	μ	[a.u.]	0.0477	0.1497	0.1503
ClF					
	$d_{\text{Cl–F}}$	[a.u.]	3.050	3.1382	3.1375
	μ	[a.u.]	0.5715	0.6210	0.6207
H_2O					
	$d_{\text{O–H}}$	[a.u.]	1.7857	1.8176	1.8173
	$a_{\text{H–O–H}}$	[°]	105.13	102.48	102.49
	μ	[a.u.]	0.8300	0.8169	0.8176
H_2S					
	$d_{\text{H–S}}$	[a.u.]	2.5216	2.5264	2.5287
	$a_{\text{H–S–H}}$	[°]	94.01	92.33	92.29
	μ	[a.u.]	0.5283	0.5120	0.5117
NH_3					
	$d_{\text{N–H}}$	[a.u.]	1.9005	1.9238	1.9233
	$a_{\text{H–N–H}}$	[°]	106.92	104.98	105.00
	μ	[a.u.]	0.6995	0.7187	0.7190
PH_3					
	$d_{\text{P–H}}$	[a.u.]	2.6698	2.6723	2.6757
	$a_{\text{H–P–H}}$	[°]	95.288	93.731	93.705
	μ	[a.u.]	0.3364	0.3261	0.3250

compares with a total MP2 correlation energy contribution of 414 kJ/mol. Interesting is also the transition from a bond-alternant and thus partially localized π-system in porphyrin (RHF/SVP C_{2v} equilibrium structure [35]) to a more delocalized D_{2h} structure [35], since it is accompanied by a substantial (MP2) correlation energy change of 82 kJ/mol; the error due to the RI approximation is merely 0.25 kJ/mol.

Tables 3 and 4 are complete in the sense that we have not omitted any examples studied so far.

5 Accuracy of RI-MP2 derivatives

We tested the accuracy of the RI-MP2 approach with respect to calculated dipole moments and equilibrium structures (cf. Table 5 and Fig. 2), by comparing them to corresponding MP2 and RHF results. Unlike the RI-MP2 derivatives, the conventional MP2 derivatives were obtained with the TURBOMOLE MPGRAD program [34] which cannot utilize the frozen core approximation in derivative calculations. From a practical point of view the results suggest that the errors introduced by the RI approximation are insignificant.

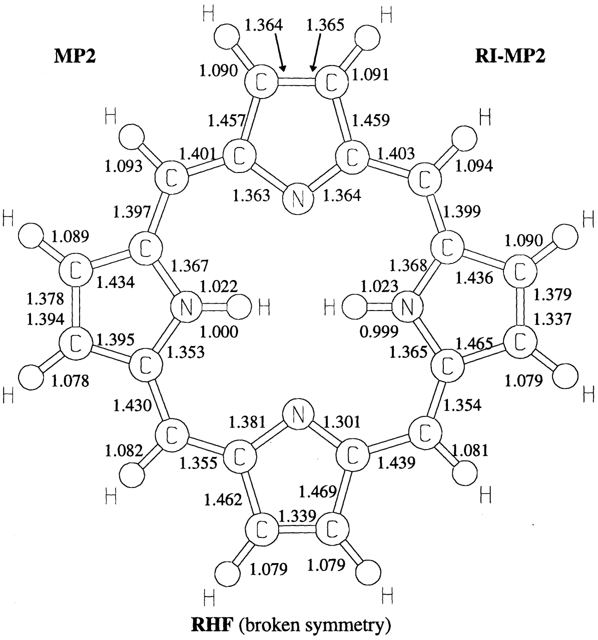

Fig. 2. Calculated bond lengths (Å) in porphyrin. Numbers in the lower half of the figure refer to the bond alternant RHF/SVP equilibrium structure (point group C_{2v}) [35]. The MP2- and RI-MP2 equilibrium structures display D_{2h} symmetry. Bond lengths in the upper left sector refer to the MP2/SVP method (frozen core approximation *not* applied) [35], those in the upper right sector to the RI-MP2/SVP approach (frozen core approximation applied)

In structure optimizations calculated RI-MP2 energies attain their exact minima (or more generally become stationary) where the first derivatives with respect to the atomic coordinates as calculated by Eq. (33) are zero.

6 Conclusions

The first implementation of RI-MP2 first derivatives has been described.

For molecules like porphyrin the RI-MP2 approach reduces the computation time for equilibrium structures and dipole moments by one order of magnitude as compared to the MP2 approach. Mass storage requirements and I/O are also reduced significantly. Modest main memory requirements – 90 MByte are sufficient for nonsymmetric molecules the size of porphyrin – indicate that corresponding structure optimizations at the RI-MP2 level of theory are possible even on personal computers.

The RI-MP2 approach does not seem to introduce additional errors of any practical significance when compared to conventional MP2 calculations. This holds for the first-order properties considered (Sect. 5) as well as for molecular interconversions that connect distant regions of a potential energy hypersurface (reaction energies, Sect. 4) like the fragmentation of porphyrin into HCN and hydrocarbons.

Clearly, future research objectives should include an implementation of a semi-canonical algorithm [30] for RI-MP2 derivatives, and the improvement of the auxiliary basis sets, in particular for the halogens. The latter objective can systematically be achieved by using the Hylleraas functional [39] in connection with transformed four-index integrals and their RI approximations, since this renders possible a variational procedure for the optimization of auxiliary basis functions. The evaluation of a combined RI-RHF/RI-MP2 approach is another important objective, since such a technique may not only save the time now spent on solving the *Z*-vector equations (cf. Sect. 3), but would also correspond to a consistent approximation of the electronic interaction operator as a whole; the techniques of perturbation theory may then be applied to recover leading corrections with respect to the exact operator.

Acknowledgements. We thank Prof. Dr. R. Ahlrichs (Universität Karlsruhe) for his generous support and many helpful discussions.

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