Møller–Plesset perturbation theory: from small molecule methods to methods for thousands of atoms

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The development of Møller–Plesset perturbation theory (MPPT) has seen four different periods in almost 80 years. In the first 40 years (period 1), MPPT was largely ignored because the focus of quantum chemists was on variational methods. After the development of many-body perturbation theory by theoretical physicists in the 1950s and 1960s, a second 20-year long period started, during which MPn methods up to order $n = 6$ were developed and computer-programed. In the late 1980s and in the 1990s (period 3), shortcomings of MPPT became obvious, especially the sometimes erratic or even divergent behavior of the MPn series. The physical usefulness of MPPT was questioned and it was suggested to abandon the theory. Since the 1990s (period 4), the focus of method development work has been almost exclusively on MP2. A wealth of techniques and approaches has been put forward to convert MP2 from a $O(M^5)$ computational problem into a low-order or linear-scaling task that can handle molecules with thousands of atoms. In addition, the accuracy of MP2 has been systematically improved by introducing spin scaling, dispersion corrections, orbital optimization, or explicit correlation. The coming years will see a continuously strong development in MPPT that will have an essential impact on other quantum chemical methods. © 2011 John Wiley & Sons, Ltd. *WIREs Comput Mol Sci* 2011 1 509–530 DOI: 10.1002/wcms.58

INTRODUCTION

Perturbation theory has been used since the early days of quantum chemistry to obtain electron correlation-corrected descriptions of the electronic structure of atoms and molecules. In 1934, Møller and Plesset[1] described in a short note of just five pages how the Hartree–Fock (HF) method can be corrected for electron pair correlation by using second-order perturbation theory. This approach is known today as Møller–Plesset perturbation theory, abbreviated as MPPT or just MP in the literature. MPPT, although in the beginning largely ignored, had a strong impact on the development of quantum chemical *ab initio* methods in the past 40 years. Another publication from the early days of quantum chemistry turned out to be very relevant for MPPT: this is the 1930 paper of

Hylleraas[2] on the description of two-electron problems with the help of perturbation theory. Second-order and third-order corrections to the energy can be determined by minimizing the *Hylleraas functionals* presented in this paper. This is more expensive than the one-step procedure Møller and Plesset suggested, but has the advantage of a free choice of the orbitals (e.g., localized rather than canonical HF orbitals) to be used in the MP calculation.

Since 1934, MPPT has seen different stages of appreciation, development, and application. For almost 40 years, quantum chemists largely ignored MPPT because the major focus in the early days of quantum chemistry was on variational theories with upper bound property such as HF or configuration interaction (CI). MPPT does not provide an upper bound for the ground state energy of the Schrödinger equation and therefore was considered as not reliable. Also, the early attempts of Hylleraas[2] to determine the energy of He and two-electron ions was not considered successful, which also gave a negative impression on the performance of perturbation

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theory. Quantum chemistry rediscovered perturbation theory in the 1960s, thanks to the work done by Brueckner, Goldstone, and other physicists on many-body perturbation theory (MBPT) to describe the interactions between nuclear particles (for a description of these developments, see review articles by Cremer[3] and Kuzelnigg,[4] or text books on MBPT[5, 6]). This work revealed that Rayleigh–Schrödinger perturbation theory (RSPT) and by this also MPPT (the latter is a special case of RSPT) is easier to carry out than its rival Brillouin–Wigner perturbation theory (BWPT) (BWPT requires knowledge of the exact energy and therefore its energy corrections can only be iteratively determined). In addition, RSPT as well as MPBT are size extensive, i.e., the energy correction calculated at a given perturbation order n all scale with the number (N) of electrons of an electronic system, whereas BWPT contains nonphysical N^p terms ($p > 1$) as a consequence of the iterative procedure of calculating perturbation energies.[3–6]

From the mid-1970s on, MPn theories were rapidly developed and programed for computer investigations of atoms and molecules.[7–20] This development strongly benefited from the competition of the Bartlett group in Florida and the Pople group in Pittsburgh in their development of MPn methods. The first approached MPPT from MBPT using diagrams and the linked cluster theorem,[3–6] whereas the latter favored a somewhat easier to understand algebraic approach, which became popular among chemists, thanks to the rapid distribution of newly developed MPn methods in form of Pople's computer programs. In this way, MP2,[7, 8] MP3,[9, 10] MP4,[10–13] and MP5[14–16] could be used by quantum chemists shortly after they had been worked out. The last development of an MPn method exclusively based on perturbation theory took place in the mid 1990s. The Cremer group worked out all 36 terms of MP6 and programed a generally applicable method.[17–20] At that time it was stated[20] that MP7 or MP8 with 141 and 583 unique terms, respectively, were outside the reach of normal development procedures, which is still valid.

Since the early 1990s, there were frequent reports on the oscillatory behavior of MPn energies and other properties. With the help of full CI (FCI) calculations, one could show that even in the case of closed shell systems, the MPn series sometimes exhibit erratic behavior or does not converge at all, which led to questions as to the physical relevance of MPn correlation energies. In the direct comparison of MPPT with coupled cluster theory (CC) on one side and density functional theory (DFT) on the other side, MPn proved to be inaccurate (compared with CC) and ex-

pensive (compared with DFT). There were voices that suggested to abandon MPPT altogether with the exception of MP2, which could be used for quick estimates of electron correlation effects.

The past 20 years have seen a development that indeed focused primarily on MP2, where two major goals were pursued: (1) to accomplish linear or at least low-order scaling for MP2, which in its conventional form scales as $O(M^5)$ (M: number of basis functions); (2) to increase the reliability of MP2 results. These developments have been extremely successful and, contrary to all prophecies of doom from the 1990s, MPPT has to considered, by the year 2010, as a method that can handle large molecules with thousands of atoms, has become rather accurate due to various improvements, and is an important tool for multiconfigurational, relativistic, DFT hybrid, quantum mechanics/molecular mechanics (QM/MM), and model chemistry methods.

THE BASIS OF MØLLER–PLESSET PERTURBATION THEORY

In perturbation theory, one transforms the Schrödinger equation defined for the exact Hamiltonian $\hat{H}$ into an eigenvalue equation for an effective Hamiltonian $\hat{H}_{\text{eff}}$. For this purpose, the Hilbert space associated with $\hat{H}$ is split into a *model space* $\mathcal{P}$ spanned by one (or more) reference function(s) (e.g., the HF wavefunction) and an *orthogonal space* $\mathcal{Q}$ (Figure 1). The corresponding projection operators $\hat{P}$ and $\hat{Q}$ project out of the exact wavefunction Ψ, model function $\Phi^{(0)}$ and correlation function χ. Furthermore, operators $\hat{P}$ and $\hat{Q}$ are used to derive the effective Hamiltonian in form of the Feshbach–Löwdin Hamiltonian.[3, 6] Applying the latter to the model function, one obtains the exact energy of the Schrödinger equation, i.e., despite the fact that one works only in model space and, accordingly, has to solve a much simpler problem, perturbation theory promises an exact energy. However, the difficulties are in the details: the Feshbach–Löwdin Hamiltonian contains an inverse of the form $(E - \hat{Q}\hat{H}\hat{Q})^{-1}$, which has to be expanded in a suitable form to calculate the exact correlation energy stepwise, i.e., order by order hoping that the perturbation series converges rapidly. In BWPT, this is done by keeping the exact energy E in the inverse, where of course E is not known, thus requiring an iterative solution. BWPT is exact for a two-electron problem, but it has, however, beside the computational burden, the problem of not being size-extensive.[3, 4, 6]

RSPT reformulates the inverse in such a way that the (known) zeroth-order energy $E^{(0)}$ replaces
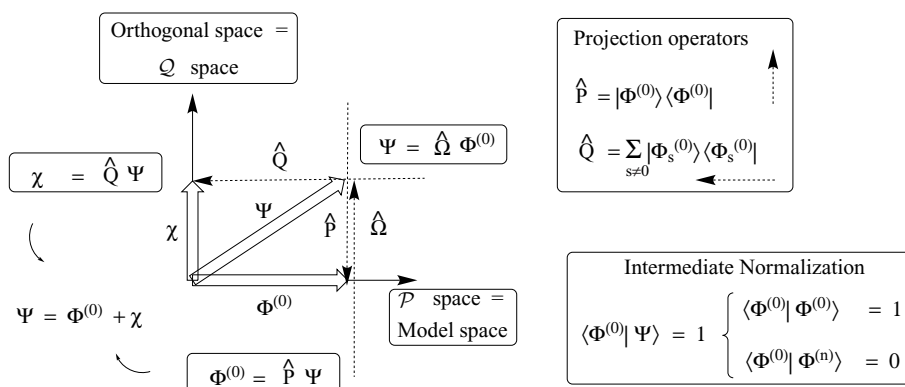
FIGURE 1 | Schematic representation of model space $\mathcal{P}$ and orthogonal space $\mathcal{Q}$, projection operators $\hat{P}$ and $\hat{Q}$, and the relationship between exact wavefunction Ψ (equal to the perturbed wavefunction), unperturbed wavefunction $\Psi^{(0)}$, and correlation function χ. The consequences of intermediate normalization are indicated.

the exact energy E.[3, 6] The orders of RSPT energy can be written with the help of a suitable operator resolvent in a compact form containing a principal term and an increasing number of so-called renormalization terms. The latter cancel with physically not meaningful parts of the principal term so that all nth-order energy corrections of the perturbation series become size-extensive. Utilizing MBPT and the linked cluster theorem,[3–6] an even more compact form results that contains only one term that is limited to linked diagrams, i.e., the interaction diagrams from quantum field theory, which identify the physically meaningful terms.[3, 4, 6]

The Møller–Plesset Perturbation Operator

MPPT differs from other RSPT approaches (e.g., the Epstein–Nesbet one[3–6]) by the choice of the perturbation operator $\hat{V}$.[1] Møller and Plesset suggested to use an HF calculation as the starting point of the perturbation expansion and accordingly they defined the zeroth-order problem as

$$\hat{H}^{(0)}\Phi_0^{(0)} = E_0^{(0)}\Phi_0^{(0)} \tag{1}$$

(the subscript of E and Φ refers to the ground state and will be dropped in the following; (n) gives the order of MPPT) where the zeroth-order Hamiltonian $\hat{H}^{(0)}$ is expressed by the sum of Fock operators:

$$\hat{H}^{(0)} = \sum_p \hat{F}(p) = \sum_p \hat{h}(p)$$
$$+ \sum_{p,i}[\hat{J}_i(p) - \hat{K}_i(p)] \tag{2}$$

with $\hat{h}(p)$ being the one-electron operator associated with the kinetic and nucleus–electron attraction part

of electron p, $\hat{J}_i(p)$ and $\hat{K}_i(p)$ being the Coulomb and exchange operator that form the HF potential and are expressed in terms of spin orbitals ψ_i:

$$\hat{J}_i(1)\psi_j(1) = \left[\int d\mathbf{r}_2 \psi_i^\star(2)\frac{1}{r_{12}}\psi_i(2)\right]\psi_j(1) \tag{2a}$$

$$\hat{K}_i(1)\psi_j(1) = \left[\int d\mathbf{r}_2 \psi_i^\star(2)\frac{1}{r_{12}}\psi_j(2)\right]\psi_i(1) \tag{2b}$$

(1 and 2 denote positions $\mathbf{r}_1$ and $\mathbf{r}_2$ of electrons 1 and 2). As zeroth-order wavefunction, the HF wavefunction is taken: $\Phi^{(0)} = \Phi^{HF}$. The corresponding eigenvalue is given by the sum of orbital energies:

$$E^{(0)} = E^{orb} = \sum_i^{occ} \epsilon_i \tag{3}$$

[occ, number of occupied orbitals; vir, number of virtual (unoccupied) orbitals]. Hence, the HF wavefunction spans the model space $\mathcal{P}$. The $\mathcal{Q}$-space is spanned by the substitution functions Φ_s, which are generated by single (S), double (D), triple (T), etc. excitations of electrons from occupied spin orbitals $\psi_i, \psi_j, \cdots$ to virtual orbitals $\psi_a, \psi_b, \cdots$ ($\psi_p, \psi_q, \cdots$ denote general spin orbitals). Functions $\Phi_s = \Phi_i^a, \Phi_{ij}^{ab}, \Phi_{ijk}^{abc}, \cdots$ are orthogonal to Φ^{HF}, which simplifies the calculation of different energy corrections. The MP perturbation operator is given by

$$\hat{V} = \hat{H} - \hat{H}^{(0)} = \sum_{p \geq q}\frac{1}{r_{pq}} - \sum_{p,i}[\hat{J}_i(p) - \hat{K}_i(p)] \tag{4}$$

Applying the perturbation operator, the first-order correction energy for $E^{(0)}$ results as

$$E_{MP}^{(1)} = \langle\Phi^{(0)}|\hat{V}|\Phi^{(0)}\rangle = V_{00} = -\frac{1}{2}\sum_{ij}\langle ij||ij\rangle \tag{5}$$

where the double bar integral is an antisymmetrized two-electron integral of the general type (given in Dirac notation):

$$\langle pq||rs \rangle = \iint \psi_p^*(1)\psi_q^*(2)\frac{1}{r_{12}}[\psi_r(1)\psi_s(2) \\ -\psi_s(1)\psi_r(2)]d\tau_1 d\tau_2 \tag{6}$$

where τ denotes integration over space and spin co-ordinates of the spin orbitals ψ.

Equation (5) reveals that the HF energy is identical to the MP1 energy:

$$E(\text{HF}) = E(\text{MP1}) = \sum_i^{\text{occ}} \epsilon_i - \frac{1}{2}\sum_{ij}^{\text{occ}} \langle ij||ij \rangle, \tag{7}$$

i.e., HF is correct up to first-order MPPT, which was first observed by Møller and Plesset.[1] This holds also for dipole moment, electron density, and other one-electron properties[1] and is known as *MP theorem*.

Second-order Møller–Plesset (MP2) Perturbation Theory

The MP2 correlation energy correction is given by Eq. (8)[1,7,8]:

$$E_{\text{MP}}^{(2)} = \sum_{s>0} \frac{V_{0s}V_{s0}}{E_0 - E_s} \tag{8}$$

where S substitutions ($\Phi_s = \Phi_i^a$) do not contribute because $< \Phi^{(0)}|\hat{V}|\Phi_i^a > = 0$ as a consequence of the Brillouin theorem. Finite matrix elements V_{0s} are only obtained for D excitations ($\Phi_s = \Phi_{ij}^{ab}$) (T, Q, etc. excitations are excluded because of the Slater–Condon rules. Compare with Figure 2).[3]

When applying Slater–Condon rules, the second-order correction takes the following form:

$$E_{\text{MP}}^{(2)} = \frac{1}{4}\sum_{ij}^{\text{occ}}\sum_{ab}^{\text{vir}} \langle ij||ab \rangle a_{ij}^{ab} \tag{9}$$

with

$$a_{ij}^{ab} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle ab||ij \rangle \tag{10}$$

being the amplitudes of the D excitations. In the closed-shell case, the formula for the MP2 correlation energy is slightly different [see *Resolution of the Identity and Density Fitting: RI/DF-MP2* Eq. (17)] because of the occupation of space orbitals ϕ_i used in this case by two electrons rather than just one electron in the case of spin orbitals ψ_i. The cost factor of an MP2 calculation is of the order $O(M^5)$ because M^4 electron repulsion integrals (ERIs) have to be calculated at the HF level, a subset of which has to be transformed from basis function to spin-orbital rep-
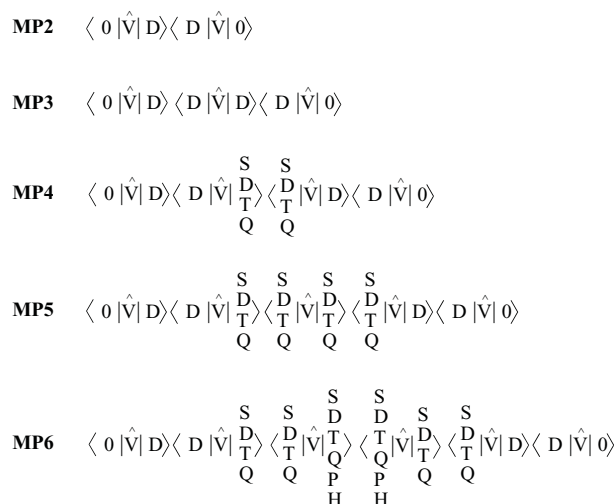
MP2 $\quad \langle 0 |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| 0 \rangle$

MP3 $\quad \langle 0 |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| 0 \rangle$

MP4 $\quad \langle 0 |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| 0 \rangle$

MP5 $\quad \langle 0 |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| 0 \rangle$

MP6 $\quad \langle 0 |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \\ \text{P} \\ \text{H} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \\ \text{P} \\ \text{H} \end{smallmatrix} |\hat{V}| \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} \rangle \langle \begin{smallmatrix} \text{S} \\ \text{D} \\ \text{T} \\ \text{Q} \end{smallmatrix} |\hat{V}| \text{D} \rangle \langle \text{D} |\hat{V}| 0 \rangle$

FIGURE 2 | Schematic representation of matrix elements and the substitution functions that make a contribution at MPn ($n = 2, 3, 4, 5, 6$). $\hat{V}$ denotes the perturbation operator, 0 the reference $\Phi^{(0)}$, S Φ_i^a, D Φ_{ij}^{ab}, T Φ_{ijk}^{abc}, Q Φ_{ijkl}^{abcd}, P Φ_{ijklm}^{abcde}, and H Φ_{ijklmn}^{abcdef}.

resentation, which, if one ERI index is transformed at a time, requires $4 \times M^5$ operations.[3]

MP2 theory accounts for dynamical, i.e., short-range pair correlation effects. In general, it is difficult to distinguish between dynamical and nondynamical correlation effects. Because the D excitations of MP2 theory do not couple, i.e., the correlation of electron pairs takes place in the available molecular space independent of each other, correlation effects are often exaggerated by MP2. Cremer and He[21] have distinguished between molecules with a balanced distribution of electrons and electron pairs (*type A systems* made up by less electronegative atoms from the left of the periodic table) and those with a strong clustering of electrons in a confined part of the molecular space due to the presence of strongly electronegative atoms, multiple bonds, transition metals, or anions (*type B systems*). For type A systems, MP2 accounts for about 70% of the total correlation energy, whereas for type B systems, 95% of the total correlation energy is accounted for (see Figure 3), which in the latter case is a result of exaggerating electron pair correlation.[21]

Owing to the fact that the mean-field orbitals of HF are not reoptimized at the MP2 level, all deficiencies of these orbitals are carried over to MP2, which can lead to problems in connection with symmetry breaking or spin contamination at the unrestricted MP2 (UMP2) level. This has to be kept in mind when trying to improve MP2 results or using MP2 in connection with other methods.
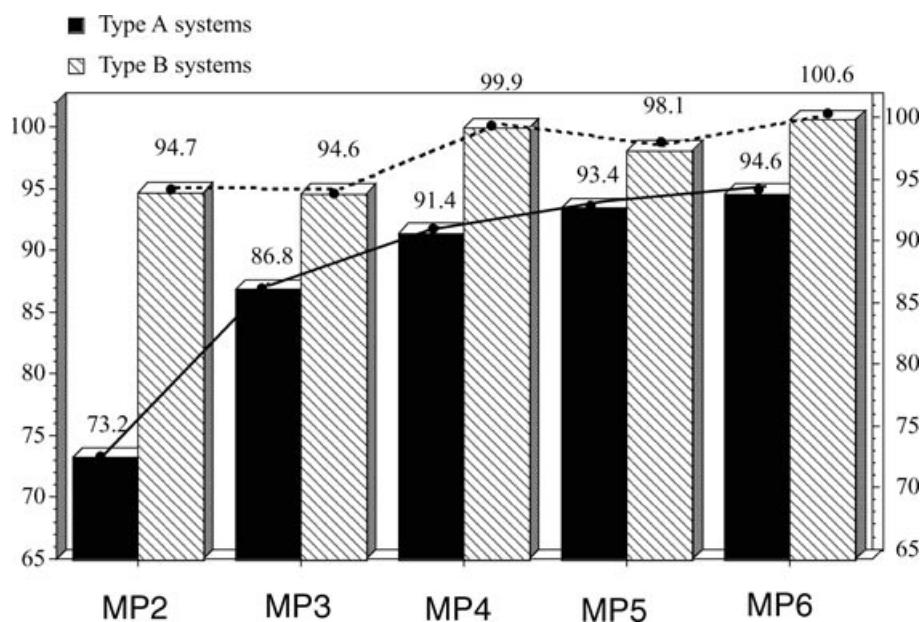
FIGURE 3 | Average MPn correlation energies given in percent of the FCI correlation energy for 14 class A and 19 class B examples.[21]

Third-order Møller–Plesset (MP3) Perturbation Theory

The MP3 correlation energy is given by[7, 9]

$$E_{MP}^{(3)} = \sum_{s>0} \sum_{t>0} \frac{V_{0s} \bar{V}_{st} V_{t0}}{(E_0 - E_s)(E_0 - E_t)} \quad (11)$$

where

$$\bar{V}_{st} = V_{st} - \delta_{st} V_{00} \quad (12)$$

Again, just D excitations contribute (Φ_s, $\Phi_t : \Phi_{ij}^{ab}$); however, the D excitations are coupled, thanks to the matrix element $\bar{V}_{st}$ (see also Figure 2). Working out the MP3 correlation energy leads to

$$E_{MP}^{(3)} = \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} \langle ij || ab \rangle b_{ij}^{ab} \quad (13)$$

The calculation of the third-order D amplitudes b_{ij}^{ab} requires $O(M^6)$ steps and it determines the cost factor of MP3. Due to the coupling between D excitations, pair correlation effects for type B systems are reduced at MP3 (see Figure 3). This is also reflected by the fact that (especially for type B systems) relative MP3 energies often revert trends found at MP2, which has led to the impression that MP3 calculations seldom lead to an improvement of MP2 results. This of course has to do with the fact that MP3 provides a more realistic description of pair correlation.

Fourth-order Møller–Plesset (MP4) Perturbation Theory

The formula for the MP4 correlation energy[11–13] combines three different substitution functions Φ_s, Φ_t, and Φ_u, which according to Slater–Condon rules implies contributions from both S, D, and T excitations:

$$E_{MP}^{(4)} = \sum_{s>0} \sum_{t>0} \sum_{u>0} \frac{V_{0s} \bar{V}_{su} \bar{V}_{ut} V_{t0}}{(E_0 - E_s)(E_0 - E_t)(E_0 - E_u)}$$
$$- \sum_{s>0} \sum_{t>0} \frac{V_{0s} V_{s0} V_{0t} V_{t0}}{(E_0 - E_s)(E_0 - E_t)^2} \quad (14)$$

By working out this formula in terms of double-bar integrals and partitioning it according to the scheme given in Figure 2, the MP4 correlation energies can given by:

$$E_{MP}^{(4)} = E_S^{(4)} + E_D^{(4)} + E_T^{(4)} + E_Q^{(4)} \quad (15)$$

In this formula, the S contribution corrects some of the changes in the orbitals due to electron correlation effects (the mean field orbitals are no longer optimal in view of the perturbation of the $\hat{H}^{(0)}$-problem). Pair correlation effects are further corrected in the D term of MP4. As new correlation effect, three-electron correlation (T excitations) is included. These correlation effects are normally small as compared with pair correlation effects; however, due to the large number of three-electron correlations, they add a significant contribution to the total correlation energy, especially in the case of type B systems with multiple bonds or a strong clustering of electrons in a confined region of

molecular space. The Q-term in MP4 results from disconnected, rather than connected, four-electron correlations, i.e., from the independent but simultaneous correlation of two electron pairs. Compared with MP3, MP4 includes new correlation effects in the perturbation description and therefore the correlation energy is distinctly improved (Figure 3). For type A systems, 91% of all correlation effects are accounted for. However, for type B systems, it is 100%, again, due to some exaggeration of correlation effects.[21]

The most expensive part of MP4 is the calculation of the T contributions, which scales with $O(M^7)$. Therefore, one has suggested to carry out MP4(DQ)[11] or MP4(SDQ) calculations[12] in those cases where in T correlation effects may play a minor role as, e.g., in the case of type A systems. Costs are reduced in this way to $O(M^6)$. Considering that CC methods such as Coupled Cluster with Single and Double (CCSD) excitations contain infinite-order effects in the SD space and disconnected T, Q, and higher correlation effects for somewhat higher cost (caused by the iterative solution of the CT equations), there seems to be little need for MP4(DQ) and MP4(SDQ) calculations nowadays.

Fifth-order and Sixth-order Møller–Plesset (MP5 and MP6) Perturbation Theory

It took 9 years after the development of MP4 in 1980[13] to set up a program to calculate the nine unique MP5 contributions to the correlation energy, although an analysis of MP5 was published already in the mid-1980s.[14] Bartlett and coworkers[15] were the first to accomplish this task, followed 1 year later by Pople and coworkers.[16] The MP5 correlation energy (see Figure 2) can similarly be partitioned as the MP4 energy (for a review on MP5 and MP6, see Ref 20). Figure 2 reveals that the new correlation effects introduced at MP4 couple at the MP5 level. This coupling leads to 14 terms of the type SS, SD, etc., where terms such as SD and DS are identical. The final equation for the MP5 correlation energy contains nine unique coupling terms[20]:

$$E_{MP}^{(5)} = E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{ST}^{(5)} + 2E_{DT}^{(5)}$$
$$+ E_{TT}^{(5)} + 2E_{DQ}^{(5)} + 2E_{TQ}^{(5)} + E_{QQ}^{(5)} \qquad (16)$$

The calculation of these terms requires $O(M^8)$ computational steps wherein the TT term is the most expensive one. Actually, the QQ term of MP5 implies $O(M^{10})$ operations; however, it can be considerably reduced in cost by breaking up multiple summations and using intermediate arrays.[20] MP5 correlation calculations (Figure 3) reveal that a coupling of T correlation effects can lead to a reduction of these con-

tributions. Similar trends are observed for S and Q correlation effects. MP5, similarly as MP3, is less attractive for correlation studies than MP4 or MP2.

MP6 was developed by He and Cremer[17–20] in the mid-1990s. As an even-order MPn method, it includes new correlation effects resulting from connected Q and disconnected pentuple (P) and hextuple (H) correlation effects. The principal MP6 term can be partitioned, in view of the coupling scheme given in Figure 2, into 55 ABC terms (A, B, C: S, D, T, Q, P, H), of which 36 are unique. He and Cremer[19] programed all 36 MP6 terms using 57 intermediate arrays to reduce costs from original $O(M^{12})$ to $O(M^9)$. They also programed the less costly MP6(M8) and MP6(M7) methods [scaling with $O(M^8)$ and $O(M^7)$] by excluding terms of higher costs from the MP6 calculation.[19] Terms such as TQT, QQQ, or TQQ are the most expensive ones in a MP6 calculation.[20] MP6 adds substantial correlation corrections to type B systems such as difluoroperoxide, FOOF.[22] However, some of these corrections may be reduced by coupling effects introduced at MP7.

Table 1 provides a summary of the *ab initio* development work as it took place in the heydays of MPPT. Also included are the calculation of high-order MPn energies with the help of CC and FCI theory (see *Advantages and Disadvantages of MP*n *Perturbation Theory*).

MPn Perturbation Theory with larger order n

MP7 contains 221 ABCD terms (coupling between S,D,T,Q,P,H excitations) of which 141 are unique, whereas MP8 has 915 ABCDE terms (S up to sevenfold and eightfold excitations; 583 unique terms). Clearly, traditional development work determining each term of a given MPn method as done for MP6 by He and Cremer[19] is no longer possible. An alternative approach to MPn is provided by CC and FCI theory. From a CCD calculation, one can extract MP2, MP3, and M4(DQ) correlation energies, from CCSD MP4(SDQ) and from CCSD(T) or CCSDT-1 the full MP4 energy: MP4(SDTQ). CCSDT is lacking just the QT term at fifth order (easily obtained by the identical TQ term) and part of the QQ term, which can be calculated with little extra work. The MP6 correlation energy can be obtained by a noniterative inclusion of Q excitations into CCSDT, thus avoiding the $O(M^{10})$ dependence of CCSDTQ. In this way, Kucharski and Bartlett[23] determined MP6 energies. Similarly, total MPn correlation energies with higher and higher orders n can be extracted from the iteration steps of an FCI calculation (see Table 1). Hence, it became

TABLE 1 | Development of MP*n* Perturbation Methods[a]

Method	Year	Authors	Cost	Ref
MP2	1974	Bartlett and Silver	$O(M^5)$	7
	1975	Binkley and Pople		8
MP3	1974	Bartlett and Silver	$O(M^6)$	7
	1976	Pople et al.		9
MP4(DQ)	1978	Bartlett and Purvis	$O(M^6)$	11
MP4(SDQ)	1978	Krishnan and Pople	$O(M^6)$	12
MP4 = MP4(SDTQ)	1980	Pople and coworkers	$O(M^7)$	13
MP5 = MP5(SDTQ)	1989	Bartlett and coworkers	$O(M^8)$	15
	1990	Pople and coworkers		16
MP6(M7)	1996	He and Cremer	$O(M^7)$	19
MP6(M8)	1996	He and Cremer	$O(M^8)$	19
MP6 = MP6(SDTQPH)	1996	He and Cremer	$O(M^9)$	18
MP*n* from CC or FCI				
MP6 from CCSDT(Q)	1995	Kucharski and Bartlett	$O(M^9)$	23
Up to MP65 from FCI	1996	Olsen et al.		26
Up to MP169 from FCI	2000	Schaefer and coworkers		29

possible to investigate the convergence behavior of the MP*n* series[24–29] once modern versions of FCI were programed (*Advantages and Disadvantages of MP*n *Perturbation Theory*).

ADVANTAGES AND DISADVANTAGES OF MP*n* PERTURBATION THEORY

MP2 is the least costly *ab initio* method to correct HF results for correlation effects. This holds also for higher MP*n* methods, provided one focuses on a special correlation effect as, e.g., connected three-electron (MP4) or connected four-electron correlations (MP6). Correlation effects can be easily analyzed using the partitioning of MP*n* energies into S, D, T, ⋯ contributions, comparing changes in response densities from order to order or describing the dependence of other correlation-corrected response properties on *n*.[30–33] These studies reveal a number of shortcomings of MP*n*, which can be summarized as follows:

1. Far reaching disadvantages result from the fact that MP*n* correlation corrections are calculated using HF mean-field orbitals with all their shortcomings. Symmetry breaking and the spin contamination at UMP*n* are connected to this problem.

2. Another disadvantage results from the MP*n* series itself. The inclusion of new correla-
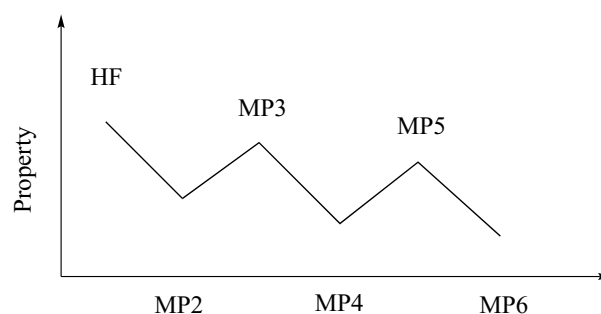

FIGURE 4 | Typical oscillatory behavior of calculated MP*n* response properties on the order *n*.

tion effects at even orders *n* and a coupling of these correlation effects at the next higher odd order can lead to an oscillatory behavior of molecular energies and other properties with increasing order *n* (Figure 4). This makes predictions of higher order MP*n* results problematic and excludes a reliable simple-minded extrapolation to FCI energies.[21, 30–33]

3. FCI studies aimed at an investigation of the MP*n* convergence behavior revealed that even for closed-shell systems, especially of type B, the MP*n* series is erratic and, in the worst case, divergent. For some time, it was speculated that this was a result of unbalanced basis sets; however, large,

well-balanced basis sets lead to the same convergence problems.[24–29]

4. MPn energies and other properties converge rather slowly to the complete basis set (CBS) limit results (corresponding to an infinitely large basis set).[34–36]

5. Conventional MPn theory is carried out with canonical (delocalized) orbitals, which contradicts the fact that dynamical electron correlation is in most cases a local phenomenon. It is obvious that some kind of local MPn theory could be much more cost-efficient than standard MPn.

6. MPn with a finite n lacks the infinite-order effects of CC methods, which make the latter much more accurate than MPPT. It also does not account for nondynamical electron correlation as CCSD(T) or CCSDT and even DFT does (although in a nonspecific way).

Several of these disadvantages and shortcomings are different consequences of the same basic deficiency of the MPn series: the perturbation operator $\hat{V}$ should be tailored newly for each electronic system investigated with MPn, which of course cannot be done with standard MPPT. In the following, we will focus first on the sometimes erratic (or even divergent) convergence behavior of the MPn series because this is most revealing and provides a physical insight into the usefulness and physical relevance of MPPT.

On the basis of the FCI calculations carried out with VDZ basis sets augmented with diffuse functions, Olsen et al.[26] reported in 1996 that the MPn series can diverge for simple closed-shell molecules such as Ne, HF, or H_2O (all class B systems). Schaefer and coworkers[29] confirmed and extended these observations by investigating MPn results for properties such as bond lengths or stretching frequencies. They found that for most class B systems augmentation of a cc-pVDZ basis set with diffuse functions leads to oscillatory or divergent behavior of the MPn series.

For the purpose of explaining the convergence behavior of the MPn series, one describes the perturbed problem with the help of a strength parameter z that switches on the perturbation: $\hat{H}(z) = \hat{H}^{(0)} + z\hat{V}$. For $z \to 1$, energy and wavefunction of the Schrödinger equation are obtained. Convergence of the MPn series can only be fulfilled if the energy spectra for $\hat{H}^{(0)}$ and the model space $\mathcal{P}$ do not overlap with that of the $\mathcal{Q}$-space. However, if an eigenvalue of the $\mathcal{Q}$-space *intrudes* the model space, it can undergo an avoided crossing with a $\mathcal{P}$-space eigenvalue of the same symmetry.[26, 28] Depending on

where the avoided crossing is located, one speaks of back-door ($-1 \leq z < 0$) and front-door intruder states ($0 < z \leq 1$). In most cases investigated, a back-door intruder state was found that reduces the convergence radius of the MPn series to a value smaller than 1 and thereby causes divergence.[37]

Goodson and coworkers,[38–40] using methods of functional analysis in the complex plane, found (in confirmation with an earlier study of Stillinger[41]) that a singularity exists on the negative real axis of z (see Figure 5). The singularity corresponds to the unphysical situation of an attractive interelectronic Coulomb potential and is associated with an ionized electron cluster free from the nucleus. In the case of a truncated basis set (corresponding to an approximate Hamiltonian), the ionization process to the continuum state cannot be described and accordingly the MPn series seems to converge. Augmenting the basis set by diffuse functions improves the description, the singularity appears, autoionization and divergence of the MPn series are observed.[38–40] In the caseof the Ar atom, singularity and autoionization state were also found for positive z, indicating that the divergence problems of the MPn series are not exclusively connected to a negative strength parameters. Sergeev and Goodson[40] have described different MP singularities (branching points, intruder states, etc.) causing varying sign patterns in the MPn series. Their conclusion is that a divergent MPn series is not necessarily useless.[40] It always depends on how convergent behavior affects low-order MPn results and how divergent or erratic convergent behavior can be summed using approximants or other means that lead to reasonable FCI energies. In a recent publication, Herman and Hagedorn[42] emphasize that the process of understanding MPn singularities is still at its beginning.

MPPT is based on the assumptions that the perturbation operator $\hat{V}$ describes a change in the unperturbed problem that is small enough to guarantee convergence. Various procedures have been applied to accelerate or to enforce convergence.[32, 33, 37, 43–45] (For a review up to 2004, see Ref 46.) These reach from extrapolation techniques to Pade approximants, summation techniques, Feenberg scaling, and sophisticated redefinitions of the model space. For example, He and Cremer[32] found when comparing the performance of Pade approximants, extrapolation formulas, and Feenberg scaling that the latter approach leads to the best reproduction of FCI energies (within 0.15 mhartree or better), provided that MPn up to MP6 energies could be used. Feenberg scaling,[43] first suggested in 1956, is based on the idea of scaling up or down the weight of the unperturbed problem with a scaling parameter λ dependent on the electronic

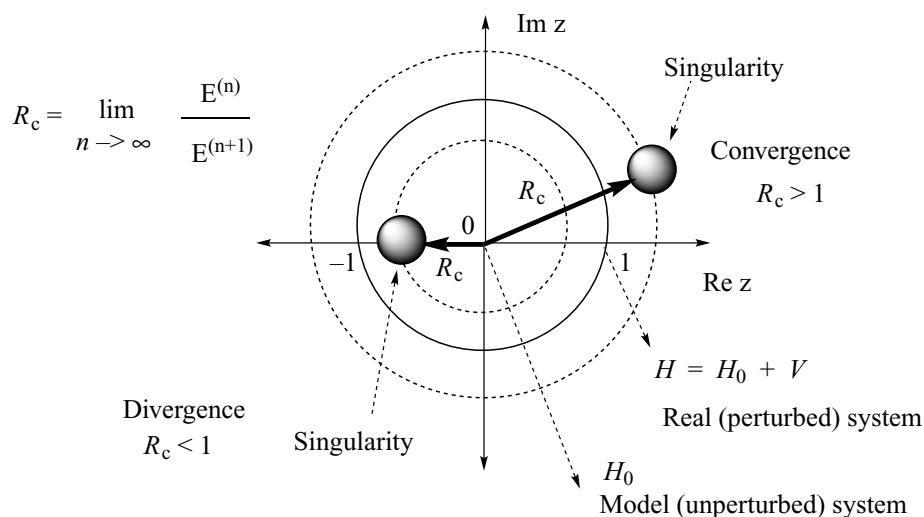$$R_c = \lim_{n \to \infty} \frac{E^{(n)}}{E^{(n+1)}}$$

FIGURE 5 | The complex plane of the strength parameter z switching on the perturbation represented by $\hat{V}$. Unperturbed (model) system and perturbed (real) system are located at $z = 0$ and $z = 1$, respectively. Singularities (poles) of two MPn series are schematically indicated by balls. For the right one, the radius of convergence R_c is larger than 1 and accordingly the MPn series is converging. In the other case, $R_c < 1$ and the MPn series is diverging (see text).

system considered. If the corrections for the correlated electron–electron interactions become too large, the weight of $\hat{H}^{(0)}$ is increased, i.e., HF electron–electron interactions are scaled up for the purpose of decreasing the perturbation. Reversely, the weight of the low-order MPn corrections are enhanced by scaling down (scaling up) $\hat{H}^{(0)}$ ($\hat{V}$). The original first-order Feenberg scaling[43–45] minimizes the MP3 correlation energy to effectively improve the first-order correction to the wavefunction. Cremer and coworkers[37] generalized this approach to second-order and *mth-order Feenberg scaling* by minimizing the fifth-order or $(2n + 1 =) m$th-order MP energy and improving the second-order or mth-order correction to the HF wavefunction. Results obtained in this way reproduce FCI energies with increasing accuracy.

Goodson and Sergeev[47,48] started from MP4, used Feenberg scaling, and then summed the resulting series applying a quadratic approximant to obtain with this *MP4-qλ* method energies better than CCSDT. Such methods will be successful if the dominant branching singularity is suitably modeled. Currently, research is continuing to investigate the convergence behavior of the MPn series, which in the year 2010 is still not solved in the sense that singularities of the MPn series can be reliably predicted for a given electronic system in dependence of the basis set used.

The many disadvantages of MPn combined with the relatively high computational cost and its limited accuracy have caused the larger part of the quantum chemical community to abandon MPPT and to use CC and DFT methods instead. There have been voices

that suggest that only lower order MPn methods such as MP2 should be used in quantum chemistry because the physical foundation of higher order MPn methods is not guaranteed. As a matter of fact, the major thrust of MPn development work has focused, in the past two decades, on the development of low-order MPn methods (MP2 and to some limited extent also MP3) that can compete with HF as timings are concerned and DFT with regard to accuracy. More than a dozen different techniques and methods have been developed to accomplish these goals, which will be discussed in the following sections.

DEVELOPMENT OF MPn METHODS WITH LOW-ORDER OR LINEAR-SCALING PROPERTIES

In the 1980s, MP2 was carried out in quantum chemical programs almost exclusively by algorithms that started from the HF canonical orbitals, had the ERIs stored on disk, and required a $O(M^5)$ transformation before calculating the MP2 correlation energy in a conventional way. This made calculations CPU time, core memory, and disk space consuming. Any increase in the size of the basis set by a factor of 10 ($M' = 10M$), e.g., investigating larger molecules led to a 100,000-fold increase in the computational-time. This excluded the use of MP2 for correlation-corrected calculations on large molecules with hundreds, if not to say thousands, of atoms. In the past two decades, this situation has been dramatically

improved due to a multitude of developments, some of which will be discussed in the following subsections *Direct and Semidirect MP2* to *Fragment Molecular Orbital Approach: FMO-MP2*. These developments focused on (1) making MP2 calculations independent of hardware limitations (*direct* and *semidirect* MP2 methods), (2) facilitating the calculation and transformation of the ERIs [*Resolution of the Identity (RI)/density fitting (DF)*, *Cholesky decomposition (CD)*, *pseudospectral(PS)*, *dual basis (DB)* methods], (3) simplifying the calculation of the MP2 energy by using other than canonical orbitals [*Laplace transformation (LT)*; *atomic-orbital-based*; *local MP (LMP)* methods), or (4) partitioning the molecular problem in smaller, easier to handle parts (divide and conquer (DC), *fragment molecular orbital (FMO)* methods]. In the past two decades, powerful MP2 methods with linear-scaling properties have been developed. If exploiting in addition the power of cluster or massively parallel computing by adjusting MP2 programs to modern computer hardware, these techniques and methods make it possible to carry out MP2 investigations for large molecules with thousands of atoms.

Direct and Semidirect MP2

In the late 1980s, Pople and coworkers[49] and independently Almlöf and Saebø[50] demonstrated that MP2 energy calculations can be carried out in an integral direct fashion (*direct MP2*) without storing partially or fully transformed ERIs on disk. In this way, MP2 calculations became independent of the available disk space. Later, an alternative approach was used that stored partly transformed ERIs (*semidirect* MP2).[51] The optimal choice of a direct or semidirect MP2 algorithm depends on the extent of utilizing the permutational symmetry of ERIs (apart from utilizing molecular symmetry), the effective prescreening of integrals for the purpose of eliminating small ERIs (exploiting the sparsity of the ERI supermatrix), and the time savings achieved when calculating the MP correlation energy.[52] Clearly, these factors have also to be related to the size and architecture of a fast memory as well as the degree of vectorization and parallelization of the available hardware. For different purposes, optimal direct or semidirect solutions have been found as is documented in a multitude of publications, only some of which can be mentioned here.[49–52]

Resolution of the Identity and Density Fitting: RI/DF-MP2

The evaluation of two-electron four-index ERIs and their subsequent transformation correspond to the major time-consuming factors in conventional MP2 calculations. The calculational work can be reduced by factorizing four-index ERIs into three-index and two-index integrals.[53, 54] These ideas were already pursued by Boys, Shavitt, and others as is summarized by Van Alsenoy[55] in a 1988 review. Their realization in the case of closed-shell MP2 was first carried out by Feyereisen et al.[53]

$$E_{\mathrm{MP}}^{(2)} = \sum_{ij}^{\mathrm{occ}} \sum_{ab}^{\mathrm{vir}} \frac{<ia|jb>[2<ia|jb> - <ib|ja>]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (17)$$

(Mulliken notation of ERIs). With the help of an orthonormal auxiliary basis set $\{\chi_A\}$, the resolution of the identity (RI) is given by

$$\mathbf{I} = \sum_A |A><A| \quad (18)$$

where Eq. (18) is only approximately fulfilled in the case of a finite set with M' functions. Inserting the identity before the operator $1/r_{12}$ of an ERI, the MP2 correlation energy takes the form:

$$E_{\mathrm{MP}}^{(2)} = \sum_{ij}^{\mathrm{occ}} \sum_{ab}^{\mathrm{vir}} \sum_{A,B}^{M'}$$

$$\frac{<iaA><A|jb>[2<iaB><B|jb> - <ibB><B|ja>]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (19)$$

In Eq. (19), $<iaA>$, etc. represent three-index overlap integrals and $<A|jb>$, etc. represent three-index ERIs, i.e., the cost of calculating the MP2 energy is reduced by an order of M. The original idea of Feyereisen et al.[53] has been improved by Almlöf and coworkers,[54] Kendall and Früchtl,[56] and Werner et al.[57] The approach has to be viewed as fitting a density distribution with a linear combination of basis function taken from an auxiliary basis[54] that can be optimized for this purpose.[58] If the residual function is minimized, several options corresponding to different metrics are possible. Almlöf and coworkers[54] demonstrated that the largest efficiency of factorizing two-electron repulsion integrals is gained while using a Coulomb metric. For the exchange integrals, the efficiency gain is smaller because a factorization of the exchange matrix similar to that of the Coulomb matrix is not possible. The same is true for the integrals needed for MP2.

It has been pointed out[57] that the RI technique involves a summation over states, whereas the procedure used is best described as DF and as such is based on a criteria absent for the RI technique. As

both terms are found in the literature, the acronyms RI/DF and RI/DF-MP2 will be used in this work.

Although the errors introduced by the RI/DF technique are nonnegligible in terms of absolute energies (about 0.1 mHartree/atom), the corresponding errors in relative energies are normally smaller than 0.1 kcal/mol. RI/DF is also justified by the fact that time savings can be as large as 1–2 orders of magnitude as compared with the costs of a conventional MP2 calculation, especially if large molecules are investigated (use of large basis sets) and RI/DF is combined with other techniques (see below) so that the linear scaling objective can be reached.[57]

Cholesky Decomposition: CD-MP2

Cholesky decomposition (CD) and RI/DF are closely related.[59–62] Beebe and Linderberg[59] already proposed in 1977 to reduce the rank of the ERI supermatrix $V_{\mu\nu,\rho\sigma}$ with the help of a Cholesky decomposition:

$$V_{\mu\nu,\rho\sigma} = < \mu\nu|\rho\sigma > \approx \sum_I^{M'} L_{\mu\nu}^I L_{\rho\sigma}^I \qquad (20)$$

The supermatrix $\mathbf{V}$ is expressed in terms of the Cholesky product $\mathbf{L}\,\mathbf{L}^\dagger$ (†: transposed) where the lower triangular matrix $\mathbf{L}$ possesses the same dimension as $\mathbf{V}$ at the start of the procedure. However, columns of $\mathbf{L}$ can be deleted in case of (approximate) linear dependence of the columns of $\mathbf{V}$, which is done in an iterative procedure utilizing recursive formulas and controlling accuracy by a suitable integral accuracy threshold [using the difference between exact ERI and approximate ERI in Eq. (20)]. In this way, $M' < M$ in Eq. (20) is achieved and the number of ERIs to be calculated is strongly reduced. CD can be considered as a RI/DF method without an auxiliary basis set.

Aquilante et al.[60, 61] improved the original CD approach by constraining the Cholesky vectors to include only products of basis functions centered at the same atom (1C-CD method) so that a molecule-specific CD procedure is obtained. In a variant, denoted as aCD, 1C-CD L-vectors are precomputed for isolated atoms. 1C-CD and aCD are very close to the original CD approach with only insignificant losses in accuracy.[60, 61]

The relationship between CD and RI/DF can be demonstrated by deriving Cholesky vectors for the latter. The major difference between the two methods is that CD represents an integral fitting using the basis functions of the MO calculation, whereas RI/DF is a density fitting method using a preoptimized auxiliary basis set for this purpose. Despite these similar-

ities, Ahlrichs and coworkers[62] see some advantages for RI/DF methods. However, a final judgment on the performance question is far from being at hand because both CD and RI/DF have to prove their usefulness in combination with other cost-reducing techniques, which may be sensitive to the inclusion of an auxiliary basis set.

Pseudospectral Approach: PS-MP2

Although not directly obvious, pseudospectral (PS) methods can be seen as another way of reducing the number of ERIs to be calculated. First of all, they are hybrid methods in the sense that they approximate conventional spectral results by using both basis functions (function space) and grid representations in three-dimensional Cartesian space (physical space).[63] The less costly one-electron integrals are analytically calculated in function space, whereas the calculation of ERIs is transformed to physical space taking advantage of the local character of the Coulomb potential. The density of electron 1 is determined by calculating N_g grid points. Then the interaction of this density with the density of electron 2 expressed by a basis function product $\chi_\rho\chi_\sigma$ is determined by N_g three-index integrals (g refers to agrid point at position $\mathbf{r}_g$). If the ERIs are expressed in this way, time savings can be achieved for the calculation and the transformation of ERIs in the course of a PS-MP2 or PS-MP3 calculation as was demonstrated by Martinez and Carter.[64] For example, the summation over grid points is facilitated by eliminating those points that contribute only insignificantly, which pays out especially for large basis sets. An additional improvement of the scaling properties of PS-MP methods can be achieved by combining the PS methodology with local correlation methods to be be discussed in the section *Local Character of Electron Correlation: LMP2*.

Dual Basis Approach: DB-MP2

For the description of electron correlation, a significantly larger basis set is required than that for an HF calculation. This is consideredin the dual basis (DB) approach, first proposed by Jurgens-Lutovsky and Almlöf.[65] In DB-MP2,[66] the density matrix of the smaller HF basis is projected onto that of the larger one to build up the corresponding $\mathbf{F}$ matrix. With the help of a one-step procedure, the HF energy of the larger basis set is approximated and, if needed, corrected by a perturbative singles contribution based on F_{ia} (occupied, virtual part of the F-matrix for the large basis). The MP2 part is calculated conventionally using the coefficients obtained for the orbitals of the large basis.

DB-MP2 energies differ only slightly from canonical MP2 energies. Costs for the HF-part of the DB-MP2 calculation are reduced by a factor of 8–10. However, by applying the RI/DF approximation, additional cost reductions can be achieved so that the overall time savings for accurate, large-basis calculations can be be more than 90%.[67]

Laplace Transformation: LT-MP2

The energy denominator of the MP2 expression is a major stumbling block for expressing the correlation problem with other than canonical orbitals. In 1991, Almlöf[68] suggested to use a Laplace transform (LT) technique to eliminate the denominator of the MP2 energy expression [Eq. (9)]:

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}$$
$$= \int_0^\infty dt \exp[(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\, t] \quad (21)$$

where t is an auxiliary parameter. The MP2 correlation energy is obtained in the form of Eq (22):

$$E^{(2)} = \frac{1}{4} \int_0^\infty dt \sum_{ij}^{occ} \sum_{ab}^{vir} <ij||ab>^2$$
$$\times \exp[(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)t] \quad (22)$$

The t-dependence of the integrand can be transferred to the orbitals: $\psi_i(t) = \psi_i(0)\exp(\frac{1}{2}\epsilon_i t)$ and $\psi_a(t) = \psi_a(0)\exp(-\frac{1}{2}\epsilon_a t)$, thus leading to

$$E^{(2)} = \int_0^\infty e^{(2)}(t)\, dt \quad (23a)$$

with

$$e^{(2)}(t) = \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} <i(t)j(t)||a(t)b(t)>^2 \quad (23b)$$

LT-MP2 provides extra flexibility in the choice of the orbitals, which is no longer constricted to canonical orbitals. By appropriate orbital rotations one can express the MP2 correlation energy, e.g., in terms of any set of basis functions (atomic orbitals; see *Use of Atomic Orbitals: AO-MP2*) or localized molecular orbitals (LMOs) (see *Local Character of Electron Correlation: LMP2*). Use of the LT technique is facilitated by substituting the integration over the exponential function in (22) by a finite sum over a relatively small number τ of grid points α.[68,69] Another advantage of the LT transformation (which can also be used for higher orders of MPn theory) is the fact that the MP2 energy can be expressed as a functional of the HF density matrix as was first shown by Surjan[122]: $E^{(2)} = E^{(2)}[P_{HF}]$. This implies that the MP2 energy can be directly calculated from the density matrix P_{HF} without knowledge of the MOs. Because the functional form of $E^{(2)}[P_{HF}]$ depends on the form of the Fock operator, the functional is not universal.

Use of Atomic Orbitals: AO-MP2

Utilizing the LT of the MP2 denominator, atomic orbital (AO)-MP2 formulations based on AOs (basis functions) rather than MOs have been developed by Häser,[70] Ayala and Scuseria,[71] and Ochsenfeld and coworkers.[72,73] For the AO-LT-MP2 method, the closed-shell correlation energy of Eq. (17) is expressed as

$$E_{AO-LT-MP2}^{(2)} = \sum_\alpha^\tau e_{JK}^{(\alpha)} \quad (24)$$

where $e_{JK}^{(\alpha)}$ is specified by Eqs. (25) (called contraction step) and (26) (called transformation step):

$$e_{JK}^{(\alpha)} = 2e_J^{(\alpha)} - e_K^{(\alpha)} = \sum_{\mu\nu\rho\sigma} <\underline{\mu}\overline{\nu}|\underline{\rho}\overline{\sigma}>^{(\alpha)}$$
$$\times [2 <\mu\nu|\rho\sigma> - <\mu\sigma|\rho\nu>] \quad (25)$$

$$<\underline{\mu}\overline{\nu}|\underline{\rho}\overline{\sigma}>^{(\alpha)} = \sum_{\mu'\nu'\rho'\sigma'} \underline{P}_{\mu\mu'}^{(\alpha)} \overline{P}_{\nu\nu'}^{(\alpha)} <\mu'\nu'|\rho'\sigma'> \underline{P}_{\rho\rho'}^{(\alpha)} \overline{P}_{\sigma\sigma'}^{(\alpha)}$$
$$(26)$$

(for details, see Refs 70–73, especially the review by Ochsenfeld et al.[72]) The occupied (underlined) and virtual pseudodensity matrices (overlined) are defined as

$$\underline{P}_{\mu\nu}^{(\alpha)} = |\omega^{(\alpha)}|^{1/4} \sum_i^{occ} C_{\mu i} \exp[\epsilon_i t^{(\alpha)}] C_{\nu i}$$
$$= |\omega^{(\alpha)}|^{1/4} \{\exp[t^{(\alpha)} \mathbf{P}^{occ} \mathbf{F}] \mathbf{P}^{occ}\}_{\mu\nu} \quad (27a)$$

$$\overline{P}_{\mu\nu}^{(\alpha)} = |\omega^{(\alpha)}|^{1/4} \sum_a^{vir} C_{\mu a} \exp[-\epsilon_a t^{(\alpha)}] C_{\nu a}$$
$$= |\omega^{(\alpha)}|^{1/4} \{\exp[-t^{(\alpha)} \mathbf{P}^{vir} \mathbf{F}] \mathbf{P}^{vir}\}_{\mu\nu} \quad (27b)$$

($\omega^{(\alpha)}$, weight factor; τ, 5–8 in most cases[68,69]).

AO-LT-MP2 approaches lead to a computational overhead arising from the calculation of τ exponential values and a more expensive transformation step. However, computational savings are gained while calculating large molecules due to the fact that the AO-formulation enables effective ERI screening or other elimination techniques for small ERIs.[71–73] Additional computational savings are gained by using only half-transformed ERIs and reordering summations within contraction and transformation.[73]

Frozen core and frozen virtual approximations can be applied and the accuracy of the calculation effectively controlled. In this way, a calculation of 16 stacked DNA basepairs with 1052 atoms (10,674 basis functions) was recently carried out.[73]

Local Character of Electron Correlation: LMP2

The *correlation domain concept* is based on the idea that dynamic electron correlation is short ranged by nature; however, the canonical HF MOs used to describe electron correlation are delocalized and thereby they complicate the description of dynamical electron correlation. The steep increase in scaling of MPn correlation methods is a consequence of using the HF wavefunction and the delocalized canonical HF orbitals as a starting point rather than being inherent in the correlation problem. This was already recognized in the 1960s and since then repeated attempts have been made to set up local correlation methods.

Localization of MOs to bond, lone pair, and core electron orbitals significantly increases the sparsity of the transformed integrals, thereby reducing storage and calculational requirements. Localized MOs (LMOs) describe that domain of the molecule where short-range correlation takes place and therefore it is attractive to formulate MPn methods in terms of LMOs. This idea was pioneered by Pulay and Saebø[74–76] and later extended or varied by Werner and coworkers,[57, 77, 78] Schütz and coworkers,[77, 78] Head-Gordon and coworkers,[79–82] and others; not all can be cited here.

Pulay and Saebø[74, 75] used the Hylleraas functional (for real functions) to obtain the second-order energy $E^{(2)}$:

$$E^{(2)} = 2 < \Phi^{(1)} | \hat{H} - E^{(0)} | \Phi^{\text{HF}} >$$
$$- < \Phi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \Phi^{(1)} > = \min \quad (28)$$

which implies a minimization process, in which the MP2 amplitudes are optimized. In this connection, $E^{(2)}$ is expressed as a sum of pair correlation energies e_{ij}:

$$E^{(2)} = \sum_{i \geq j} e_{ij} \quad (29)$$

described by LMOs rather than canonical MOs. This approach increases the calculational costs, leads however to the advantage of describing pair correlation in correlation domains. Weak electron pairs that contribute to the correlation energy less than a given threshold, e.g., 3 mhartree or less, can easily be identified and discarded.[74, 75]

Another advantage is that the virtual (correlation) space can be spanned by projected basis functions χ_μ [projected atomic orbitals (PAOs) because the occupied space has to be projected out] where each occupied LMO is associated with just those PAOs that are located in the spatial vicinity of the LMO. In this way, a *local correlation space* or *pair domain* is generated, which includes covalent virtual pairs $|a_i b_j >$ ($|a >$ close to $|i >$; $|b >$ close to $|j >$) and ionic virtual pairs $|a_i b_i >$ and $|a_j b_j >$ (both $|a >$ and $|b >$ close to the same occupied LMO), thus drastically reducing each pair domain of canonical MP2 (all virtual pairs are included).

The AOs are orthogonalized with regard to the occupied LMOs; however, they are nonorthogonal among each other. Nonorthogonality is important in the context of LMP2 because it helps to remove the localization tails. Further advantages result for the integral transformation from basis function to LMO space because integral prescreening can be effectively used and/or distant pairs can be treated by a multipole expansion.[77] LMP2 recovers a large percentage (more than 98%) of the canonical MP2 correlation energy. The LMP methods have been extended to third and fourth order,[74, 75] various versions including AO-based MP2 theory and a splitting of the Coulomb operator in short- and long-range part[78] have been presented, and LMP2 has been combined with the RI/DF technique.[57] In this way, low-order scaling[77, 78] or fast linear-scaling LMP2 versions have been obtained.[57]

A different approach to LMP2 has been taken by Head-Gordon and coworkers[79–82] who developed the local *diatomics-in-molecules* and *triatomics-in-molecules* (DIM and TRIM) MP2 methods. DIM-MP2[79] is a single-step procedure, based on a parameter-free description of the local correlation space and formulated in terms of nonorthogonal atom-centered orbitals in both the occupied and the virtual spaces. The expression of MP2 in terms of nonorthogonal orbitals is more complicated than the canonical one; however, it can be simplified by imposing that the local MP2 energy becomes invariant to rotations of the AO basis on each atom. Costs are reduced to cubic scaling, and 99.8% of the canonical MP2 energy is recovered. TRIM-MP2 extends the D excitation pattern from an exclusive local (atomic) one as in DIM to a more general one that also includes nonlocal D excitations.[81]

Divide and Conquer Approach: DC-MP2

A divide and conquer (DC) strategy was originally suggested by Yang[83] for DFT and later developed as

DC-MP2 by Kobayashi et al.[84–86] for MPPT. The approach is based on the partitioning of large electronic systems into many small fragments, the independent quantum chemical description of each fragment, and finally the recombination of the fragment results to get the energy for the original electronic system.[83] DC-MP2 has the advantage of reducing computational cost to a linear dependence on the size of the system and providing a suitable starting point for parallelization of a MP2 program. If a molecule is partitioned into N subsystems, N local eigenvalue problems have to be solved. This implies the determination of a subsystem density matrix with the help of a suitable partitioning matrix, which describes each basis function as being located inside the subsystem, its buffer region, or outside both subsystem and buffer region.[83–85]

DC-MP2 scales with $O(Nm^5)$, i.e., the number m of basis functions in a subsystem and the number N of subsystems, where for large molecules $m << N$. This leads to large time savings (e.g., $m = 10$, $N = 100$; $10^7 << 10^{15}$) and enables linear scaling with the size of a large molecule.[85]

Fragment Molecular Orbital Approach: FMO-MP2

Fragment molecular orbital (FMO) theory was developed over the past 10 years by Fedorov, Kitaura, and coworkers.[87–90] A large molecule is divided into N fragments and all molecular properties of the target molecule are then calculated from the fragments and a limited number of their conglomerates, e.g., their dimers (FMO2) or trimers (FMO3). The FMO2 energy[87]

$$E = \sum_I^N E_I + \sum_{I>J}^N (E_{IJ} - E_I - E_J) \qquad (30)$$

(E_I, monomer energies; E_{IJ}, dimer energies) is calculated by variationally optimizing each monomer in the Coulomb field of the total molecule (environment) and neglecting exchange and charge-transfer effects between the monomer and the environment, which are assumed to be of local nature. FMO is variational only with regard to the monomers, whereas the dimer (or trimer) corrections are determined in a perturbational sense. Dangling bonds between fragments are electrostatically saturated, thus excluding the necessity of other capping means. The FMO2-MP2 correlation energy, $E_{FMO2}^{(2)}$, is calculated in a similar way[88]:

$$E_{FMO2}^{(2)} = \sum_I^N E_I^{(2)} + \sum_{I>J}^N [E_{IJ}^{(2)} - E_I^{(2)} - E_J^{(2)}]$$
$$+ \text{corr. Terms} \qquad (31)$$

The correction terms are based on the electrostatic potential and response densities of monomers and dimers. Time savings are similar as in the case of DC-MP2, where again additional time savings are gained by excluding dimer (or trimer) terms for distantly separated monomers. Calculations with 3000 and more basis functions have been carried out. In those cases where conventional MP2 energies are available, errors in the FMO2-MP2 energy are in the mHartree range.[88]

Parallelization of MP2 Programs

Rapid developments in computer hardware in the form of either multicore, cluster, or massively parallel processors had a strong influence on quantum chemical program design. Common to these developments is the degree and the mode of parallelization that has been improved, whereas the processor clock speed has remained essentially the same. There is a distinct trend to combine more cores per motherboard in the next years and consequently quantum chemical program development has and will have to adjust to this trend.

The parallelization of quantum chemical codes up to the year 2008 and the availability of parallelized quantum chemical programs have been discussed in a recent monograph by Janssen and Nielsen,[91] who devoted extra chapters to the parallelization of the MP2 and LMP2 methods (see also Ref 92 of the same authors). There, the relevant work of Pulay,[93] Nagase and coworkers,[93, 94] are summarized. An efficient parallel algorithm has been developed for RI/DF-MP2 to perform energy calculations for large molecules on distributed memory processors.[94] Impressive accomplishments have been made using massively parallel vector computers. For example, Mochizuki et al.,[95] utilizing earlier program developments,[95] have carried out FMO-MP2 calculations on an influenza HA antigen–antibody system comprising 14,086 atoms (921 residues) with 78,390 basis functions.[96] Calculations were completed within 53 min using 4096 vector processors, where the cost factor relative to the FMO-HF calculation was just 2.7.[96]

Combination Methods and Linear Scaling

In the past two decades, a wealth of new methods and techniques has been developed to speed up the lower order MPn methods. In the case of MP2, either the prefactor or the actual $O(M^5)$ scaling problem itself has been effectively reduced. By combining some of the 10 procedures described above, even more powerful MP2 algorithms result, varying of course with regard to the accuracy of the calculated MP2 energy,

the ease of implementing analytical energy derivatives for MP2 response property calculations, or the degree of parallelization of the corresponding programs. It would require an extra section to discuss these possibilities with regard to advantages and disadvantages, which is beyond the scope of this review. Therefore, just a few examples are mentioned here.

Low- or even linear-scaling efficiency[72] has been obtained by combination methods such as RI/DF-LMP2,[57] RI/DF-TRIM,[82] PS-LMP2,[97] DB-DC-MP2,[86] FMO-LMP2,[98] FMO-RI/DF-MP2,[99] FMO-CD-MP2,[100] RI/DF-AO-LT-MP2,[101] or RI/DF-CDD (Cholesky-decomposed pseudodensity)-LT-MP2.[102]

These methods have helped to apply MP2 to larger and larger molecules. Recently, Ochsenfeld and coworkers[123] have applied multipole-based integral estimates (MBIE)-SOS-AO-LT-MP2 to an RNA system comprising 1664 atoms and 19,182 basis functions, making this one of the largest *ab initio* calculations ever done. FMO-MP2 calculations have been carrid out for even larger systems (see *Parallelization of MP2 Programs*). So far it was not possible to assess the accuracy of FMO-MP2 calculations of huge molecular systems that are not amenable to comparative calculations yielding accurate MP2 energies. Currently, it is difficult to make a judgement on the usefulness of FMO-MP2 for the investigation of biomolecules and other large systems. Considering, however, the manifold of MP2 techniques available today, it is reasonable to expect that routine MP2 calculations for biomolecules with 10,000 and more atoms become feasible within the next 5 years.

IMPROVEMENT OF LOW ORDER MP*n* METHODS

Low-order MP*n* methods do not reach the accuracy of CCSD(T) and other high-order CC methods. Often MP2 or MP3 are even less reliable than modern DFT hybrid methods based on empirical corrections. Therefore, a second goal of the MP*n* development work of the past two decades has been the improvement of the MP methodology. Improvements were first strictly in an *ab initio* sense; however, in the last decade, they adopted an empirical touch, obviously influenced by the developments in the area of DFT, which were often based on just observation rather than first principles due to the inherent problems of density functionals. Today, one can say that these empirical corrections of MP*n* theory triggered more solid development work, which otherwise may not have taken place. This is especially true for spin scaling (section *Spin-Scaled MP*n), its rational-

ization in terms of Feenberg scaling, and the follow-up work on orbital-optimized MP2 (section *Orbital-Optimized MP*).

Spin-Scaled MP*n*

HF theory includes exchange correlation, i.e., same-spin electron correlation as a result of the Pauli principle and the antisymmetrization of the wavefunction. Accordingly, MP2 is biased toward same-spin (ss) excitations and ss-electron correlation.[103] Analyzing this situation, Grimme developed spin-component-scaled (SCS) MP2, in which ss-correlation effects are scaled back by a factor of 3 ($f_{ss} = 1/3$), whereas opposite-spin (os) correlation effects are increased by the factor $f_{os} = 1.2$.[103] In a second paper, Grimme[103] extended spin-scaling to SCS-MP3. Both SCS-MP2 and SCS-MP3 yield improved molecular properties such as atomization energies, bond lengths, or vibrational frequencies.[103–105]

In view of the small f_{ss}-value of Grimme,[103] and Head-Gordon and coworkers[106] suggested to completely suppress the ss-component of the MP2 correlation energy. Although their spin-opposite scaled (SOS) MP2 method is based on $f_{os} = 1.3$ and $f_{ss} = 0$ (exchange integrals are eliminated), the accuracy of SCS-MP2 is not lost. The advantage of SOS-MP2 approach is that by dropping the more difficult exchange (ss)-part, MP2 speed up techniques such as RI/DF and LT[106] are more easily applied to convert a $O(M^5)$ into a $O(M^4)$ scaling method. Lochan et al.[107] pointed out that both SCS- and SOS-MP2 fail to correctly describe long-range correlation between two nonoverlapping systems. For the purpose of leaving short-range scaling intact, but at the same time introducing a desired long-range scaling factor $f_{os} = 2$ that recovers the asymptotic MP2 interaction energy of distant closed-shell fragments, they split the electron interaction operator $1/r_{12}$ in a short-range and a long-range part and scaled the latter to correct the long-range behavior of MP2 correlation. This *modified opposite spin* (MOS)-MP2 method performs better than SOS-MP2 for a variety of problems involving both short-range and long-range interactions.[107]

It soon became obvious that the scaling factors depend on the electronic system considered. In some cases, scaling factors opposite to those originally suggested lead to better results. This has led to a fundamental analysis of spin scaling in terms of Feenberg scaling[108] and to the development of MP*n* method improvements that may lead to a more systematic improvement of MP*n* theory (see section *Orbital-Optimized MP*). Apart from this, it could be expected that the benefits of spin scaling would have an impact on other *ab initio* methods such as CC theory. Several

steps have been made in this direction, and a development as in the case of low-order MPn methods is foreseeable.

Dispersion Corrected MPn

Various authors have pointed out that MP2 has a tendency of overestimating dispersion interactions.[109, 110] In view of the importance of van der Waals interactions in general and dispersion interactions in specific in many fields of chemistry, attempts have been made to improve the MPn description of dispersion interactions either by spin scaling, the addition of a Lennard–Jones term or in form of hybrid methods. As an example for the first group of dispersion-corrected MPn methods, the SMP3 (scaled MP3) and MP2.5 (average of MP2 and MP3 correlation correction) methods may be mentioned.[111, 112] These methods intend to reproduce CCSD(T) results for the S22 benchmark set of noncovalently bonded interaction complexes[109] according to:

$$E[CCSD(T), \text{large}] \approx E[\text{SMP3}, \text{large}]$$
$$= E[\text{MP2}, \text{large}] + f_{\text{MP3}} E^{(3)}[\text{small}] \quad (32)$$

(large and small refers to the size of the basis set) where the second term on the right side approximates the CCSD(T) correction, $\Delta E[CCSD(T), \text{small}] = E[CCSD(T), \text{small}] - E[\text{MP2}, \text{small}]$, of a given problem calculated with a small basis set. Because basis set and correlation corrections are separated, the method corresponds to a scaled MP method taking advantage of the oscillating behavior of the MPn series (MP2 overestimating, MP3 underestimating pair correlation due to a coupling of D excitations in the latter method).

An empirically corrected MP2 method, dubbed MP2 + ΔvdW, has been worked out by Tkatchenko et al.[113] They improved the long-range interaction potential of MP2 by adding correction terms of the Lennard–Jones type, C_n / R^n (C_n, dispersion coefficient; R, distance between monomers). In this way, a reasonable agreement with CCSD(T) binding energies is obtained.[113]

Cybulski and Lytle[110] and later Heßelmann[114] have developed MP2 dispersion-corrected methods (henceforth called *MP2C* for *MP2 coupled*) that focus directly on the deficiencies of supermolecular MP2 interaction energies as described by intermolecular perturbation theory. The uncoupled HF (UCHF) dispersion energy contained in the MP2 dispersion energy can overestimate dispersion by 15% and more.[110] Because of this, these authors replaced the UCHF dispersion energy with the coupled dispersion energy of a time-dependent HF (TDHF) or time-dependent DFT (TDDFT) approach.[114] MP2C offers considerable improvements in the case of dispersion-only complexes as well as for H-bonded complexes (deviation from CCSD(T)/CBS 0.25 kcal/mol in case of the S22 set).[115]

Orbital-Optimized MP

MPPT based on the HF wavefunction as reference suffers from the shortcomings of the mean-field orbitals. A remedy of these problems can be achieved by optimizing orbitals at the MP level and using those for the calculation of the MP correlation energy. These ideas were pursued already in the 1980s by various authors such as Adamowicz or Bartlett who used an energy-optimizing principle based on the second-order Hylleraas functional to obtain improved virtual orbitals. In 2009, Neese, Grimme et al.[116] followed a similar approach to develop an orbital-optimized spin-component scaled MP2, OO-SCS-MP2, method. In the minimization process, the mean-field orbitals are adjusted to MP2 correlation, thus largely suppressing some of their shortcomings. Neese et al.[116] combine the OO-MP2 procedure with spin-component scaling and the RI/DF technique in form of OO-RI/DF-SCS-MP2. Errors in calculated RI/DF-SCS-MP2 radical stabilization energies are reduced by a factor of 3–5 [reference: CCSD(T)/CBS energies], whereas time requirements are enlarged by a factor of 8–12.

Lochan and Head-Gordon[117] had already developed, in 2007, an OO-MP2 method for the purpose of alleviating the shortcomings of mean-field orbitals in open-shell calculations. OO-MP2 enhanced the stability of MP2 results by leading to a better handling of spin contamination and symmetry breaking problems.[117] Recent work by Kurlancheek and Head-Gordon[118] demonstrates that orbital optimization at OO-MP2 is an effective means to cure violations of N-representability by UMP2 (i.e., natural orbital occupation numbers larger 2 or smaller 0).

Explicitly Correlated MP

It is a general observation that MP2 results converge slowly only to complete basis set (CBS) limit results, which can be expressed by saying that the true form of the MP2 Coulomb hole is difficult to assess from truncated basis set calculations. In 1929, Hylleraas showed in his seminal work on the helium atom that the correlation cusp is correctly described by introducing the distance r_{12} between two electrons into an explicitly correlated electronic wave function. For decades, explicitly correlated or r_{12} calculations were limited to few electron systems because of the

mathematical difficulties in calculating M^6 or M^8 three-electron and four-electron integrals required for the exact minimization of the Hylleraas functional for the second-order correlation energy. (For a recent review, see Klopper.[119])

Kutzelnigg and Klopper[119] solved the three-ERI and four-ERI problem with the help of the RI approach and developed MP2-R12 that corresponds to a MP2 theory inwhich the first-order pair functions contain terms linear in the interelectronic distances r_{pq}. Explicitly correlated methods such as MP2-R12 speed up the convergence of the one-electron basis so that already quadruple zeta basis sets provide a reliable estimate of the CBS limit energy. MP-R12 has been improved in the last years to MP2-F12 by using the Slater-type geminal correlation factor $\exp(-\zeta r_{12})$ rather than linear r_{12} terms.[120] MP2-F12 outperforms other correlation factors tested. The method has led to the most accurate MP2 correlation energies obtained so far. Both MP2-F12 and MP2-R12 have been employed to estimate MP2 CBS limit energies. Current developments concentrate on reducing the high costs of MP2-R12 or MP2-F12 by utilizing RI/DF, where a breakthrough has been obtained recently by Werner and coworkers[121] who used LMP2-F12. There is strong indication that in the near future the combination of MP2-F12 with RI/DF and correlation domain techniques will become a powerful tool for getting reliable correlation-corrected energies and other molecular properties.

CONCLUSIONS AND OUTLOOK

Whenever a new MPn method is developed, a number of concomitant tasks have to be solved: (1) Restricted closed-shell, unrestricted, and restricted open-shell versions of the new method have to be made available; in the case of UMPn, the need and possibility of spin-Projected UMPn (PUMPn) versions also have to be checked. (2) For each of these versions, analytical energy derivatives have to be worked out for the calculation of response properties. (3) Direct (semidirect), parallelized, and low order scaling versions have to be made available. (4) Also, it has to be checked and the necessary steps have to be taken to combine the new method with GVB, CASSCF, and multireference methods. (5) An important area is the use of MPn *in* relativistic theory. (6) Similarly, the method may have some relevance for getting better double-hybrid DFT methods or might be combined with TDDFT. (7) There is also the possibility of using a new, more accurate MPn methods in connection with model chemistry approaches such as Pople's Gm or related approaches. In short, any useful new MPn method may trigger a dozen or more follow-up developments, most of which are not routine and may require months of additional programming work.

Owing to space limitations, this review cannot report on the work on PUMPn, restricted open-shell MP (ROMP), and other related methods. The problems of spin contamination and orbital symmetry breaking in UMPn theory have been investigated for years and this has helped understanding the problems connected with MPPT. Similarly, there is no space available to describe the development of multireference MPn methods, relativistic MPn, double-hybrid DFT, and other methods, which would require long sections or additional review articles focusing especially on one of these topics. Furthermore, it would have been useful to give an account on high-accuracy MPn properties, the use of MPn methods in model chemistry methods, or the discussion of typical MPn results. Also, not touched by this review is the use of MPPT in connection with molecular vibrational problems. These topics have to be left to other reviews in this volume or forthcoming reviews in other publication media.

In this review, the four different, partly overlapping stages of MPPT development during the past 80 years have been outlined. The first one was characterized by little interest or even disregard of MPPT. Then, after a revival of MPPT triggered by the success of MBPT in nuclear physics, the actual *sturm and drang* time of MPn in quantum chemistry followed, closely connected with the names of Bartlett and Pople. At the end of the 1980s, doubt and criticism as to the physical meaning of MPn led to a short period of turning away from MPPT and replacing it by the more attractive CC and DFT methods. But almost simultaneously the focus on MP2 and the conversion of the method into a linear scaling method brought about a new interest into MPPT. Improvement of MP2, especially in the last decade, has made MP2 one of the two or three major tools (the other being HF and DFT) while investigating very large molecules.

In the years to come, quantum chemists have to master the huge task of selecting the most useful MPn method (first MP2, later perhaps MP3) out of a multitude of possibilities, thanks to linear scaling properties, that can be used for the investigation of large molecules with thousands of atoms. This method has to fulfill a number of properties:

1. It must be size-extensive.
2. It must reproduce conventional MP2 properties as closely as possible; in any case, calculated trends (relative energies, etc.) must be

identical to those obtained with conventional methods.

3. The determination of analytical energy derivatives must be straightforward.

4. Time savings must apply to both the method itself and the calculation of energy derivatives. In this connection, it is relevant that some of the techniques discussed above offer significant advantages when calculating the analytical energy gradient and higher derivatives.

5. The method in question must provide a continuous representation of the PES (this requirement is overlapping with 3; however, is more general then the latter).

Clearly, orbital-optimized MP*n* methods and MP*n*-F12 methods will play a prominent role in the future. A method such as RI/DF-LMP2-F12 has already been found to be both affordable and very accurate,[121] in which the linear scaling properties are achieved by applying local F12, local RI/DF, and local RI, the latter for the F12 part. Up to 87 atoms and 3128 basis functions were calculated. (Werner and coworkers[121] suggest in this connection that the method is a suitable starting point for future RI/DF-LCCSD(T)-F12 calculations.) If, at the same time, better than mean-field orbitals can be used, MP2 theory will become a powerful tool in the hands of the quantum chemists.

The coming years have to clarify which of the methods suggested is the best linear scaling MP2 method fulfilling requirements 1–5. This method may strongly change the way QM/MM methodology is set up and how large molecules will be investigated in the future. Probably, the MM part will be used exclusively for the description of the solvent, whereas biomolecules such as proteins or DNA can be fully described at the MP2 level, improving perhaps the description of the core by employing CC theory. MP3, previously considered to be a superfluous method, can turn out to replace MP2 more and more. There is no doubt that what takes place currently in single-reference MPPT will have a stronger impact on multireference MPPT, relativistic MPPT, and DFT-MPPT hybrid methods. It is also clear that many of the techniques developed for MP2 will be transferred to CC methods. It could be that, once low-scaling MP3 is found to be more attractive than MP2, another paradigm shift from MPPT to CC theory could occur because a method such as CCSD is only somewhat more costly than MP3, but includes contrary to MP3, orbital relaxation and infinite order effects. The first steps in this direction have already been done. Now in the year 2010, a huge development task is ahead of quantum chemists, which involves probably more research groups than ever before. It is not difficult to foresee that within the next 3–5 years, this review will become outdated because a wealth of new MP*n* methods will emerge from what is available today in MPPT.

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