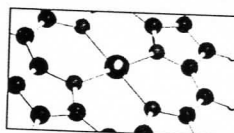# Volume 3
M–P

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ENCYCLOPEDIA OF COMPUTATIONAL CHEMISTRY

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Møller–Plesset Perturbation Theory

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Abbreviations

BWPT = Brillouin–Wigner perturbation theory; EN = Epstein–Nesbet; FCI = full CI; MBPT = many-body perturbation theory; MRS PT = multireference state perturbation theory; PT = perturbation theory; RSPT = Rayleigh–Schrödinger perturbation theory; SRS PT = single-reference state perturbation theory.

1 INTRODUCTION

Most electronic structure investigations start with a Hartree–Fock (HF) calculation (see *Density Functional Theory (DFT), Hartree–Fock (HF), and the Self-consistent Field*), which provides a reasonable description of energy, wavefunction, electron density distribution and other properties of atoms and molecules. However, because of its well-known simplification of the description of electron interactions (each electron moves in the average field of all other electrons), HF suffers from an exaggeration of electron repulsion. One has to apply a suitable correlation corrected method that describes electron interactions in a better way to obtain more reliable atomic and molecular properties. During the 1960s and early 1970s, *electron correlation* was mostly introduced by *configuration* interaction (CI) theory (see *Configuration Interaction*); however, since the mid-1970s the most often used correlation corrected *ab initio* method is many-body *perturbation theory* (MBPT) with the Møller–Plesset perturbation operator (often denoted as MP theory).[1]

1.1 Historical Background

Møller and Plesset[1] were the first to develop a perturbation theory (PT), in which the HF *wavefunction* and energy are taken as zero-order solutions to the exact wavefunction and energy. The difference between the exact *Hamiltonian* and the HF Hamiltonian is considered as a small perturbation, which corrects the average-field approximation of HF theory in such a way that the correlated movement of the electrons is explicitly considered. In 1934, Møller and Plesset published their work in a short paper of just five pages, which for more than 40 years had little impact on quantum chemistry, but later became very popular among quantum chemists, and today is considered as one of the milestone papers dealing with the electron correlation problem. In the 1930s and also in the following decades, the focus of quantum chemists was primarily on HF theory and its possible improvement in the form of CI theory. When electronic structure calculations first became available for a larger audience due to the advent of computers in the mid-1950s, development work concentrated on various HF and CI solutions and their implementation in the form of computer programs. Little attention was paid to the possibilities of PT. The situation was different among nuclear physicists since the interaction potential between nucleons is strongly repulsive and, therefore, HF theory, which allows two particles to occupy the same region in space, was not applicable within nuclear theory. Therefore, nuclear physicists used the model of noninteracting particles and included interactions by PT using either the Brillouin–Wigner (BW) or the Rayleigh–Schrödinger (RS) variant. It soon became obvious that the second-order BW energy contrary to the second-order RS energy is not proportional to the number N of particles. In an important paper, Brueckner[2] investigated the application of RSPT to *fermions* and found that the third-order energy $E^{(3)}$ and higher order perturbation energies $E^{(p)}$ contain terms that are proportional to N^2, N^3, etc., but that these terms are canceled by other terms in the energy formula so that all remaining terms are 'linked cluster' terms proportional to N. Brueckner could not give a general proof of what is known today as the 'linked cluster theorem' for any order p. This was given two years later by Goldstone[3] using a diagrammatic representation of PT, which was stimulated by developments in field theory connected with the names of Feynman, Dyson, and Wick in the late 1940s and early 1950s. The work of Brueckner, Goldstone, and others presented the start of MBPT in its present form as the PT that considers just the linked cluster contributions to the energy and, therefore is 'extensive' (i.e., scales with N) at all orders of PT. Within a couple of years Feshbach formulated an effective Hamiltonian that could be used to get (in principal) exact energies even though applied to model wavefunctions, Bloch and later des Cloizeaux made the first steps toward quasidegenerate MBPT, and a generalization of MBPT to open-shell systems was started.[4]

In 1963, Kelly[5] demonstrated the applicability of the Brueckner–Goldstone MBPT in electronic structure calculations on atoms. In the 1960s and early 1970s, only a few MBPT investigations on atoms and the H_2 molecule were published. This changed in the 1970s when Bartlett and, independently, Pople developed MBPT methods from second- to fourth-order for general use in electronic structure calculations within a relatively short period of about five years.[6–12] Bartlett and his co-workers made the lead in these developments following the diagrammatic approach to MBPT in the tradition of Goldstone,

Hugenholtz, Brandow and others. Although diagram language provided an elegant approach to developing appropriate formulas for calculating the perturbation energy, it was unfamiliar to many chemists and, therefore, there was a certain relief among those willing to apply perturbation theory to chemical problems when Pople's parallel developments of low-order MBPT discarded diagram language and followed what is known today as the algebraic approach to PT. Since Pople directly connected his work to the outline provided by Møller and Plesset on second-order PT, he coined the terms MP2, MP3, MP4, etc. for second-, third-, fourth-, etc. order MBPT with the MP perturbation operator. Bartlett preferred the notation MBPT(2), MBPT(3), MBPT(4), etc. for the same methods, indicating that his developments closely followed the linked cluster theorem of MBPT. Of course, both notations can be used interchangeably; in this summary Pople's MP notation is used.

Subsequently both the Pople and the Bartlett group independently pushed the routine use of PT methods in electronic structure calculations by inventing analytical energy derivative techniques in connection with PT, introducing direct methods for the investigation of large molecules and, finally, developing fifth-order PT (MBPT(5) or MP5) in the mid (Bartlett and co-workers[13,14]) to late 1980s (Pople and co-workers).[15] The competition between both groups led to rapid progress and application of MP (MBPT) methods. It helped considerably that, in particular, Pople made it a strategy to make newly developed programs available to a broad public of interested users. Because of this the MP methods are closely connected with the name of Pople although it is fair to say that both Pople and Bartlett made equally large contributions to the field. Only few contributions came from other groups. As examples, the work by Gauss and Cremer on MP3 and MP4 analytical derivatives[16,17] or the development of a sixth-order MP (MP6) method for routine calculations by He and Cremer[18] are mentioned here.

1.2 Reasons for the Popularity of MP Methods

Today, MP methods are the most popular correlation corrected *ab initio* methods in quantum chemistry for calculating dynamic electron correlation effects. MP2 theory has become the routine method for obtaining a fast, reasonably accurate account of electronic structure. In this regard it has replaced HF methods when medium-sized and even larger molecules are investigated. Today, MP2 calculations on molecules as large as fullerenes are not an exception. The popularity of MP methods results from several reasons:

(a) MP theory leads to a hierarchy of well-defined methods, which provide increasing accuracy with increasing order p. MP2 theory leads to a major improvement of HF results since it already covers the most important correlation effects. MP4 theory provides reasonably accurate results while MP6 approaches full CI (FCI) results rather closely.

(b) Correlation effects are included stepwise in a systematic manner that facilitates their analysis and the understanding of the correlation problem. Therefore, it is not difficult to understand error trends and to predict the results of higher order MP calculations.

(c) Most important is the fact that, contrary to CI methods, all MP methods are size-extensive,[19,20] i.e., calculated

MP energies scale linearly with the number of electrons as was first shown by Brueckner[2] and Goldstone.[3]

(d) Up to fourth-order, MP energies can be calculated at relatively small computational cost since calculations involve just single, noniterative evaluation steps. MP2 requires just $O(M^5)$ operations where M is the number of basis functions used in the calculation. MP3 and partial MP4 scale with $O(M^6)$ and full MP4 with $O(M^7)$. Using modern supercomputers calculations with 150–200 basis functions are feasible with an $O(M^7)$ method such as MP4.

Another factor has influenced the popularity of MP methods considerably. That is the availability of easy to handle computer programs that can carry out MP calculations for almost any property with almost any reference wavefunction. Pople and his group pioneered the development, design, and distribution of such *ab initio* programs. In particular, Pople invented a monolithic program package, which performs all steps of an *ab initio* calculation in an uninterrupted sequence so that the user has to provide just a very simple input file containing information on atoms and geometry of the molecule and some simple commands in the form of keywords that decide on the method and the type of calculation to be used.[21] It played also an important role that Pople's program was (and still is) available to any interested user after a rather short delay between development of the new method and applying it. By this a major problem of *ab initio* theory was solved, namely the problem of reproducing and testing the results of a new method that in most other cases was only accessible to a small group of experts.

There are also some disadvantages of MP theory which have to be mentioned. (a) MP methods are not variational, i.e., MP energies can become more negative than FCI energies obtained with the same set of basis functions for the same molecular geometry. (b) At a given order p of MP PT, there does not exist a well-defined wavefunction, which makes it impossible to uniquely calculate a molecular property in form of an expectation value. (c) One observes often an oscillatory or erratic rather than monotonic convergence behavior of calculated MP energies with increasing order p.[22,23]

The first two problems are of just minor consequence. For example, it is more important to use a size-extensive rather than a variational method for calculating electron correlation effects. Also, one can calculate molecular properties in the form of response properties (see *Molecular Magnetic Properties*) using analytical energy derivatives without ever referring to a wavefunction.[23] However, the third problem is more serious: it was early observed that the MP energy can strongly oscillate for small values of p before it converges to the FCI energy value, which is identical with the infinite-order MP energy. In some cases, MP energies even diverge, i.e., there is no infinite-order MP correlation energy equal to the FCI correlation energy. Oscillations are also found for other properties such as the internal coordinates of molecular geometries, dipole moments, vibrational frequencies or infrared intensities.[23] Clearly, these oscillations make the use of MP methods less attractive, which is one of the major reasons why coupled cluster (CC) methods (see *Coupled-cluster Theory*) have replaced MP methods more and more in the 1990s when high-accuracy *ab initio* calculations are required.

There is reason to believe that higher order correlation effects will make it possible to successfully apply single determinant theory even in the case of typical multireference problems. Apart from this, the analysis of higher order correlation effects provides a basis for the understanding of the convergence behavior of the MP series. Once the convergence behavior of the MP series is well understood, the prediction of reliable FCI energies from MP energies for low p becomes possible.[24]

2   METHODOLOGY

2.1   The Necessity of Correlation Corrections

2.1.1   The Correlated Movement of the Electrons

Since electrons are negatively charged particles, they repel each other according to the Coulomb law. Within an atom or molecule their movement is correlated, i.e., each electron moves in a way that avoids the instantaneous positions of the other electrons. *Ab initio* methods can be classified according to the way they treat the correlated movement of the electrons. In HF theory an electron is considered to move through the space of an atom or molecule under the influence of the positive charges of the nuclei and the negative charge cloud created by the time-averaged positions of all other electrons (effect 1). This description will be improved if *Coulomb repulsion* between individual electrons according to their instantaneous positions is explicitly considered. Hence, there should be a low probability of finding an electron in the vicinity of another electron. Their movements should be 'correlated' in such a way that any close approach to another electron is avoided as much as possible thus keeping Coulomb repulsion low (Coulomb correlation, effect 2). Apart from this, electrons are fermions, which implies that their wavefunction is antisymmetric and that they obey the *Pauli exclusion principle*. There is a zero probability that two electrons with the same spin are found at the same position, which is denoted by the term 'exchange correlation' (effect 3).

The three effects are illustrated for the H_2 molecule in Figures 1–4 where the probability distribution of one electron
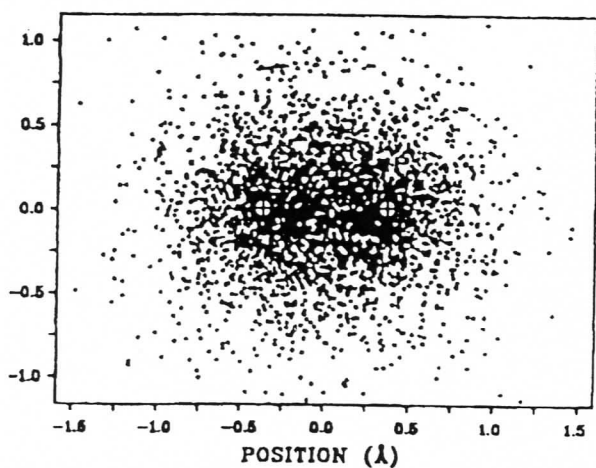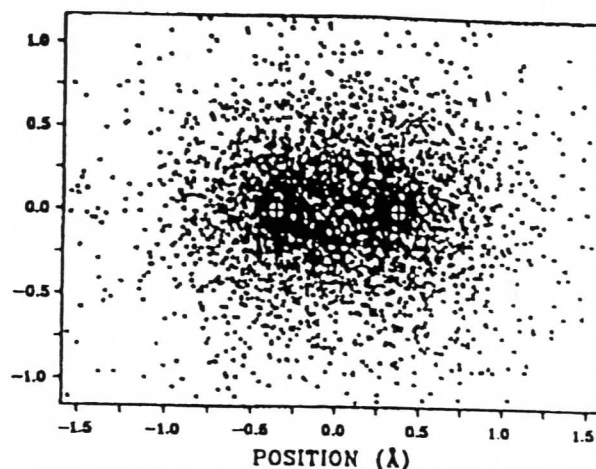

Figure 2   Probability distribution for one of the electrons in the H_2 ground state, as obtained from the HF wavefunction. Reproduced with permission from R. C. Dunbar, *J. Chem. Educ.*, 1989, **66**, 463–466. Copyright (1989) American Chemical Society

dependent upon the position of the other is shown in form of a dot representation.[25] Figure 1 gives as an appropriate reference a one-electron distribution for an H_2 molecule with completely independent electrons: There are no electron–electron interactions at all in this case and the one electron considered moves free in the field of the two H nuclei, i.e., the distribution shown in Figure 1 is identical with that of the H_2^+ molecule. If the electron interactions are described within HF theory, the probability distribution for one electron shown in Figure 2 will result. The distribution is somewhat more diffuse than in Figure 1, but basically there is not much difference between the distributions shown in Figures 1 and 2. If the interactions between the two electrons of H_2 are correctly described by using the exact wavefunction for the calculation of the probability distribution; it is no longer sufficient to use just one picture as in the HF case. For each position of electron 2, a different distribution results for electron 1. From Figure 3, which gives the probability distribution of electron 1 for three different positions of electron 2 (indicated by white circles), it can be seen that Coulomb repulsion has a strong effect on the distribution of the other electron, which tries to avoid the location of electron 2. In Figure 4, the same three positions of electron 2 are shown for the situation of the triplet state of H_2, which has an electron with α-spin in the bonding σ_g MO of H_2 and an electron with α-spin in the antibonding σ_u MO. Because of exchange correlation, the probability of finding electron 1 at the position of electron 2 is zero and the antisymmetrization of the wavefunction leads to a nodal surface that always passes through the position of electron 2.

This example shows that the largest correlation effect is due to exchange or Fermi correlation (effect 3): the two electrons strongly avoid each other (*Fermi hole*). A substantial effect is also due to Coulomb correlation (effect 2), while qualitatively there seems to be little difference between a description assuming an electron moving through the averaged Coulomb field of all other electrons (effect 1) and a description assuming noninteracting electrons. HF theory covers effects 1 and 3; effect 3 (Fermi correlation) is clearly the more important one. Strictly seen, HF is a correlation corrected method since it describes exchange correlation correctly. However, it is

Figure 1   Probability distribution of the single electron in H_2^+. The positions of the two protons are indicated by crosses. Reproduced with permission from R. C. Dunbar, *J. Chem. Educ.*, 1989, **66**, 463–466. Copyright (1989) American Chemical Society
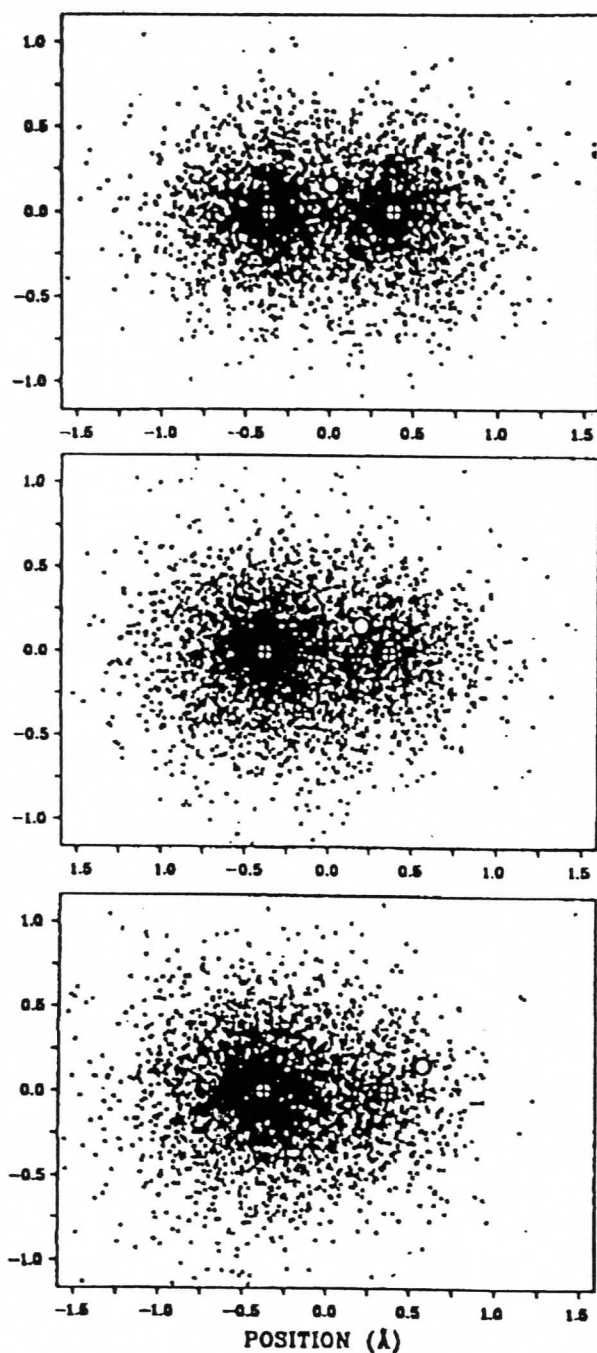
Figure 3 Probability distribution of electron 1 in the *ground state* of H_2 for three different positions of electron 2 (white circles), as obtained from the exact wavefunction. Reproduced with permission from R. C. Dunbar, *J. Chem. Educ.*, 1989, **66**, 463–466. Copyright (1989) American Chemical Society

Figure 4 Probability distribution of electron 1 in the triplet state of H_2 for three different positions of electron 2 (white circles), as obtained from the exact wavefunction. Reproduced with permission from R. C. Dunbar, *J. Chem. Educ.*, 1989, **66**, 463–466. Copyright (1989) American Chemical Society

common practice to confine the term correlation to Coulomb correlation and to consider just those methods which include effect 2 (Coulomb correlation) to some extent as correlation corrected methods.

2.1.2 Shortcomings of the HF Approach

Because of the simplified treatment of Coulomb repulsion between electrons, it is possible that within an HF description
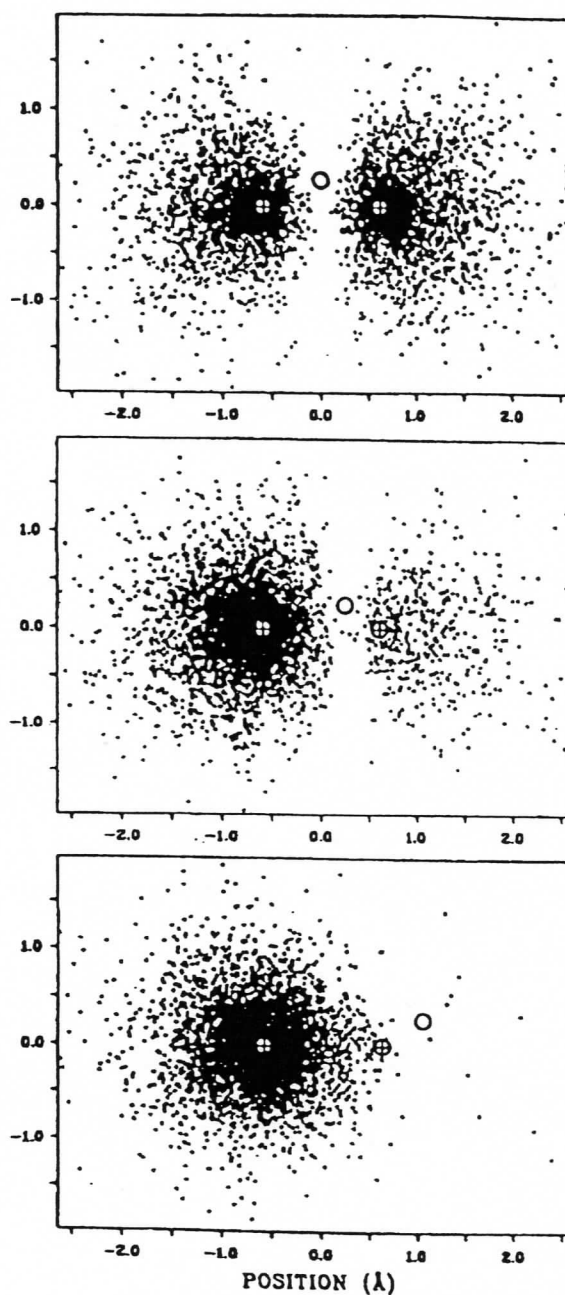
electrons cluster too strongly around the nuclei. This leads to an increase of stabilizing electron–nucleus attraction and to a shielding of the nucleus. Nucleus–nucleus repulsion is under-estimated and *bond lengths* calculated at the HF level are too short, this effect becoming larger with increasing size of the basis set. As soon as Coulomb correlation is explicitly consid-ered, a clustering of electrons in the vicinity of the nucleus is no longer possible, the nucleus is deshielded, nucleus–nucleus repulsion increases and the bond length is enlarged toward its correct value (for opposite effects, see Section 3.4). Clustering of electrons around the nucleus is particularly strong in the case

of electronegative atoms, which means that HF exaggerates bond polarities (the electropositive atom in a bond becomes too positively charged, the electronegative atom too negatively charged). This leads to an overestimation of *dipole moments* and also influences calculated bond angles in such a way that both the underestimation of bond lengths and the exaggeration of bond polarities causes bond angles to widen. Another consequence of an artificial shortening of bond lengths is the overestimation of stretching force constants and harmonic stretching frequencies. In a similar way, one can explain trends in *vertical ionization potentials*, electron affinities, polarizabilities, infrared intensities and other molecular properties calculated at the HF level.[23] Consideration of Coulomb correlation effects, e.g., by MP theory, leads to significant improvements of calculated molecular properties where remaining errors depend on the basis set used, higher order correlation effects not covered by a given MP method, the necessity of relativistic corrections or the inclusion of environmental effects.

The correlation effects described so far are summarized under the term dynamic electron correlation, since they depend on the correlated movement of the electrons in atomic or molecular space. They have to be distinguished from so-called nondynamic or static electron correlation (near-degeneracy correlation) effects, which have to do with the question of whether the HF wavefunction provides a suitable description for the electron system in question. This is certainly the case for most stable closed-shell systems in their equilibrium geometry. However, it is no longer true if such a closed-shell system dissociates in a homolytic fashion. The correct description of such a chemical process requires at least two rather than one *Slater determinant* (*configuration state function*) since during dissociation two (or more) electronic states become nearly degenerate. In general, any atomic or molecular system either in equilibrium or in a dynamical process that possesses nearly degenerate states is poorly described by an HF wavefunction (based on a single determinant). Examples are homolytically dissociating molecules, biradicals, molecules with low lying excited states, etc. Appropriate corrections will be obtained if a two-configuration or multiconfiguration method such as TCSCF, GVB or MCSCF is used to determine an appropriate starting wavefunction for the atomic or molecular problem in question. The energy difference between HF and the multiconfiguration method defines the static *correlation energy*. Clearly, once static correlation is appropriately described, an additional correction has to be made to account for the dynamic correlation of the electrons.

Dynamic correlation is the correlated movement of two or more electrons at a relatively short distance around the cusp region. Static correlation normally leads to a relatively large separation of two electrons in a pair as, e.g., in the bond breaking situation (one electron staying at the first atom, the other at the second atom) or in the near-*degeneracy* situation of ground and *excited states* experienced for molecules such as ozone (one electron staying in a contracted ground state *molecular orbital* localized in the vicinity of the nuclear framework, the other occupying an excited state orbital extending far beyond the nuclear framework).

2.1.3 Definition of the Correlation Energy

The correlation energy E_{corr} for a given state with regard to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the HF approximation. In this definition, which was first given by Löwdin,[26] both static and dynamic correlation energy are included in E_{corr}, which makes sense in so far as in the general case it is no longer possible to distinguish between dynamic and static correlation effects. For example, methods that typically cover dynamic correlation effects include at high-order also some of the static correlation effects and vice versa. On the other hand, one can take the point of view of always using a reference wavefunction that covers near-degeneracy effects so that the difference between the exact energy and the reference energy (calculated at HF, TCSCF, MCSCF, etc.) is just the dynamic correlation energy. Again, it is hardly possible to keep static and dynamic correlation effects separated as soon as high-order correlation effects are included in the calculation.

The definition of the correlation energy given above does not consider the basis set used. Numerical HF calculations, if possible, provide the HF limit and if the Schrödinger energy is derived with the help of experimental data, a total correlation energy can be determined.[27] However, in most cases the HF energy is just known for a finite basis set. If an FCI calculation with the basis set in question is possible, one can calculate the exact correlation energy for this particular basis. Otherwise, one has to use an approximate method X for the basis set Y and obtains the X/Y-based correlation energy where also the geometry of a molecule has to be considered.

Since correlation keeps Coulomb repulsion, which corresponds to a positive, destabilizing energy contribution, small, the correlation energy is always negative (stabilizing). Compared to the *total energy* of an atom or molecule, the correlation energy is typically less than 0.5%, e.g., 0.38 hartree in the case of the Ne atom, which is just 0.3% of its total energy (-129.06 hartree). Nevertheless, this corresponds to 238 kcal mol^{-1} and is larger than most bond and reaction energies. Since the correlation energy depends on the electronic structure, correlation effects on relative energies cancel only in exceptional cases. If chemical accuracy (1 kcal mol^{-1}) is required, correlation energies have to be calculated in a consistent manner.

2.1.4 Pair Correlation Effects

Electronic structure calculations confirm what is anticipated from the Pauli exclusion principle, spin considerations and symmetry constraints, namely that electrons prefer to pair and to occupy certain regions of molecular space: (a) the inner-shell regions of atoms, (b) the bond regions, (c) certain non-bonding regions. Hence, dynamic correlation effects should be particularly strong within an electron pair but less between different electron pairs separated in space. The main contribution to the correlation energy E_{corr} should be electron pair correlation where intrapair correlation should be larger than interpair correlation. Accordingly, the correlation energy can be approximated by equation 1:

$$E_{corr} = \frac{1}{2} \sum_p \sum_q \varepsilon_{pq} \qquad (1)$$

where ε_{pq} is the correlation energy of the electrons p and q coupled in the pair pq.

There are three important types of pair correlation effects that should always be considered, namely left-right correlation, angular (up-down) correlation, and in-out correlation.

They are explained below for the case of the Li_2 molecule, which has the *electron configuration* $(1\sigma_g)^2$, $(1\sigma_u)^2$, $(2\sigma_g)^2 = core(2\sigma_g)^2$.

Left–right correlation. One of the two bonding $2\sigma_g$ electrons prefers to stay close to the left, one close to the right Li nucleus. In the wavefunction, this type of correlation is included by mixing in the $(2\sigma_u)^2$ configuration, which requires a double (D) excitation from the $2\sigma_g$ to the $2\sigma_u$ orbital (Figure 5). Linear combinations of the $2\sigma_g$ and $2\sigma_u$ orbitals lead to new orbitals $2\sigma_g + c_{lr}2\sigma_u$ and $2\sigma_g - c_{lr}2\sigma_u$, which have a larger amplitude either on the left or the right Li nucleus as is schematically indicated in Figure 5. Adding left–right correlation to the HF description of dissociating Li_2, a charge transfer relative to the HF description as indicated in equation (2)

$$Li^+ \cdots Li^- \longrightarrow Li^\bullet \cdots Li^\bullet \qquad (2)$$

is caused and dissociation of Li_2 is qualitatively correctly described. Therefore, the D excitations leading to a description of left–right correlation are also called dissociative excitations.

Angular (up–down) correlation. The two bonding $2\sigma_g$ electrons of Li_2 prefer to stay at opposite sides of the bond axis to avoid each other. In the wavefunction, this type of correlation is included by mixing in the $(1\pi_u)^2$ configuration, which requires a D excitation from the $2\sigma_g$ to the $1\pi_u$ orbital (Figure 5). Linear combinations of the $2\sigma_g$ and $1\pi_u$ orbitals lead to new orbitals $2\sigma_g + c_a 1\pi_u$ and $2\sigma_g - c_a 1\pi_u$, which have a larger amplitude either above or below the bond axis (see Figure 5). For the separated atoms, this type of excitation corresponds to a transfer of a 2s electron to a 2p orbital. In this way, the spherical charge distribution of a Li atom is polarized in the direction of the p orbital. A polarized state of the Li atom is a prerequisite to describing dispersion forces between Li atoms correctly and, therefore, one speaks of dispersive excitations in this case.

In–out correlation. If the two bonding $2\sigma_g$ electrons of Li_2 both happen to be near to one Li nucleus, then one will stay close to the nucleus while the other electron will move into the nonbonding region farther away from the nucleus. In the

wavefunction, this type of correlation is included by mixing in the $(3\sigma_g)^2$ configuration, which requires a D excitation from the $2\sigma_g$ to the $3\sigma_g$ orbital (Figure 5). Linear combinations of the $2\sigma_g$ and $3\sigma_g$ orbitals lead to new orbitals $2\sigma_g + c_{io}3\sigma_g$ and $2\sigma_g - c_{io}3\sigma_g$, which have a larger amplitude either in the bonding or the nonbonding region as is schematically shown in Figure 5. For obvious reasons, this type of excitation is also called a dispersive excitation.

By including the most important left–right, angular, and in–out pair correlation effects the Li_2 *bond dissociation energy* ($D_e = 1.05$ eV) is reproduced with a small error of 6% while at the HF level ($D_e = 0.17$ eV) the error is larger than 80%.[28] Mostly it is sufficient to consider just the correlation effects of valence electron pairs. Inner-shell correlation effects can be ignored (frozen core description). However, for larger atoms the core is polarized and inner-shell correlation becomes important.

2.1.5 Higher Order Correlation Effects

In the language of *ab initio*, theory, D excited configurations are described by the symbol Φ_{ij}^{ab}, where i and j denote spin orbitals ψ_i and ψ_j occupied in the HF ground state wavefunction Φ_0, while a and b denote virtual orbitals ψ_a and ψ_b, which become occupied in the D excited configuration. It is common custom to use indices $i, j, k, \ldots$ to label occupied spin orbitals and indices $a, b, c, \ldots$ to label unoccupied (virtual) spin orbitals. In cases where both types of spin orbitals are considered indices $p, q, r, \ldots$ are used. In particular, left–right, angular, and in–out pair correlation effects are included by adding to the ground state wavefunction of Li_2 the D excitations $\Phi_{2\sigma_g,\overline{2\sigma_g}}^{2\sigma_u,\overline{2\sigma_u}}$, $\Phi_{2\sigma_g,\overline{2\sigma_g}}^{1\pi_u,\overline{1\pi_u}}$, $\Phi_{2\sigma_g,\overline{2\sigma_g}}^{3\sigma_g,\overline{3\sigma_g}}$ (a bar indicates a β spin orbital), which possess additional nodal planes that help to keep electrons apart.

However, when this is done the HF orbitals are no longer the best orbitals for the new physical situation, with (partially) correlated electron pairs. Accordingly, the occupied orbitals should be reoptimized, which corresponds to a new mixing with the virtual (unoccupied) orbitals. This is done in a MCSCF method, but not in methods such as MP that describe just dynamic electron correlation. Instead, single (S) excitations Φ_i^a are mixed (via D excitations) into the wavefunction; these describe orbital relaxation effects, i.e., the orbitals are partially readjusted to accommodate correlated electron pairs. S excitations cannot compensate for an orbital reoptimization within a MCSCF calculation, however they represent an useful orbital relaxation correction, which compared to pair correlation effects is considerably smaller.

By mixing in higher and higher excited configurations such as triple (T) Φ_{ijk}^{abc}, quadruple (Q) Φ_{ijkl}^{abcd}, pentuple (P) Φ_{ijklm}^{abcde} or hextuple (H) excitations Φ_{ijklmn}^{abcdef} higher and higher correlation effects are covered. For example, T excitations describe three-electron correlation effects (from the correlated movement of three electrons dependent upon each other) as well as a combination of pair correlation effects and orbital relaxation. Similarly, Q excitations can cover genuine four-electron correlation effects and combinations of lower order correlation effects. It is clear that with increasing number of electrons connected all-electron correlations become less and less probable. However, there is a relatively large probability that, e.g., a Q excitation describes a pair correlation taking
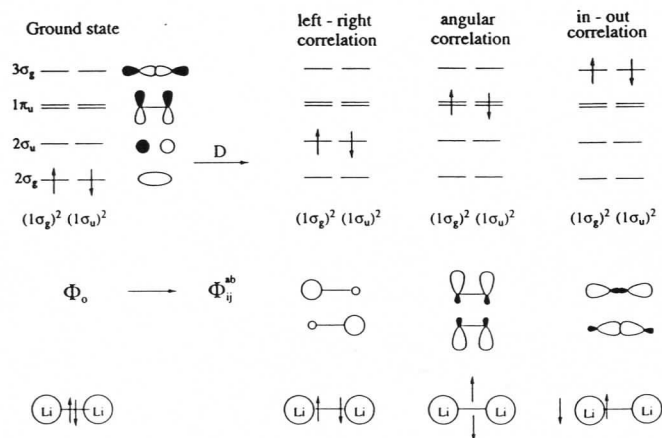

Figure 5 Left–right, angular, and in–out pair correlation in the case of Li_2 as described by appropriate D excitations. MO diagrams for ground (left side) and doubly excited states are given. Orbitals and the bond electron pair (from left to right: uncorrelated in the bond region, left–right correlated, angular correlated, in–out correlated) are schematically shown

place in one part of a molecule and another pair correlation taking place at the same time, but independently of the first in another part of the molecule. One speaks in this case of disconnected correlation effects, of which the disconnected pair–pair correlations are the most important ones.

Connected P and H correlation effects should be of minor importance, while disconnected H correlation effects resulting from three independently correlating pairs can be rather important, e.g., for a conjugated molecule such as benzene with its three delocalized π-electron pairs. One can view higher order excitations such as a Q excitation as a D excitation on top of another D excitation. Since D excited configurations are also important in setting up a reasonable reference wavefunction for a near-degeneracy problem it is clear that one can no longer distinguish which part of the higher order (disconnected) excitations describes nondynamic and which part dynamic correlation effects. Or in other words, the more higher order excitations are mixed into the HF reference wavefunction, the larger is the chance of getting away with a single-reference (determinant) description such as HF even in the case of a typical multireference (near-degeneracy) system. Of course, an exact solution in the latter case is only provided by a FCI description, which considers all possible excitations up to n-tuple for an n-electron system. An FCI calculation with a limited basis set covers all (dynamic and nondynamic) correlation effects that can be described with the basis set chosen.

2.1.6 *Correlation Corrected Methods*

Figure 6 provides an overview of the most frequently used correlation corrected *ab initio* methods in quantum chemistry and, by this, indicates the position of MP methods among these methods.

As indicated, MC methods extend the application of HF theory to problems with strong nondynamic electron correlation. Therefore, the MC methods represent a separate class of correlation corrected methods, actually closer to HF than dynamic electron correlation methods.

There are three classes of methods that describe dynamic correlation effects, namely PT methods, of which MP methods are the most prominent ones, CI methods, and CC methods. MP methods are computationally the simplest ones while CC methods are the most complicated, most expensive, but also the
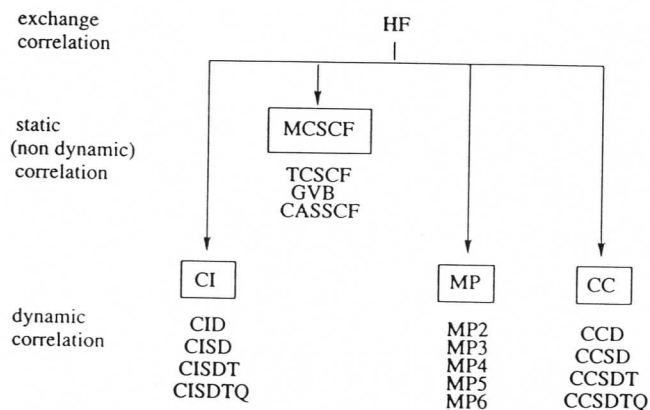
most accurate ones. The three types of methods, even though conceptually different, have many connections and, therefore, it is useful when discussing MP methods to compare the corresponding CI and CC methods. A detailed discussion of the latter will be presented by P. Csarsky (see *Configuration Interaction*) and J. Gauss (see *Coupled-cluster Theory*).

2.2 The Formalism of Perturbation Theory

A solution of the many-electron nonrelativistic electronic *Schrödinger equation* in its time-independent form

$$\hat{H}\Psi = E\Psi \qquad (3)$$

($\hat{H}$: Hamiltonian or energy operator; Ψ: exact wavefunction; E: exact energy; the ground state is considered, i.e., $\Psi_I = \Psi_0 = \Psi$) is not possible for an n-electron system with $n > 1$ and, therefore, one has to work with approximate solutions of equation (3). Suppose that an approximate form of equation (3), namely

$$\hat{H}_0\Phi^{(0)} = E^{(0)}\Phi^{(0)} \qquad (4)$$

has been solved. If both $E^{(0)}$ and $\Phi^{(0)}$ are not very different from the true energy E and the true wavefunction Ψ, energies and wavefunctions can be considered as being related by a perturbation where equation (4) describes the unperturbed problem and equation (3) the perturbed problem. Accordingly, the true Hamiltonian $\hat{H}$ is split into unperturbed Hamiltonian $\hat{H}_0$ and perturbation operator $\hat{V}$:[4]

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \qquad (5)$$

By switching on the perturbation with the help of a dimensionless parameter λ, the unperturbed solution is smoothly transferred into the perturbed solution corresponding to the Schrödinger equation (3).

$$\left.\begin{array}{c} E^{(0)} \longrightarrow E \\ \Phi^{(0)} \longrightarrow \Psi \end{array}\right\} \quad \lambda \longrightarrow 1$$

By expanding E and Ψ in the form of a Taylor series in λ, one obtains

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots + \lambda^p E^{(p)} + \cdots \qquad (6)$$

$$\Psi = \Phi^{(0)} + \lambda\Phi^{(1)} + \lambda^2\Phi^{(2)} + \cdots + \lambda^p\Phi^{(p)} + \cdots \qquad (7)$$

where $E^{(p)}$ and $\Phi^{(p)}$ are the pth order correction to the reference energy $E^{(0)}$ and the reference wavefunction $\Phi^{(0)}$ of the unperturbed problem. Inserting the Hamiltonian (5) and equations (6) and (7) into the Schrödinger equation, one obtains

$$(\hat{H}_0 + \lambda\hat{V})(\Phi^{(0)} + \lambda\Phi^{(1)} + \cdots)$$
$$= (E^{(0)} + \lambda E^{(1)} + \cdots)(\Phi^{(0)} + \lambda\Phi^{(1)} + \cdots) \qquad (8)$$

Since all terms in expansion (8) are linearly independent, the equation must be satisfied for each order p.

$$\text{order } 0: \quad (E^{(0)} - \hat{H}_0)\Phi^{(0)} = 0 \qquad (9)$$

$$\text{order } 1: \quad (E^{(0)} - \hat{H}_0)\Phi^{(1)} = (\hat{V} - E^{(1)})\Phi^{(0)} \qquad (10)$$

exchange correlation		HF		
static (non dynamic) correlation		MCSCF		
		TCSCF GVB CASSCF		
	CI		MP	CC
dynamic correlation	CID CISD CISDT CISDTQ		MP2 MP3 MP4 MP5 MP6	CCD CCSD CCSDT CCSDTQ

Figure 6 Overview of correlation corrected *ab initio* methods used in quantum chemistry

order 2 : $\quad (E^{(0)} - \hat{H}_0)\Phi^{(2)} = (\hat{V} - E^{(1)})\Phi^{(1)} - E^{(2)}\Phi^{(0)}$ (11)

$$\vdots$$

order p : $\quad (E^{(0)} - \hat{H}_0)\Phi^{(p)} = (\hat{V} - E^{(1)})\Phi^{(p-1)} - \sum_{k=2}^{p} E^{(k)}\Phi^{(p-k)}$

(12)

All wavefunctions are determined only up to an arbitrary constant, which is frequently chosen to set the integral (13)

$$\int \Psi^* \Psi \, d\tau = \langle \Psi | \Psi \rangle = 1 \qquad (13)$$

equal to one to provide a convenient probability interpretation. In PT, it is more convenient to choose the intermediate normalization

$$\langle \Phi^{(0)} | \Psi \rangle = 1 \qquad (14)$$

which is equivalent to

$$\langle \Phi^{(0)} | \Phi^{(0)} \rangle = 1 \quad \text{and} \quad \langle \Phi^{(0)} | \Phi^{(p)} \rangle = 0 \quad \text{for all } p > 0 \quad (15)$$

In this way, simple energy expressions are obtained from equations (9)–(12)

order 0 : $\quad E^{(0)} = \langle \Phi^{(0)} | \hat{H}_0 | \Phi^{(0)} \rangle$ (16)

order 1 : $\quad E^{(1)} = \langle \Phi^{(0)} | \hat{V} | \Phi^{(0)} \rangle$ (17)

order 2 : $\quad E^{(2)} = \langle \Phi^{(0)} | \hat{V} | \Phi^{(1)} \rangle$ (18)

$$\vdots$$

order p : $\quad E^{(p)} = \langle \Phi^{(0)} | \hat{V} | \Phi^{(p-1)} \rangle$ (19)

where the energy for $p = 0$ is known from the unperturbed problem and calculation of the first-order, second-order, etc. energy correction seems to require knowledge of the first-order, second-order, etc. correction to the wavefunction of the unperturbed problem.

order 1 : $\quad \Phi^{(1)} = (E^{(0)} - \hat{H}_0)^{-1}(\hat{V} - E^{(1)})\Phi^{(0)}$ (20)

order 2 : $\quad \Phi^{(2)} = (E^{(0)} - \hat{H}_0)^{-1}$

$$\times \, [(\hat{V} - E^{(1)})\Phi^{(1)} - E^{(2)}\Phi^{(0)}] \qquad (21)$$

$$\vdots$$

order p : $\quad \Phi^{(p)} = (E^{(0)} - \hat{H}_0)^{-1}[(\hat{V} - E^{(1)})\Phi^{(p-1)}$

$$- \sum_{k=2}^{p} E^{(k)}\Phi^{(p-k)}] \qquad (22)$$

Detailed analysis of the perturbation formulas reveals that the pth order correction to the wavefunction, $\Phi^{(p)}$, is actually sufficient to calculate all energy corrections up to $E^{(2p+1)}$, which is the content of the Wigner theorem.

$$\left.\begin{array}{l} \Phi^{(0)} \longrightarrow E^{(0)}, E^{(1)} \\ \Phi^{(1)} \longrightarrow E^{(2)}, E^{(3)} \\ \Phi^{(2)} \longrightarrow E^{(4)}, E^{(5)} \\ \Phi^{(3)} \longrightarrow E^{(6)}, E^{(7)} \\ \quad\quad \vdots \\ \Phi^{(p)} \longrightarrow E^{(2p)}, E^{(2p+1)} \end{array}\right\} \; \text{Wigner Theorem} \qquad (23)$$

The Hamiltonian $\hat{H}_0$ is a Hermitian operator with a complete set of eigenfunctions $\Phi_I^{(0)} (I = 0, 1, 2, \ldots)$ corresponding to ground state wavefunction $\Phi_0^{(0)}$ of the unperturbed problem and the excited state wavefunctions $\Phi_1^{(0)}$, $\Phi_2^{(0)}$, $\Phi_s^{(0)}$, etc. The latter can be used to determine the correction terms $\Phi_0^{(p)}$ for $\Phi_0^{(0)}$ to obtain the exact ground state wavefunction Ψ_0 of the perturbed problem. Working out the corresponding formulas, one obtains

$$E_0^{(1)} = \langle \Phi_0^{(0)} | \hat{V} | \Phi_0^{(0)} \rangle = \langle 0 | \hat{V} | 0 \rangle = V_{00} \qquad (24)$$

$$E_0^{(2)} = \sum_{s>0} \frac{V_{0s}V_{s0}}{E_0 - E_s} \qquad (25)$$

$$E_0^{(3)} = \sum_{s>0} \sum_{t>0} \frac{V_{0s}\overline{V}_{st}V_{t0}}{(E_0 - E_s)(E_0 - E_t)} \qquad (26)$$

$$E_0^{(4)} = \sum_{s>0} \sum_{t>0} \sum_{u>0} \frac{V_{0s}\overline{V}_{su}\overline{V}_{ut}V_{t0}}{(E_0 - E_s)(E_0 - E_t)(E_0 - E_u)}$$

$$- \sum_{s>0} \sum_{t>0} \frac{V_{0s}V_{s0}V_{0t}V_{t0}}{(E_0 - E_s)(E_0 - E_t)^2} \qquad (27)$$

$$\Phi_0^{(1)} = \sum_{s>0} \frac{V_{s0}}{E_0 - E_s} \Phi_s^{(0)} \qquad (28)$$

$$\Phi_0^{(2)} = \sum_{s>0} \sum_{t>0} \frac{V_{st}V_{t0}}{(E_0 - E_s)(E_0 - E_t)} \Phi_s^{(0)}$$

$$- \sum_{s>0} \frac{V_{00}V_{s0}}{(E_0 - E_s)^2} \Phi_s^{(0)} \qquad (29)$$

where $\quad V_{st} = \langle \Phi_s^{(0)} | \hat{V} | \Phi_t^{(0)} \rangle$

and $\quad \overline{V}_{st} = V_{st} - \delta_{st}V_{00}$ (30)

and $\quad E_0^{(0)} = E_0$ and $E_s^{(0)} = E_s$.

2.3 Møller–Plesset Perturbation Theory

2.3.1 The MP Perturbation Operator

In 1934, Møller and Plesset published a 'note on an approximate treatment for many electron systems', in which they suggested using the HF wavefunction and HF energy as the zeroth-order approximation to exact wavefunction and energy. Accordingly, the HF Hamiltonian $\hat{H}^{HF}$ was regarded as the appropriate $\hat{H}_0$ operator for the unperturbed problem:

$$\hat{H}_0' = \hat{H}^{HF} = \sum_p \hat{F}(p) - \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij})$$

$$= \sum_p \hat{F}(p) - G^{HF} \qquad (31)$$

The Fock operator for electron p

$$\hat{F}(p) = \hat{h}(p) + \hat{v}(p) = \hat{h}(p) + \sum_i [\hat{J}_i(p) - \hat{K}_i(p)] \qquad (32)$$

is an effective one-electron operator, which depends on the one-electron operator $\hat{h}(p)$ that covers kinetic energy and nucleus–electron attraction, and the HF potential $\hat{v}(p)$ constructed from Coulomb operators $\hat{J}_i(p)$ and exchange operators $\hat{K}_i(p)$ both being expressed in terms of spin orbitals ψ_i.

The Fock operators are Hermitian operators that are associated with the set of one-electron eigenvalue problems:

$$\hat{F}(p)\psi_i(p) = \varepsilon_i\psi_i(p) \tag{33}$$

Equation (33) represents the kernel of HF theory specifically and MO theory in general since they define the spin orbitals ψ_i and their orbital energies ε_i as eigenfunctions and eigenvalues of the Fock operators. Since the sum of orbital energies covers the electron interaction energy G^{HF} twice, the HF Hamiltonian contains besides the sum of Fock operators also the correction term $-G^{\text{HF}}$.

Since the exact Hamiltonian is given by

$$\hat{H} = \sum_p \hat{h}(p) + \frac{1}{2}\sum_p\sum_q \frac{1}{r_{pq}} \tag{34}$$

the perturbation operator takes the form

$$\hat{V}' = \hat{H} - \hat{H}^{\text{HF}} = \frac{1}{2}\sum_p\sum_q \frac{1}{r_{pq}} - \sum_p \hat{v}(p) + G^{\text{HF}} \tag{35}$$

where the expectation value of $\hat{V}'$ is

$$\langle\hat{V}'\rangle = \langle\hat{H} - \hat{H}^{\text{HF}}\rangle = G^{\text{exact}} - 2G^{\text{HF}} + G^{\text{HF}} = G^{\text{exact}} - G^{\text{HF}} \tag{36}$$

This is most likely a small quantity so that the basic assumption of PT, namely that the perturbation operator is associated with a relatively small electron interaction correction, is fulfilled. However, there is the problem that G^{exact} cannot be calculated, unless one reverts again to the average-field approximation of HF theory. In this case, the expectation value of the perturbation operator becomes zero, which is not useful at all. To get out of this dilemma, the shift term G^{HF} is used to define the new operators $\hat{H}_0$ and $\hat{V}$

$$\hat{H}_0 = \hat{H}^{\text{HF}} + G^{\text{HF}} = \sum_p \hat{F}(p) \tag{37}$$

$$\hat{V} = \hat{V}' - G^{\text{HF}} = \frac{1}{2}\sum_p\sum_q \frac{1}{r_{pq}} - \sum_p \hat{v}(p) \tag{38}$$

The expectation value of $\hat{V}$ adopts a finite value when calculated on the basis of the average-field assumption.

The HF wavefunction is an eigenfunction of $\hat{H}_0$ and the sum of orbital energies $E^{\text{orb}} = \sum_i \varepsilon_i$ is the corresponding eigenvalue.

$$\Phi_0^{(0)} = \Phi_0^{\text{HF}} = \Phi_0; \quad E_0^{(0)} = E_0^{\text{orb}} \tag{39}$$

$$\hat{H}_0\Phi_0 = E_0^{\text{orb}}\Phi_0 \tag{40}$$

The substitution functions Φ_s generated by exciting electrons from occupied spin orbitals ψ_i, ψ_j, etc. to virtual spin orbitals ψ_a, ψ_b, etc. are also eigenfunctions of $\hat{H}_0$ and, accordingly, are orthogonal to each other.

2.3.2 *Calculation of MP Energies: Integral Transformation*

The evaluation of MP correlation energies requires the calculation of matrix elements of the type V_{0s}, V_{st}, etc. and denominators such as $E_0 - E_s$ (see equations 25–29). Calculation of the denominators is facilitated by the fact that

for a substitution function Φ_s such as Φ_{ij}^{ab} the following relations hold:

$$\hat{H}_0\Phi_{ij}^{ab} = E_{ij}^{ab}\Phi_{ij}^{ab} \tag{41}$$

$$E_{ij}^{ab} = \sum_{k\neq i,j}\varepsilon_k + \varepsilon_a + \varepsilon_b = E_0 - \varepsilon_i - \varepsilon_j + \varepsilon_a + \varepsilon_b \tag{42}$$

$$E_0 - E_s = E_0 - E_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \tag{43}$$

and similar formulas for higher excitation functions Φ_s.

Since the MP perturbation operator involves a two-electron operator, the standard Slater rules for orthonormal spin orbitals can be applied when calculating V_{0s}, V_{st}, etc. All matrix elements can be expressed in terms of double-bar integrals $\langle ij\|ab\rangle$, which are antisymmetrized two-electron integrals of the general type $\langle pq\|rs\rangle$:

$$\langle pq\|rs\rangle = \int\int \psi_p^*(1)\psi_q^*(2)\frac{1}{r_{12}}[\psi_r(1)\psi_s(2) - \psi_s(1)\psi_r(2)]d\tau_1 d\tau_2 \tag{44}$$

From an HF calculation two-electron integrals $\langle\mu\nu|\lambda\sigma\rangle$ over basis functions χ_μ are available, which means that for MP calculations some or all two-electron integrals have to be transformed into the basis of spin orbitals ψ_i. The cost factor for transformation (45)

$$\langle ij|kl\rangle = \sum_\mu\sum_\nu\sum_\lambda\sum_\sigma \langle\mu\nu|\lambda\sigma\rangle c_{\mu i}c_{\nu j}c_{\lambda k}c_{\sigma l} \tag{45}$$

(coefficients $c_{\mu i}$ are the LCAO coefficients obtained in the HF calculation) seems to be rather large since the cost of the one-step transformation (45) is proportional to $O(M^8)$, where M denotes the number of basis functions used in the HF calculation. This can be seen by realizing that about M^4 two-electron integrals over basis functions χ_μ have to be calculated at the HF level (this is the reason why the cost of an HF calculation is proportional to $O(M^4)$), which are transformed into M^4 two-electron integrals over spin orbitals. However, Nesbet[29] and later Bender[30] realized that the M^8 transformation of equation (45) can be dissected into a sequence of four M^5 transformations by calculating *intermediate arrays* $\langle\mu\nu|\lambda l\rangle$, $\langle\mu\nu|kl\rangle$, and $\langle\mu j|kl\rangle$ which represent partially transformed two-electron integrals:

$$\langle\mu\nu|\lambda l\rangle = \sum_\sigma \langle\mu\nu|\lambda\sigma\rangle c_{\sigma l} \tag{46}$$

$$\langle\mu\nu|kl\rangle = \sum_\lambda \langle\mu\nu|\lambda l\rangle c_{\lambda k} \tag{47}$$

$$\langle\mu j|kl\rangle = \sum_\nu \langle\mu\nu|kl\rangle c_{\nu j} \tag{48}$$

$$\langle ij|kl\rangle = \sum_\mu \langle\mu j|kl\rangle c_{\mu i} \tag{49}$$

In this way, the integral transformation can be carried out at a cost level which is not much higher than that of an HF calculation. On the other hand, it is clear that any correlation corrected *ab initio* calculation involves at least $O(M^5)$ computational steps because of equations (46)–(49).

The use of intermediate arrays to reduce the computational cost of an MP calculation becomes rather important when higher order MP energy corrections have to be calculated. It

is kind of an art in itself that once suitable energy formulas of the type shown in equations (25)-(29) are found, these are converted into double bar integrals in such a way that computational cost are kept minimal. For fourth-order and higher order MP energies, this requires increasing use of intermediate arrays.[18]

2.3.3   First-order MP Energy and MP Theorem

The first-order correction to the energy E_0^{orb} is given by

$$E_{MP}^{(1)} = \langle \Phi_0 | \sum_{p<q} \frac{1}{r_{pq}} - \sum_p \hat{v}(p) | \Phi_0 \rangle$$
$$= V_{00} = -\frac{1}{2} \sum_{ij} \langle ij \| ij \rangle \tag{50}$$

i.e., it reduces the orbital energy E_0^{orb} by the electron interaction energy G^{HF}. Hence, the first-order MP energy is identical to the HF energy:

$$E(\text{HF}) = E(\text{MP1}) = E_0^{\text{orb}} + E_{\text{MP}}^{(1)} = \sum \varepsilon_i - \frac{1}{2} \sum_{ij} \langle ij \| ij \rangle, \tag{51}$$

which means that the HF energy is correct up to first-order. Correlation corrections do not come in before second-order. Møller and Plesset were the first to show this.[1] They also showed that the HF electron density and other one-electron properties such as the dipole moment are correct through the first-order of PT. This is today known as the Møller–Plesset theorem.

2.3.4   Second-order MP Energy

The second-order correction to the energy was given by equation (25)

$$E_0^{(2)} = \sum_{s>0} \frac{V_{0s} V_{s0}}{E_0 - E_s} \tag{25}$$

where a priori the substitution functions could be S excitation functions Φ_i^a and D excitation functions Φ_{ij}^{ab}. However, because of the Brillouin theorem all matrix elements $\langle \Phi_0^{(0)} | \hat{V} | \Phi_i^a \rangle$ are identical to zero. Only D excitations interact directly with the ground state wavefunction and, therefore, the s-index in equation (25) is equal to D. If equation (25) is converted into double bar integrals utilizing equation (43) in the case of the denominator, one obtains

$$E_{\text{MP}}^{(2)} = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle a_{ij}^{ab} \tag{52}$$

where a_{ij}^{ab} are the D amplitudes that are given by

$$a_{ij}^{ab} = (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)^{-1} \langle ab \| ij \rangle \tag{53}$$

Møller and Plesset were the first to derive the formula for the second-order correlation energy.[1] Calculation of the MP2 correlation energy requires just $O(M^5)$ operations and, therefore, MP2 calculations represent one of the cheapest ways of getting correlation corrections. As shown before, D excitations describe pair correlation effects and, therefore, the MP2 correction covers the largest part of the correlation energy defined

by a given basis set. It has to be stressed that the D excitations couple via $\hat{V}$ only with the HF ground state wavefunction (matrix elements V_{0s}), however not among themselves and, therefore, they 'do not see each other'. As a consequence, the whole atomic or molecular space is used to separate the electrons within a pair irrespective of the fact that the electrons of another pair may occupy the same space. This leads to an overestimation of pair correlation effects, which has to be considered when analyzing MP2 correlation energies.

2.3.5   First-order MP Wavefunction

Since determination of the MP2 correlation energy requires the calculation of the D amplitudes a_{ij}^{ab} (equation 53), the first-order correction to the wavefunction is readily available within a MP2 calculation:

$$\Phi_{MP}^{(1)} = \frac{1}{4} \sum_{ij} \sum_{ab} a_{ij}^{ab} \Phi_{ij}^{ab} \tag{54}$$

The correction $\Phi_0^{(1)}$ is fully determined by all D excitations. Its magnitude is measured by

$$\langle \Phi_{MP}^{(1)} | \Phi_{MP}^{(1)} \rangle = T^2 = \frac{1}{4} \sum_{ij} \sum_{ab} (a_{ij}^{ab})^2 \tag{55}$$

2.3.6   Third-order MP Energy

In the case of the third-order correction, again only D excitations are included, which means that the third-order energy covers just pair correlation effects. However due to the fact that matrix elements V_{st} are included in the correction formula (equation 26), where Φ_s and Φ_t represent excitations D and D', the third-order correction includes a coupling between different D excitations, which leads to a correction of pair correlation effects overestimated at the second-order level.

The two-electron integral formula of the third-order energy correction is given by

$$E_{\text{MP}}^{(3)} = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle b_{ij}^{ab} \tag{56}$$

where the second-order D excitation amplitudes depend in a somewhat complicated way on the first-order D amplitudes of equation (53):

$$b_{ij}^{ab} = (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)^{-1} \left[\frac{1}{2} \left(\sum_{ef} \langle ab \| ef \rangle a_{ij}^{ef} + \sum_{mn} \langle mn \ ij \rangle a_{mn}^{ab} \right) - \sum_{me} \sum_P (-1)^P P(i/j|a/b) \langle mb \| je \rangle a_{im}^{ae} \right] \tag{57}$$

The permutation symbol $P(i/j|a/b)$ denotes the product $P(i/j)P(a/b)$, and $P(i/j)$ (or $P(a/b)$) gives the sum of the identity and the permutation of $i(a)$ and $j(b)$. The calculation of the b_{ij}^{ab} amplitudes requires $O(M^6)$ steps and, accordingly, the determination of the MP3 correlation energy is an $O(M^6)$ operation.

2.4 Size-extensivity of MP Methods and the Linked Diagram Theorem

PT in its present form was first developed for the investigation of continuous media such as nuclear matter, solids, electron gas, etc. where the properties of interest are extensive (see Section 1.1). When doubling the size of the system investigated and keeping the particle density constant, the energy of the system should double. This property is called size-extensivity. For an atom or molecular system, the particle density does not remain constant when its size is increased. Nevertheless, a physically reasonable description by PT (or any other method) must lead to a linear dependence of the energy on the number N of electrons. Energy terms that have a nonlinear dependence on N are unphysical and prevent a comparison of atomic or molecular energies in connection with the investigation of molecular stability and reactivity.

Brueckner was the first to show for the lower orders of PT that all terms having a nonlinear dependence on N mutually cancel each other. Both $E_0^{(0)}$, $E_0^{(1)}$, and $E_0^{(2)}$ have only terms linear in N, which is the reason why HF and MP2 are size-extensive. This can be shown by adding stepwise electron pairs to a closed-shell system with N_0 electrons. For example, the zeroth-order energy increases in this case according to equation (58):

$$E_0^{(0)}(N_0 + 2 + 2 + 2 + \cdots) = \sum_i 2\varepsilon_i + 2\varepsilon_j + 2\varepsilon_k + 2\varepsilon_l + \cdots \quad (58)$$

where the extra electrons occupy MOs ϕ_j, ϕ_k, etc. The more electron pairs are added, the more the orbital energies of the newly occupied MOs approach the value $\varepsilon = 0$. For very large N the difference between the ε values of newly occupied MOs becomes so small that by a first approximation the orbital energy can be considered as a constant ε and the zeroth-order energy becomes

$$E_0^{(0)}(N) = N\varepsilon \quad (59)$$

i.e., $E_0^{(0)}$ scales with the number of electrons N. Similar considerations apply to first- and second-order energy, thus confirming that HF and MP2 are size-extensive.

The situation is somewhat different for the third-order energy given in equation (26), which can be rewritten in the following way:

$$E_0^{(3)} = \sum_{s \neq} \sum_{t > 0} \frac{V_{0s} V_{st} V_{t0}}{(E_0 - E_s)(E_0 - E_t)} + \sum_{s = t > 0} \frac{V_{0s} V_{ss} V_{s0}}{(E_0 - E_s)^2}$$
$$- E_0^{(1)} \sum_{s > 0} \frac{V_{0s} V_{s0}}{(E_0 - E_s)^2} \quad (60a)$$

$$E_0^{(3)} = \Gamma_1^{(3)} + \Gamma_2^{(3)} - E_0^{(1)} \Gamma_3^{(3)} \quad (60b)$$

In the third term, $\Gamma_3^{(3)}$ corresponds to the second-order energy reduced by an extra denominator. Hence, both $E_0^{(1)}$ and $\Gamma_3^{(3)}$ scale with N and their product with N^2. Using the relationship $\overline{V}_{st} = V_{st} - \delta_{st} V_{00}$ in connection with the second term one can rewrite $\Gamma_2^{(3)}$ according to

$$\Gamma_2^{(3)} = \sum_{s > 0} \frac{V_{0s} \overline{V}_{ss} V_{s0}}{(E_0 - E_s)^2} + V_{00} \sum_{s > 0} \frac{V_{0s} V_{s0}}{(E_0 - E_s)^2} \quad (61a)$$

$$= \sum_{s > 0} \frac{V_{0s} \overline{V}_{ss} V_{s0}}{(E_0 - E_s)^2} + E_0^{(1)} \Gamma_3^{(3)} \quad (61b)$$

where the first term scales with N and the second again with N^2. Clearly, part of the second term cancels the third term of the third-order energy so that the latter just scales with N rather than $N + N^2$. Similar considerations apply to fourth and higher orders of MP PT.

It is useful to examine what would happen if the third-order energy were given by equation (62)

$$E_0^{(3)'} = \Gamma_1^{(3)} - E_0^{(1)} \Gamma_3^{(3)} \quad (62)$$

which no longer would be size-extensive. If equation (62) were used to calculate the energy of the dissociation reaction $AB \rightarrow A + B$, where AB would represent a 10-electron molecule and fragments A and B, 6- and 4-electron systems respectively, then one would obtain a third-order correction for the reaction energy according to (62):

$$\Delta E^{(3)} = E_{AB}^{(3)} - E_A^{(3)} - E_B^{(3)}$$
$$= [e_{AB}^N(10) - e_{AB}^{N^2}(100)] - [e_A^N(6) - e_A^{N^2}(36)]$$
$$- [e_B^N(4) - e_B^{N^2}(16)] \quad (63)$$

where the partial third-order correction energies e depending on N or N^2 are always negative since they represent correlation corrections. Because of the N^2 dependence, the correction term e^{N^2} raises the absolute energy of AB more than those of the fragments A and B. In this way, the fragments become too stable relative to AB and, accordingly, the dissociation energy ($\Delta E > 0$) becomes too small, which is a typical error when using methods that are not size-extensive. The error can be quantified by calculating a supermolecule ($A \cdots B$), in which the fragments are 10 or more Å apart so that their interaction is negligible. The corresponding reaction energy is given by

$$\Delta E^{(3)} = [e_{AB}^N(10) - e_{AB}^{N^2}(100)] - [e_{A \cdots B}^N(10) - e_{A \cdots B}^{N^2}(100)] \quad (64)$$

i.e., the size-extensivity error cancels, although the method used to calculate ΔE is still not size-extensive. The difference in the energies obtained from equations (63) and (64) gives the size-extensivity error, which can be up to 5 kcal mol^{-1} and larger, depending on the number of electrons involved.

While size-extensivity is a property that can only be proven for very large numbers of electrons of a given atom or molecule, as shown in equation (59), it is much easier to demonstrate its consequences for dissociation or related chemical reactions. In this connection the term size-consistency was coined by Pople.[19] Very often size-consistency and size-extensivity are used interchangeably, however this is not correct because the property of size-consistency is a special case of the more general property of size-extensivity as has nicely been shown by Bartlett.[20]

While Brueckner[2] proved size-extensivity just for the first-orders of RSPT, Goldstone[3] could show in 1957 that all unphysical terms contained in the energy formulas of RSPT cancel through all orders of the perturbation series, i.e., MP PT is size-extensive at all orders. It is possible to express the energy terms of PT in terms of diagrams.[3] Similarly, one can describe operators by diagrams since an operator can always be expressed within a given basis with the help of matrix

elements that in turn are represented by diagrams. Expression and analysis of the PT formulas in terms of diagrams are the subjects of diagrammatic PT. One can show that the energy terms possessing a linear dependence on N are represented by linked diagrams (all parts of the diagram are connected, the diagram is closed and possesses no open, external lines), while the unphysical energy terms with a nonlinear N-dependence are represented by unlinked diagrams (there are separated, disconnected closed parts of the diagram). This observation is summarized in the 'linked diagram theorem' (also called 'linked cluster theorem'), which says that the energy correction at order p, $E^{(p)}$, is fully determined by all linked diagrams since all unlinked diagrams representing unphysical terms cancel.[3]

It is useful to start with the linked diagram theorem and to use only linked diagrams in the perturbation expansion. Clearly, in this way the time-consuming handling of unphysical terms, which will cancel anyway for a size-extensive PT method, can be avoided. This is the strategy of MBPT, which can be considered as that PT which is size-extensive for any number of electrons since it is based on the linked diagram theorem. MP theory is an MBPT with the MP perturbation operator and, therefore, it is reasonable to speak of MBPT(2), MBPT(3), etc., instead of MP2, MP3, etc.

2.5   Position of MP Theory in the Framework of General Perturbation Theory

The central idea of PT is to transform the Schrödinger equation for the exact Hamiltonian defined in Hilbert space into an eigenvalue equation for an effective Hamiltonian $\hat{H}_{eff}$ defined in a model space (reference space). Although the operator $\hat{H}_{eff}$ has its eigenfunction in the model space, its eigenvalue is the exact energy. The advantage of this transformation is that the problem of determining the exact energy can be solved in the smaller model space. This is done by expanding $\hat{H}_{eff}$ in the perturbation operator $\hat{V}$. Different effective Hamiltonians have been suggested and investigated and, accordingly, different perturbation series have been obtained. They differ in every finite order, but are equivalent in the limit of infinite order.
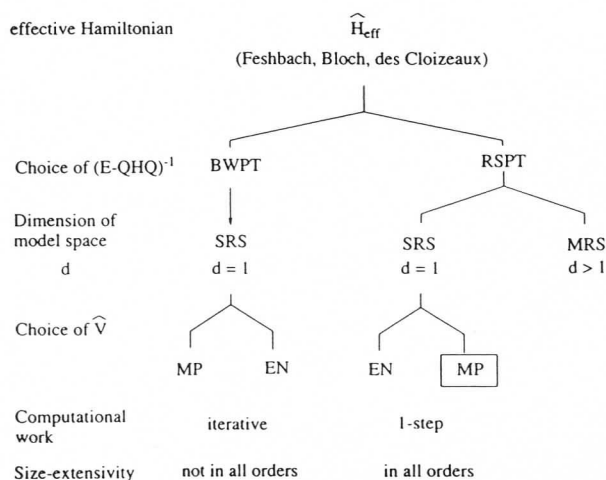
Figure 7 gives an overview of some of the PTs that are used to study the electron correlation problem. Much work has been done with the Feshbach–Löwdin effective Hamiltonian, from which BWPT (sometimes also called Lennard-Jones–Brillouin–Wigner PT) and RSPT are derived. In the simplest case, the model space is spanned by one suitable reference function, which is sufficient by most closed shell systems in their equilibrium geometry. In this case, one speaks of single-reference state (SRS) PT. For problems with a low lying excited state, which is almost degenerate (quasidegenerate) with the ground state, such an approach is not sufficient and one has to span the model space by two (or more) reference wavefunctions. This leads to multireference state (MRS) PT. Contrary to BWPT, both SRS and MRS PT are possible in case of RSPT. Furthermore, RSPT has the advantage of being size-extensive, i.e., the most elegant formulation of RSPT is given by MBPT. Depending on the choice of the perturbation operator one can distinguish between MP, Epstein–Nesbet (EN), and other theories. It has to be noted that the MP perturbation operator can also be applied within the framework of BWPT, or for both SRS and MRS RSPT and, therefore, one should indicate in the general case which approach is taken in connection with MP perturbation operator. The MP theory described here is RS–SRS–MP–PT theory as indicated in Figure 7.

To get a somewhat better understanding of the role of RS–SRS–MP–PT in general and its higher orders in particular, some basic terms of general PT are briefly described.[4,31–33]

2.5.1   Model and Orthogonal Space

The partitioning of the Hilbert space (target space) in model space (reference space, P-space) and orthogonal space (outer space, Q-space) is illustrated in Figure 8.

Projection operators $\hat{P}$ and $\hat{Q}$ which project out of the exact wavefunction Ψ the component parallel to the model function $\Phi_0^{(0)}$ and the correlation function χ, respectively, are given by

$$\hat{P} = |\Phi_0^{(0)}\rangle\langle\Phi_0^{(0)}| \tag{65}$$

$$\hat{Q} = \sum_{s \neq 0} |\Phi_s^{(0)}\rangle\langle\Phi_s^{(0)}| \tag{66}$$

Figure 7   Overview of some of the perturbation theories used in quantum chemistry (see text)
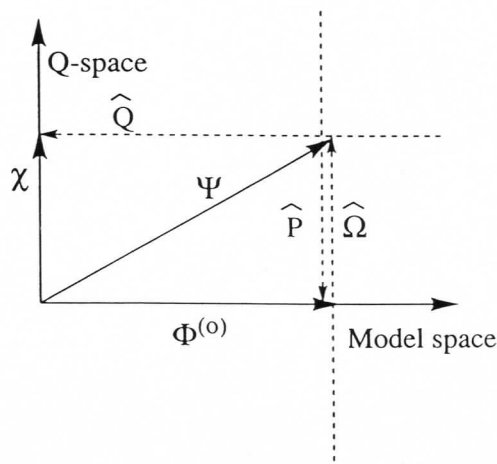

Figure 8   Simple illustration of model space and orthogonal space

with $\hat{P} + \hat{Q} = \hat{I}$. The operator $\hat{\Omega}$, which generates out of the model function $\Phi_0^{(0)}$ the exact wavefunction Ψ, is called the wave operator.

$$\Psi = \hat{\Omega}\Phi_0^{(0)} \qquad (67)$$

When using intermediate normalization, i.e., $\langle\Psi|\Phi_0^{(0)}\rangle = 1$, wave operator $\hat{\Omega}$ and projection operator $\hat{P}$ are 'antiparallel' as indicated in Figure 8. In this case, the following relationship holds:

$$\Psi = (\hat{P} + \hat{Q})\Psi = \hat{P}\Psi + \hat{Q}\Psi = \Phi_0^{(0)} + \chi \qquad (68)$$

i.e., the exact wavefunction is expressed in terms of model and correlation function.

2.5.2 Choice of the Effective Hamiltonian

In SRS-PT, the Feshbach–Löwdin Hamiltonian $\hat{H}_{\text{eff}}$, which is obtained by partitioning the exact Hamiltonian with the help of the projection operators $\hat{P}$ and $\hat{Q}$, is best known.

$$[\hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\hat{Q}(E - \hat{Q}\hat{H}\hat{Q})^{-1}\hat{Q}\hat{H}\hat{P}]|\Phi_0^{(0)}\rangle = \hat{H}_{\text{eff}}|\Phi_0^{(0)}\rangle$$
$$= E|\Phi_0^{(0)}\rangle \qquad (69)$$

Hence, the exact energy is obtained by operating with $\hat{H}_{\text{eff}}$ on the model function $\Phi_0^{(0)}$, which is known, e.g., from an HF calculation.

Depending on how the inverse $(E - \hat{Q}\hat{H}\hat{Q})^{-1}$ is expanded according to

$$(\hat{A} - \hat{B})^{-1} = \sum_{k=0}^{\infty} \hat{A}^{-1}(\hat{B}\hat{A}^{-1})^k \qquad (70)$$

different types of PT result.

2.5.3 Brillouin–Wigner Perturbation Theory (BWPT)

This theory results from the choice $\hat{A} = E - \hat{H}_0$ and $\hat{B} = \hat{V}$:

$$\hat{A} - \hat{B} = E - \hat{H} = E - (\hat{H}_0 + \hat{V}) \qquad (71)$$

Eigenvalue equation and energy take the following form:

$$\left[\hat{P}\hat{H}_0\hat{P} + \hat{P}\hat{V}\hat{P} + \hat{P}\hat{V}\hat{Q}\left[(E - \hat{H}_0)^{-1}\right.\right.$$
$$\left.\left. \times \sum_{k}^{\infty}(\hat{V}(E - \hat{H}_0)^{-1})^k\right]\hat{Q}\hat{V}\hat{P}\right]|\Phi_0^{(0)}\rangle$$
$$= E|\Phi_0^{(0)}\rangle \qquad (72)$$

$$E = E^{(0)} + \langle\Phi_0^{(0)}|\hat{V} + \hat{V}\frac{\hat{Q}}{E - \hat{H}_0}\hat{V} + \cdots|\Phi_0^{(0)}\rangle \qquad (73a)$$

$$= E^{(0)} + \langle 0|\hat{V} + \hat{V}\hat{R}\hat{V} + \hat{V}\hat{R}\hat{V}\hat{R}\hat{V} + \cdots|0\rangle \qquad (73b)$$

$$= E^{(0)} + E^{(1)} + E^{(2)} + \cdots + E^{(p)} + \cdots \qquad (73c)$$

$$= E^{(0)} + \langle 0|\hat{W}|0\rangle \qquad (73d)$$

with

$$E^{(p)} = \langle 0|\hat{V}(\hat{R}\hat{V})^{p-1}|0\rangle, \qquad (74)$$

$|0\rangle = |\Phi_0^{(0)}\rangle$ and the resolvent $\hat{R}$ being defined as

$$\hat{R} = \frac{\hat{Q}}{E - \hat{H}_0} = \sum_{s \neq 0}\frac{|s\rangle\langle s|}{E - E_s} \qquad (75)$$

The operator $\hat{W}$ is the reaction operator, which has the same effect when operating on the reference function as $\hat{V}$ has on Ψ, i.e., it is an effective interaction operator:

$$\hat{V}|\Psi\rangle = \hat{W}|\Phi_0^{(0)}\rangle \qquad (76)$$

Although BWPT looks conceptually simple, it has the disadvantage that the effective Hamiltonian depends in this case on the exact energy, which means that correlation corrections can only be calculated iteratively to get a self-consistent solution. A direct consequence of this is that only SRS PT is possible for BWPT. Another disadvantage is that not all orders of BWPT are size-extensive.

2.5.4 Rayleigh–Schrödinger Perturbation Theory (RSPT)

If one transforms the Brillouin–Wigner operators $\hat{A}$ and $\hat{B}$ by a shift term $E - E^{(0)} = \Delta E = E_{\text{corr}}$, i.e.,

$$\hat{A} - \hat{B} = (E^{(0)} - \hat{H}_0) - (\hat{V} - \Delta E) = E - \hat{H}, \qquad (77)$$

then one will obtain RSPT, which has the advantage of using a (reduced) resolvent $\hat{G}_0$ that depends on the known eigenvalue $E^{(0)}$ rather than the exact energy E:

$$\hat{G}_0 = \frac{\hat{Q}}{E^{(0)} - \hat{H}_0} = \sum_{s \neq 0}\frac{|s\rangle\langle s|}{E^{(0)} - E_s} \qquad (78)$$

The following resolvent formulas result for the corrections to reference function and reference energy:

$$|\Phi^{(1)}\rangle = \hat{G}_0\hat{V}|0\rangle \qquad (79)$$

$$|\Phi^{(2)}\rangle = \hat{G}_0\hat{V}|\Phi^{(1)}\rangle - E^{(1)}\hat{G}_0|\Phi^{(1)}\rangle \qquad (80)$$

$$|\Phi^{(3)}\rangle = \hat{G}_0\hat{V}|\Phi^{(2)}\rangle - E^{(1)}\hat{G}_0|\Phi^{(2)}\rangle - E^{(2)}\hat{G}_0|\Phi^{(1)}\rangle \qquad (81)$$

$$E^{(2)} = \langle 0|\hat{V}|\Phi^{(1)}\rangle = \langle 0|\hat{V}\hat{G}_0\hat{V}|0\rangle = \langle\hat{V}\hat{G}_0\hat{V}\rangle \qquad (82)$$

$$E^{(3)} = \langle 0|\hat{V}|\Phi^{(2)}\rangle = \langle 0|\hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V}|0\rangle - E^{(1)}\langle 0|\hat{V}\hat{G}_0\hat{G}_0\hat{V}|0\rangle$$
$$= \langle 0|\hat{V}\hat{G}_0\overline{V}\hat{G}_0\hat{V}|0\rangle \qquad (83)$$

The two terms for $E^{(3)}$ are the *principal (leading)* and *renormalization term*, respectively, where the renormalization term corresponds to $E^{(1)}\Gamma_3^{(3)}$ of equation (60). It represents an unphysical term depending on N^2 that is canceled by part of the leading term. This is expressed by the $\overline{V}$ notation of equation (83).

The number r of renormalization terms increases with order p:

$\dfrac{(2p-2)!}{p!(p-1)!}$	order p	1	2	3	4	5	6	
	total terms	1	1	2	5	14	42	(84)
	r terms	0	0	1	4	13	41	

For $E^{(4)}$, there are already four renormalization terms beside the principal term:

$$E^{(4)} = \langle 0|\hat{V}|\Phi^{(3)}\rangle \qquad (85)$$

$$= \langle 0|\hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V}|0\rangle - \langle 0|\hat{V}\hat{G}_0\hat{V}\hat{G}_0\langle\hat{V}\rangle\hat{G}_0\hat{V}|0\rangle$$
$$- \langle 0|\hat{V}\hat{G}_0\langle\hat{V}\rangle\hat{G}_0\hat{G}_0\hat{V}|0\rangle - \langle 0|\hat{V}\hat{G}_0\langle\hat{V}\rangle\hat{G}_0\langle\hat{V}\rangle\hat{G}_0\hat{V}|0\rangle$$
$$- \langle 0|\hat{V}\hat{G}_0\langle\hat{V}\hat{G}_0\hat{V}\rangle\hat{G}_0\hat{V}|0\rangle$$

Again, the four renormalization terms represent unphysical contributions depending on N^2 and N^3, which are canceled by parts of the leading term. Using the $\overline{V}$ notation, a simple formula results for $E^{(4)}$, which is normally found in textbooks:

$$E^{(4)} = \langle 0|\hat{V}\hat{G}_0\overline{V}\hat{G}_0\overline{V}\hat{G}_0\hat{V}|0\rangle - \langle 0|\hat{V}\hat{G}_0\langle\hat{V}\hat{G}_0\hat{V}\rangle\hat{G}_0\hat{V}|0\rangle \quad (86a)$$
$$= \langle 0|\hat{V}\hat{G}_0\overline{V}\hat{G}_0\overline{V}\hat{G}_0\hat{V}|0\rangle - E^{(2)}\langle 0|\hat{V}\hat{G}_0\hat{G}_0\hat{V}|0\rangle \quad (86b)$$

Since $\langle\hat{V}\hat{G}_0\hat{V}\rangle$ is the $E^{(2)}$ energy, the second term is proportional to N^2 and is often called 'MP4 renormalization term'. It represents disconnected Q excitations that are canceled by an equivalent term in the Q part of the leading term.

The energy correction $E^{(p)}$ can be written in a simplified form

$$E^{(p)} = \langle 0|\hat{V}(\hat{G}_0\hat{V})^{(p-1)}|0\rangle + \text{renormalization terms}, \quad (87)$$

which in the language of MBPT becomes

$$E^{(p)} = \langle 0|\hat{V}(\hat{G}_0\hat{V})^{(p-1)}|0\rangle_L \quad (88)$$

where L indicates limitation to linked diagrams. Another expression of $E^{(p)}$ in terms of the wave operator at order $p-1$ is also rather useful:

$$E^{(p)} = \langle 0|\hat{V}\hat{\Omega}^{(p-1)}|0\rangle \quad (89)$$

where the wave operator $\hat{\Omega}$ at order p is given by

$$\hat{\Omega}^{(p)} = \hat{G}_0\left[\hat{V}\hat{\Omega}^{(p-1)} - \sum_{k=1}^{p-1} E^{(k)}\hat{\Omega}^{(p-k)}\right] \quad (90)$$

2.6 Higher Orders of MP Perturbation Theory

MP theory is practical up to fourth order. Higher orders become more and more problematic because of the complexity of the energy formulas and the time requirements for doing actual calculations. In recent years, the MP5 and MP6 correlation energies have been worked out and computer programs are available to do MP5[14,15] and MP6 calculations.[18] It is useful to consider the question of what correlation effects are covered at these and even higher orders.

2.6.1 Excitations Included at Order p of MP Theory

Utilizing equations (79)–(86) and the form of the resolvent G_0 (equation 78), one can write down the leading term in a simplified form, which considers just the numerator and abbreviates substitution functions $|\Phi_s^{(0)}\rangle$ by $|S\rangle = |\Phi_i^a\rangle$, $|D\rangle = |\Phi_{ij}^{ab}\rangle$, $|T\rangle = |\Phi_{ijk}^{abc}\rangle$, $|Q\rangle = |\Phi_{ijkl}^{abcd}\rangle$, etc.

$$|\Phi^{(1)}\rangle : \hat{G}_0\hat{V} \quad \langle D|\hat{V}|0\rangle|D\rangle$$

$$|\Phi^{(2)}\rangle : \hat{G}_0\hat{V}\hat{G}_0\hat{V} \quad \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V}|D\rangle \right. \langle D|\hat{V}|0\rangle \left. \middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle$$

$$|\Phi^{(3)}\rangle : \hat{G}_0\hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V} \quad \left\langle \begin{matrix} S \\ D \\ T \\ Q \\ P \\ H \end{matrix} \middle| \hat{V} \middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle$$

$$\times \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V}|D\rangle \right. \langle D|\hat{V}|0\rangle \left. \middle| \begin{matrix} S \\ D \\ T \\ Q \\ P \\ H \end{matrix} \right\rangle \quad (91)$$

$$E^{(2)} : \langle 0|\hat{V}|D\rangle \; \langle D|\hat{V}|0\rangle$$

$$E^{(3)} : \langle 0|\hat{V}|D\rangle \; \langle D|\hat{V}|D\rangle \; \langle D|\hat{V}|0\rangle$$

$$E^{(4)} : \langle 0|\hat{V}|D\rangle \; \langle D|\hat{V}\middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V}|D\rangle \; \langle D|\hat{V}|0\rangle$$

$$E^{(5)} : \langle 0|\hat{V}|D\rangle \; \langle D|\hat{V}\middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V} \middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V}|D\rangle \; \langle D|\hat{V}|0\rangle$$

$$E^{(6)} : \langle 0|\hat{V}|D\rangle \; \langle D|\hat{V}\middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V} \middle| \begin{matrix} S \\ D \\ T \\ Q \\ P \\ H \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \\ P \\ H \end{matrix} \right.$$

$$\times \hat{V}\middle| \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ D \\ T \\ Q \end{matrix} \middle| \hat{V}|D\rangle\langle D|\hat{V}|0\rangle \quad (92)$$

This notation reveals that at even orders new excitations and at the next higher odd order couplings between the new excitations are included. Hence, at MP2 D excitations are included while MP3 covers D, D couplings. At MP4, the new excitations are S, T, Q, which are coupled at MP5. At MP6, P and H, at MP8 septuple and octuple excitations, etc. are added.

2.6.2 Partitioning of MP Energies

It is common custom to partition correlation energies $E^{(p)}$ according to those excitations that appear in the central matrix element(s) of equation (92). Hence the MP4 energy is given by

$$E^{(4)} = E_S^{(4)} + E_D^{(4)} + E_T^{(4)} + E_Q^{(4)} \quad (93)$$

MP5 covers 14 energy terms of the type $E_{AB}^{(5)}$, which because of $E_{AB}^{(5)} = E_{BA}^{(5)}$ can be contracted to nine unique terms. They describe the coupling between S, D, T, and Q excitations.

$$E^{(5)} = E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{ST}^{(5)}$$
$$+ 2E_{DT}^{(5)} + E_{TT}^{(5)} + 2E_{DQ}^{(5)} + 2E_{TQ}^{(5)} + E_{QQ}^{(5)} \quad (94)$$

At MP6, there is a total of 55 terms of the type $E_{ABC}^{(6)}$, of which 36 are unique (see Figure 9).

Table 1 reveals that the number of terms increases exponentially with order p. It also gives the calculational cost and

MP5 (14 / 9)															pt	pq	hq
	SS	SD	ST	DS	DD	DT	DQ	TS	TD	TT	TQ	QD	QT	QQ			
MP4					SDTQPH Space for MP6 (55 / 36)												
S	SSS	SSD	SST	SDS	SDD	SDT	SDQ	STS	STD	STT	STQ						
D	DSS	DSD	DST	DDS	DDD	DDT	DDQ	DTS	DTD	DTT	DTQ	DQD	DQT	DQQ			
T	TSS	TSD	TST	TDS	TDD	TDT	TDQ	TTS	TTD	TTT	TTQ	TQD	TQT	TQQ	QPT	QPQ	QHQ
Q				QDS	QDD	QDT	QDQ	QTS	QTD	QTT	QTQ	QQD	QQT	QQQ	TPT	TPQ	

Figure 9 MP6 terms can be derived from MP4 and MP5 terms considering Slater rules

Table 1 Comparison of MP Methods

MP	Number of total terms	Number of unique terms	Cost (without intermediate arrays)	Most expensive term	Cost (intermediate arrays included)	Most expensive terms
MP2	1	1	M^5		M^5	(ij‖ab)
MP3	1	1	M^6		M^6	b-amplitudes
MP4	4	4	M^8	Q	M^7	T
MP5	14	9	M^{10}	QQ	M^8	TT
MP6	55	36	M^{12}	QHQ	M^9	TQT, QQQ, and TQQ
MP7	221	141	M^{14}	QHHQ	M^{10}	TQQT, etc.
MP8	915	583	M^{16}	QHOHQ	M^{11}	TQS_7QT, etc.

the terms causing the highest cost factor. At MP5 and higher levels of MP PT, the development of an efficient computer program is directly connected with the derivation of suitable intermediate arrays. By defining the right intermediate arrays, the mathematical algorithms for MP5, MP6, etc. can be executed on a computer in a minimum of time. This is indicated in Table 1 for MP5 and MP6, which are reduced from $O(M^{10})$ to $O(M^8)$ and $O(M^{12})$ to $O(M^9)$ procedures by using series of intermediate arrays. One can say that the development of higher order MP correlation methods focuses (a) on how to get rid of unwanted unlinked diagram contributions and (b) on how to set up the right intermediate arrays in the two-electron integral equations.

2.6.3 Strategies for Deriving Higher Orders of MP Theory

There are two different ways of developing MP methods, namely the algebraic approach and the diagrammatic approach. The first is based on an algebraic derivation of matrix elements from general PT formulas. It works well for low-order PT[7,8,11,12] but becomes problematic for higher orders since the number of renormalization terms increases rapidly with order p. The linked diagram theorem[3] shows that it is superfluous to evaluate the renormalization terms since these are all canceled

by appropriate parts of the principal term. Only the linked diagram contributions of the principal term determine the MP correlation energy at order p.

Because of the linked diagram theorem it is of advantage to derive the MP energy formulas by diagrammatic techniques, which immediately identify those terms that really contribute to the correlation energy. Accordingly, diagrammatic derivations of MP3, MP4, and MP5 energy have been worked out, which clearly demonstrate superiority over the algebraic approach.[9,10,13,14] However, the diagrammatic approach has also its disadvantages. This becomes obvious when considering the increase in linked diagrams contributing to the correlation energy. If one uses Brandow diagrams, there are 1, 3, 39, 840, and 28 300 antisymmetrized diagrams for $p = 2, 3, 4, 5$, and 6, respectively. This means that it is hardly possible to explicitly derive the sixth-order correlation energy in terms of linked diagrams.

Therefore, a third approach for developing higher order PT formulas was proposed,[18,24] which is based on a combination of algebraic and diagrammatic techniques and comprises the following steps.

1. The principal term is derived from the general PT formula. 2. Since it is clear that all renormalization terms will be canceled by parts of the principal term, derivation of the

MP energy formula concentrates just on the principal term. This is dissected into various parts according to the excitations involved at the corresponding order of PT. The various parts are written in a cluster operator form. 3. Each part of the principal term characterized by S, D, T, Q, P, H, etc. excitations can be described as representing connected or disconnected energy diagrams according to the nature of the cluster operators appearing in the energy formula. 4. All connected (closed) energy terms correspond to linked diagram contributions and enter the formula for the correlation energy, while the disconnected energy terms represent unlinked diagram contributions that can be discarded. 5. The final cluster operator form of the linked diagram contributions is transformed into two-electron integral formulas. This is facilitated by the fact that all those terms that originally involved disconnected cluster parts can be simplified by using intermediate arrays.[34]

This approach, which avoids both the derivation of superfluous energy contributions typical of the algebraic derivation and a tedious analysis of all linked diagram terms, was successfully applied to deriving the MP6 energy formula.[18,24,34]

Nevertheless, the derivation of 141 unique MP7 terms is too complicated to be done by hand and, therefore, any future developments of higher orders than MP6 will require some form of automated method development strategy based on computer algebra languages.

Of course, there is also the possibility of generating higher orders of MP theory during the iterations of a FCI calculation.[35,36] For smaller atoms and molecules, for which FCI calculations are still possible, this has been done by various authors evaluating MP correlation energies up to order $p = 43$[35] and even $p = 65$.[36] A similar approach is based on CC theory. Independent work by Adamowicz and co-workers[37] and Bartlett and co-workers[38] has led to a derivation of CCSDTQ, which was used to calculate the MP6 correlation energy.[39] For this purpose, a simplified CCSDTQ method corrected through sixth order with a noniterative inclusion of some connected Q contributions was used.

2.7 Convergence of the MP Series

A major problem of MP theory is that convergence of the MP series is not guaranteed. It is well known that the MP series exhibits different convergence behavior for different electronic systems:

1. The MP series can decrease monotonically approaching the FCI correlation energy for $p \to \infty$.
2. There are initial oscillations in the MP series before it converges to the FCI value.
3. The MP series diverges and does not lead to the FCI correlation energy for $p \to \infty$.

Clearly, initial oscillations or divergence of the MP series make it rather problematic to use MP correlation energies in electronic structure investigations. For example, relative energies such as differences between electronic states of an atom or molecule, reaction energies, etc. will become erroneous in the case of erratic convergence behavior.

2.7.1 Convergence Behavior and Electronic Structure

Cremer and He[24] carried out an MP investigation of 29 electronic systems, for which FCI correlation energies are available. They found two types of initial convergence behavior when calculating MP correlation energies up to $E_{MP}^{(6)}$:

1. For one class of electronic systems (class A), monotonic convergence of the MP series is observed.
2. For the second class (class B), convergence is erratic, in particular initial oscillations occur.

These two situations are illustrated in Figure 10, where calculated MP correlation energies are scaled with exact (FCI) correlation energies and averaged over all class A or class B systems calculated.

For class A systems, the correlation energy increases monotonically from 73% (MP2) to 87% (MP3), 91% (MP4), 93% (MP5) and finally 95% (MP6) obviously approaching the FCI limit rather slowly but asymptotically. For class B systems, the MP2 energy already covers 95% of the FCI correlation energy, which could mean that pair correlation is much more important for class B systems than for class A systems or that MP2 exaggerates pair correlation by a considerable amount. Most likely both factors are responsible for the large MP2 correlation energy in the case of class B systems. At MP3 the correlation energy is 0.1% smaller (for class A, 14% larger) than the MP2 correlation energy, which suggests that the MP3 contribution covers not only stabilizing (negative) but also large destabilizing (positive) pair correlation contributions thus correcting partially the exaggeration of pair correlation effects at MP2. MP4 correlation effects lead to another 5% increase of the total correlation energy, which is larger than the corresponding increase calculated for class A systems (4%, Figure 10). Again, one can speculate that S, T, and Q correlation corrections added at MP4 are more important for class B systems than for class A systems. Alternatively, these effects (as well as the pair correlation effects) may be overestimated at MP4. The latter effect seems to be corrected by a relatively large positive MP5 correlation contribution, decreasing the correlation energy by almost 2% at the MP5 level. MP6 correlation contributions increase the absolute value of the correlation energy to 100.6% thus slightly overshooting the FCI correlation energy. This suggests that at MP6 certain correlation effects are still exaggerated, which is confirmed by the fact that for class B
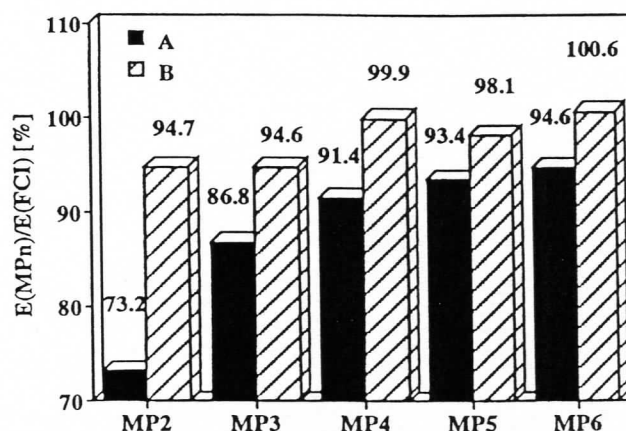

Figure 10 Coverage of the FCI correlation energy at a given order p, separated for classes A and B. Reproduced with permission from D. Cremer and Z. He, *J. Phys. Chem.*, 1996, **100**, 6173–6188. Copyright (1996) American Chemical Society

MP6 correlation energies are on average 6% larger than for class A (4.7% at MP5, Figure 10).[24]

For class A systems the MP series possesses normal convergence behavior. Each higher level of MP theory represents a better approximation to the correct correlation energy, with the MP6 energy presenting the best approximation feasible at the moment when using standard MP procedures. For class B systems, the MP series initially oscillates, which leads to an exaggeration of calculated correlation energies at even orders.

Cremer and He[24] showed that the convergence behavior of the MP series depends on magnitude and sign of the T contributions: 1. A relatively small importance of T contributions is typical of class A systems and seems to guarantee monotonic convergence of the MP series provided higher terms resulting from P, H, etc. excitations are also small and do not play a significant role. 2. A relatively large importance of T contributions, combined with an alternation of the sign of the T contribution $E^{(p)}(T)$ with order p is typical of class B systems and seems to lead to initial oscillations in the MP series.

Analysing S, D, T, Q, P, and H contributions to the low-order MP correlation energies, Cremer and He came to the conclusion that differences in their contributions reflect the fact that the electronic systems of class A and B basically differ with regard to their electron distribution. Class A covers those molecules for which bond electron and lone pairs are well separated and distributed over the whole space of the molecule. For example, in BH, $^1\Sigma^+$, core electron pair, bonding electron pair and lone pair are localized in different parts of the molecule. The same is true in the case of alkanes, boranes, Li or Be compounds, etc. Because the electron pairs of class A systems are well separated, the importance of three-electron correlations and couplings between the correlation modes of the various electron pairs is moderate and the molecular correlation energy is dominated by pair correlation effects.

For class B systems, a clustering of electron pairs in certain regions of an atom or molecule is observed. For example, for electronegative atoms such as F or Ne, seven or eight electrons share the available space in the valence sphere, which is rather limited due to the orbital contracting and charge attracting force of the nucleus. The same is true for electron systems with two or more electron pairs in a confined region of space, as for example for molecules with multiple bonds or molecules with atoms that undergo hypervalent bonding.

If electrons cluster in certain regions of atomic or molecular space, three-electron correlations become important since they provide a simple mechanism to protect the region of an electron pair against occupation by other electrons. Accordingly, T correlation effects can become as large as or even larger than pair correlation effects. Even the connected Q effects at MP6 cannot be neglected since they become important for the correlated movement of many electrons in a confined space encountered for class B systems. Clearly, dynamic electron correlation is more important for class B than class A systems. If the correlation problem has to be handled just by pair correlations at MP2, their effects are exaggerated, in particular since the electrons of a pair are separated without considering that there are other pairs in the same region of space. This leads to relatively large positive corrections at MP3 since coupling effects are quite important for class B systems. At MP5, positive T contributions correct an exaggeration of certain correlation effects at MP4 and since the T effects dominate the fifth-order energy for class B systems, the latter becomes

positive. An exaggeration and correction of certain correlation effects will probably also occur at higher orders of MP PT and, therefore, the MP series oscillates for class B systems.

With an increasing number of electrons, there will be more systems with a clustering of electron pairs in certain regions of atomic or molecular space. Hence, class B systems probably represent the normal case and oscillatory behavior of the MP perturbation series is most likely the rule rather than the exception. Class A systems and monotonic convergence of the MP series, on the other hand, probably represent the exception, which so far has not become clear since the convergence behavior of the MP series can only be investigated for rather small systems.

2.7.2 Improvement of the Convergence Behavior of the MP Series

Different techniques are available to improve the convergence behavior of the MP series and to predict FCI correlation energies by appropriate extrapolation techniques. Best known in this connection is the use of Padé approximants,[40] Feenberg scaling[41] or the application of simple extrapolation formulas.[24,34]

Calculations of the MP series are always terminated at some finite order p neglecting residuals of order $p + 1$. According to Padé,[40] the MP series can be considered as one of the $(p + 1)$ approximants that are given by the ratio of a polynomial of order k to a polynomial of order ℓ, where $k + \ell = p$. The coefficients of these polynomials are determined in such a way that each approximant differs from the energy only by residuals of order $p + 1$. Formulas for approximants $[k, \ell]$ have been worked out and can be found in the literature. They have been applied with varying success.[18]

Another possibility of improving the convergence of the MP series is based on Feenberg scaling of the Hamiltonian operator according to equation (95)[18,41,42]

$$\hat{H} = \frac{1}{1-\eta}\hat{H}_0 + \left(\hat{V} - \frac{\eta}{1-\eta}\hat{H}_0\right) \quad (95a)$$

$$= \tilde{H}_0 + \tilde{V} \quad (95b)$$

where η is a scalar parameter. The scaling of $\hat{H}_0$ leads to a transformation of the MP series where each term is obtained now as a polynomial in η:[41,42]

$$E_\eta^{(p)} = \sum_{k=1}^{p-1} C_{k-1}^{p-2}\eta^{p-k-1}(1-\eta)^k E_{MP}^{(k+1)} \quad (p \geq 2) \quad (96)$$

Feenberg[41] suggested that the value of η is obtained by minimizing the third-order correlation energy $\sum_{k=2}^{3} E_\eta^{(k)} = \Delta E_\eta^{(3)} = E_\eta^{(2)} + E_\eta^{(3)}$, which leads to

$$\eta^{(3)} = 1 - \frac{E_{MP}^{(2)}}{E_{MP}^{(2)} - E_{MP}^{(3)}} \quad (97)$$

Substituting η in equation (96) by $\eta^{(3)}$, the Feenberg energy series $E_\eta^{(p)}$ is obtained. This is called first-order Feenberg scaling since it is based on an improvement of the first-order wavefunction. Cremer and co-workers[18,24] have derived formulas for second-order (minimization of the fifth-order MP energy), third-order and even higher order Feenberg scaling.[43]

They have shown that with second-order Feenberg scaling and the use of MP6 correlation energies accurate predictions of FCI correlation energies are possible even in those cases in which the MP series oscillates at lower orders.

Some success has also been achieved by using extrapolation formulas such as the one suggested by Pople and co-workers[44]

$$\Delta E(\text{extrap, MP4}) = \frac{E_{MP}^{(2)} + E_{MP}^{(3)}}{1 - \frac{E_{MP}^{(4)}}{E_{MP}^{(2)}}}, \quad (98)$$

which is correct up to fourth order and is based on the assumption that $E_{MP}^{(5)}$ bears the same relationship to $E_{MP}^{(3)}$ as $E_{MP}^{(4)}$ does to $E_{MP}^{(2)}$. Even and odd order terms of the MP series are supposed to form a geometrically progressive energy series, where the ratio of successive even order terms is similar to the ratio of successive odd order terms. This, of course, is not justified since the MP series possesses both oscillatory and monotonic convergence behavior.

Therefore, extensions of formula (98) for both class A and class B systems have been suggested by Cremer and He:[24]

$$\Delta E^{(A)}(\text{extrap, MP6}) = \sum_{k=2}^{4} E_{MP}^{(k)} + \frac{E_{MP}^{(5)}}{1 - \frac{E_{MP}^{(6)}}{E_{MP}^{(5)}}} \quad (99)$$

$$\Delta E^{(B)}(\text{extrap, MP6}) = E_{MP}^{(2)} + E_{MP}^{(3)} + (E_{MP}^{(4)} + E_{MP}^{(5)})e^{\frac{E_{MP}^{(6)}}{E_{MP}^{(4)}}} \quad (100)$$

Actually, both $1/(1-x)$ and e^x lead to similar series. However, in the exponential series higher powers k of x are scaled down by prefactors $1/k!$. In this way, higher excitation effects are reduced in equation (100). Use of these extrapolation formulas leads to FCI estimates only slightly inferior to those obtained by Feenberg scaling.

2.7.3 Divergent Behavior of the MP Series

The basic assumption of SRS MP theory based on an HF reference wavefunction (used in more than 90% of all investigations) is that the wavefunction is dominated by just one single configuration. This assumption, of course, will no longer be valid if systems with rather low lying excited states are considered such as the Be atom for which the first excited ^1S state resulting from the $1s^2 2p^2$ configuration is not far above the ^1S, $1s^2 2s^2$ ground state energy. In this case, the energy spectrum of model space and outer space (Q-space) are no longer well separated (they may even overlap). When varying the perturbation parameter λ (which in the general case is a complex number) from 0 to 1, a state from Q-space can intrude the model space and cross with the state of the model space. For states of the same symmetry this leads to an avoided crossing situation. It has been shown[45] that if the avoided crossing occurs for $\lambda < 1$, the MP series becomes divergent. Various procedures have been suggested to deal with the intruder state problem,[32,33,45] of which the simplest is an enlargement of the model space by including the intruder state.

Recent FCI investigations by Christiansen and co-workers[46] have provided evidence that the MP series can diverge even in the case of single reference dominated systems when using extended basis sets. The authors investigated the Ne atom and found for $\lambda = -0.82$ an avoided crossing ('back door intruder state') between the HF dominated state and a state dominated by P and higher excitations. Hence, a degeneracy for $|\lambda| \leq 1$ is encountered and divergent behavior of the MP series results. However, the MP series becomes convergent when a smaller basis set is used. This observation is rather alarming for two reasons. First, there seems to be no guarantee that a single-reference dominated electron system with high lying excited states is also a system for which the MP series converges. Since the intruder state is relatively high lying, the usual remedy for an intruder state problem, namely including the intruder state in the model space, will not work. Secondly, the use of an extended basis set is actually the prerequisite for the accurate calculation of molecular properties using MP theory and, therefore, the use of extended basis sets cannot be avoided.

On the other hand, one has to realize that divergent behavior of the MP series was observed in the Ne example at MP15, i.e., at an order where 80% of all excitations are of the P or even higher type. Hence, divergence in this case does not indicate that all the lower orders of MP theory are physically not reasonable and cannot be used for describing chemical reactions and calculating molecular properties. Even estimates of the FCI energy based on lower order MP energies should be reasonable despite the fact that infinite-order MP theory will not reproduce the FCI result in a case of divergence.

3 APPLICATIONS

3.1 Available MP Methods

The routine application of MP methods as well as any other correlation corrected *ab initio* method depends on two prerequisites:

1. The method in question has to be developed for any useful reference wavefunction.
2. Analytical energy derivatives have to be available.

MP methods have been developed for both *spin-restricted HF (RHF)*, *spin-unrestricted HF (UHF)*, and *restricted open-shell HF (ROHF)* wavefunctions[47,48] to investigate both closed- and open-shell systems (see Table 2). For the calculation of electron systems with multireference character such as biradicals various multireference state (MRS) MP methods have been developed (Table 2).[50-52] All these methods describe atoms, molecules, and reaction systems in the gas phase. However, many chemical reactions take place in solution phases. For this purpose, MP methods are available that start from a solvent corrected wavefunction where mostly polarizable continuum models are used[53,54] (see *Self-consistent Reaction Field Methods*).

Quantum mechanically, a one-electron property is defined as the expectation value of the corresponding operator expressed with the help of wavefunction Ψ or because this is mostly not available with the approximate wavefunction Φ. In the case of MP theory, this leads to problems because an MP method at given order p does not possess a well-defined wavefunction. According to the Wigner theorem (see equation 23), the function $\Phi^{(p)}$ is associated with both $E^{(2p)}$ and $E^{(2p+1)}$. However, this does not represent a real disadvantage of MP theory since one-electron properties can be expressed as response properties once analytical energy derivatives are

Table 2 Available MP Methods (Numbers Refer to References)

	MP2	MP3	MP4	MP5	MP6
1 RHF/UHF	6,7	6,8	9–12	13–15	18,39
	MP2: direct (61–63) and parallel implementations (66)				
a) PUMP	49	49	49		
b) analytical 1st deriv.	55	16	16,17		
c) analytical 2nd deriv.	56	57	57		
d) GIAO	58	59	59,60		
2 ROHF	47,48	47	47		
	MP2: direct versions and analytical derivatives available				
3 GVB	50	51	51		
4 Multireference	52				
5 Solvent methods	various versions are available for MP2, MP3, MP4, see e.g., 53				

available.[23] Most important are the first derivatives with regard to the position coordinates of the nuclei of a molecule. They determine the forces exerted on the nuclei in a nonequilibrium situation. Since all forces have to vanish at the *stationary points* of the *potential energy surface* (the *energy gradient* vanishes for minima and saddle points), routine calculation of the forces is a prerequisite for calculating equilibrium geometries and transition state geometries (see *Geometry Optimization: 1* and *Gradient Theory*). Calculation of the forces requires the evaluation of the response density matrix, which covers orbital relaxation effects caused by the perturbation λ. With the help of the MP response density matrix evaluated at order p, any one-electron property such as electron density distribution, dipole moment, higher multipole moments, etc. can be calculated.

Second derivatives of the energy are needed to calculate second-order properties such as harmonic force constants, electric polarizabilities, infrared intensities or nuclear magnetic resonance (NMR) shieldings. Second derivatives of the energy with regard to nuclear displacement coordinates are required to calculate vibrational frequencies and force constants in the harmonic approximation. Harmonic infrared intensities can be determined as derivatives of the dipole moment components with regard to nuclear displacement coordinates or, considering that the dipole moment components themselves can be viewed as derivatives of the energy with regard to the electric field components, the infrared intensities are evaluated as second derivatives of the energy with regard to the components of the electric field and nuclear displacement coordinates. Second derivatives with regard to the electric field are associated with the electric *polarizability* tensor. Second derivatives with regard to the nuclear magnetic moment and the magnetic field determine NMR shieldings and, by this, NMR chemical shifts. For the calculation of NMR shieldings and chemical shifts with finite basis sets, results must be made independent of the choice of origin of the coordinate system ('gauge origin' problem), which can be achieved by using basis functions with individual local gauge origin (GIAOs: 'gauge including atomic orbitals').

As is indicated in Table 3, almost all molecular properties that can be evaluated at the HF level can also be determined at the MP2 level since analytical first and second energy derivatives are available.[55] This applies to RHF, UHF, and ROHF wavefunctions, however not to GVB or other multireference wavefunctions. Analytical first derivatives have

Table 3 Molecular Properties that can be Calculated with MP Methods

	MP2	MP3	MP4	MP5	MP6
Energy	y	y	y	y	y
Geometry	y, a	y, a	y, a	y, n	y, n
Electron density	y	y	y		
Dipole moment and higher moments	y	y	y		
Frequencies	y, a	y, a	y, a	y, n	y, n
Polarizabilities	y	y	y		
Infrared intensities	y	y	y		
NMR chemical shifts	y	y	y		

y: yes; a: analytically; n: numerically

also been worked out for MP3 and MP4[16,17] while so far no attempts have been made to extend derivative techniques to MP5 or MP6. In the latter cases, geometry optimizations are made possible by using numerical techniques to calculate forces and the energy gradient. Analytical second derivatives for MP2 have been used for some time.[56] Recently, Gauss and Stanton[57] have worked out second derivatives for MP3 and MP4, however, these methods are not generally available so far and, therefore, MP3 and MP4 frequencies are still calculated with numerical techniques. Gauss has developed GIAO-MP2,[58] GIAO-MP3, and GIAO-MP4[59,60] so that NMR shieldings and chemical shifts can be calculated, which in view of the importance of NMR chemical shifts in chemistry has considerably extended the range of applicability of MP methods to chemical problems (see *NMR Chemical Shift Computation: Ab Initio* and *NMR Chemical Shift Computation: Structural Applications*).

There are also some technical considerations which determine the usefulness of a correlation corrected method. One of these is the availability of direct methods that largely avoid the storage of two-electron integrals and, therefore, extend the applicability of a correlation corrected method to large molecules. Direct methods have been worked out for MP2[61–63] and GIAO-MP2[64] that make calculations with 1000 basis functions and more possible. With the advent of parallel computers, there is also work to set up MP methods in the most efficient way for this new hardware and to increase the range of applicability for MP methods. Promising work is with the 'resolution of the identity' MP2 (RI-MP2) method,[65] which requires a fitting basis to replace the computationally expensive

four-center two-electron repulsion integrals by combinations of two- and three-center integrals. In a test calculation with 461 basis functions and a fitting basis of 1227 primitive functions the computing time of a normal MP2 calculation could be reduced by 95% from 30 000 to 1500 seconds with the help of a parallel implementation of RI-MP2.[66]

3.2   Basis Sets for MP Calculations

The selection of an appropriate basis set for a given method, a given property, and a given molecule is an art by itself. Nevertheless, there are some basic rules that should be considered when carrying out correlation corrected calculations in general and MP calculations in particular.

1. A relatively large basis set has to be used for a reasonable description of correlation effects. *Minimal basis sets* or split valence basis sets are not suitable for carrying out MP or other correlation corrected *ab initio* calculations. One needs at least a DZ + P(VDZ + P) or TZ + 2P basis set to get reasonable energies, geometries and first-order properties. For second-order properties, TZ + 2P or QZ + 3P basis sets are needed. (DZ + P = *double-zeta* plus polarization; VDZ = valence DZ; TZ = triple-zeta; QZ = quadruple-zeta.)

2. Correlation consistent basis sets (see *Basis Sets: Correlation Consistent Sets*), which have been optimized at a correlation corrected level such as CISD, should be used rather than basis sets optimized at the HF level.

3. Any time one has to reduce a basis set selected along the lines of points 1 and 2 because of computational considerations, one should have a sufficient amount of reference data available, which provide a detailed insight into errors caused by the basis set reduction.

4. Different properties of a molecule depend on the molecular charge distribution in different ways. There are properties that depend more on the charge distribution close to the nucleus (e.g., electric field gradients), and others that depend more on diffuse charge distribution relatively far away from the nuclear framework (e.g., dispersion forces, infrared intensities). Property optimized basis sets exploit these relationships by just describing the more important parts of the density distribution correctly and reducing in this way the size of the basis set. This leads to efficient basis sets, which of course are no longer generally applicable and, in addition, have to be checked considering point 3.

Apart from these general considerations, the applicability of each basis set has to be seen against the background of results obtained for a related well-understood problem with the same correlation method and the same basis set. Accordingly, it is often better to use a well-documented basis set, which in terms of number and type of basis functions included may not be the best for the problem in question, rather than a more extended basis set, which has to be tested first since it has hardly been used before in the literature.

3.3   Which MP Method Covers What Correlation Effects?

As mentioned before, MP2 includes all D excitations and, accordingly, describes the most important pair correlation

effects. There is no coupling between the D excitations at second order and, therefore, each pair correlation correction is determined as if no other electron pairs are present in the molecule. This leads to an overestimation of pair correlation effects. At the MP3 level of theory, couplings between D excitations are included and an exaggeration of pair correlation effects at MP2 is partially corrected.

In Figure 11, the various correlation contributions at MP4 and MP5 are given in the form of bar diagrams ('MP spectra')[24,34] separated for class A (systems with well-separated electron pairs) and class B electronic systems (systems with electron clustering) where each contribution is given as a fraction of the total MP4 or MP5 correlation contribution and averaged over all electronic systems of a given class. At MP4, the S, D, and T correlation contributions are always negative while the Q correlation effects are always positive. Pair correlation is dominant for class A systems. Orbital relaxation (S excitations) and three-electron correlation effects (T
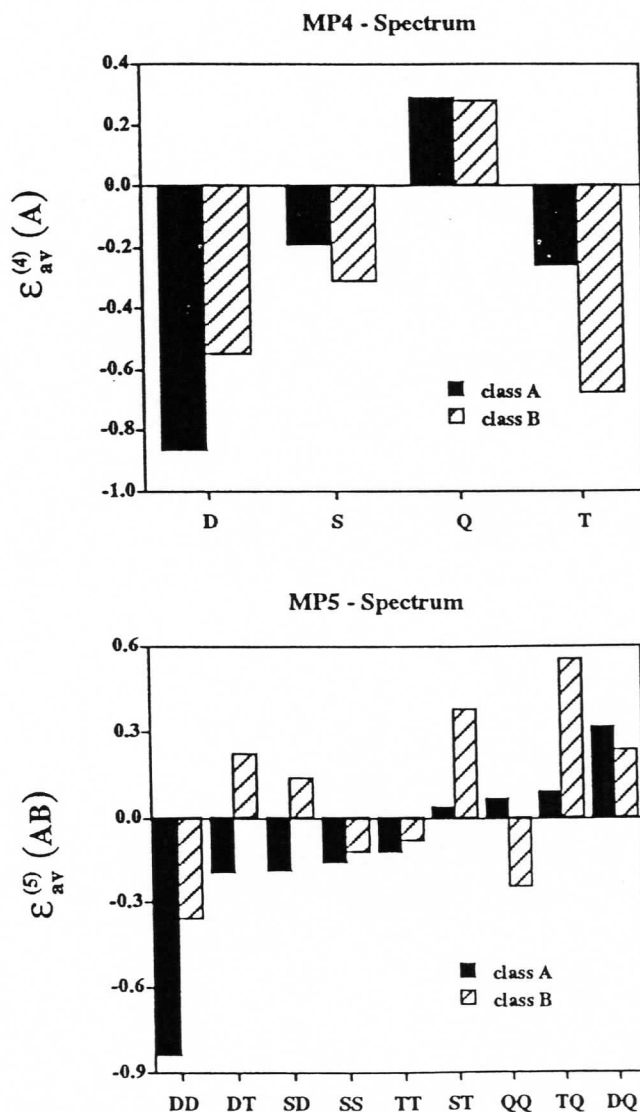

Figure 11   MP4 and MP5 spectra for class A and class B molecules. Reproduced with permission from D. Cremer and Z. He, *J. Phys. Chem.*, 1996, **100**, 6173–6188. Copyright (1996) American Chemical Society

excitations) are clearly smaller. The (connected) T excitations are generally smaller than pair correlation effects. However, since each electron pair can correlate with any of the other electrons in a three-electron situation, the number of three-electron combinations is much larger than the number of core, bond, and lone pairs. Because of their large number, T effects lead to sizeable contributions to the correlation energy. The T effects can even become rather large if electron pairs are packed closely together in a particular area of a molecule as in the case of class B systems. For the latter, three-electron correlation becomes as important as pair correlation and even orbital relaxation becomes larger. Q effects at MP4 correspond to disconnected Q, i.e., they do not describe the correlation of four electrons (which would be rather small) but the simultaneous correlation of two electron pairs. For both class A and class B systems, Q contributions are positive since they cover a considerable part of the pair–pair couplings that correct for an exaggeration of pair correlation effects.

For class A systems, MP4(SDQ), which is cheaper than full MP4 (MP4 scales with $O(M^7)$, MP4(SDQ) with $O(M^6)$), is sufficient for a reasonable description while class B systems definitely require full MP4 calculations. This becomes even more obvious when one considers that T effects are larger in this case than the sum of S, D, and Q contributions since there is some cancellation among the latter terms.

T and Q correlation effects can be exaggerated at MP4 for the same reason pair correlation effects are exaggerated at MP2. MP5 introduces the coupling between S, D, T, and

Q excitations in form of SS, SD, ST, DD, DT, DQ, TT, TQ, and QQ correlation effects and, therefore, MP5 gives a better account of (connected) T and (disconnected) Q effects. The MP5 spectrum in the case of class A systems reveals that there is a dominance of the DD pair correlation effects corrected somewhat by positive DQ and QQ contributions while the T terms are all relatively small. The QQ term still represents a disconnected term, i.e., it involves four-electron pairs rather than two correlating four-electron ensembles. For class B systems, positive TQ, ST, and DT terms lead to an overall positive MP5 contribution. One can directly understand that the TQ term is positive because it describes the coupling between three-electron effects with pair–pair correlation. Three-electron correlation effectively helps to correct pair correlation and to keep different pairs apart where this effect is tested against the pair–pair couplings described by the Q excitations. The TQ contribution will become positive if pair correlation effects are overestimated at lower orders. Hence, at MP5 the correlation energy of class B systems is predominantly corrected with regard to an exaggeration of correlation effects that occurs at a lower MP level.[24,34]

At MP6, the correlation effects, which are newly introduced, are disconnected P and disconnected H excitations in the form of couplings between pair and three-electron correlation effects (P) and couplings between three correlating electron pairs (H). In addition, there are (connected) four-electron correlation effects. For a long time, these were considered as being rather unimportant, however MP6 calculations for
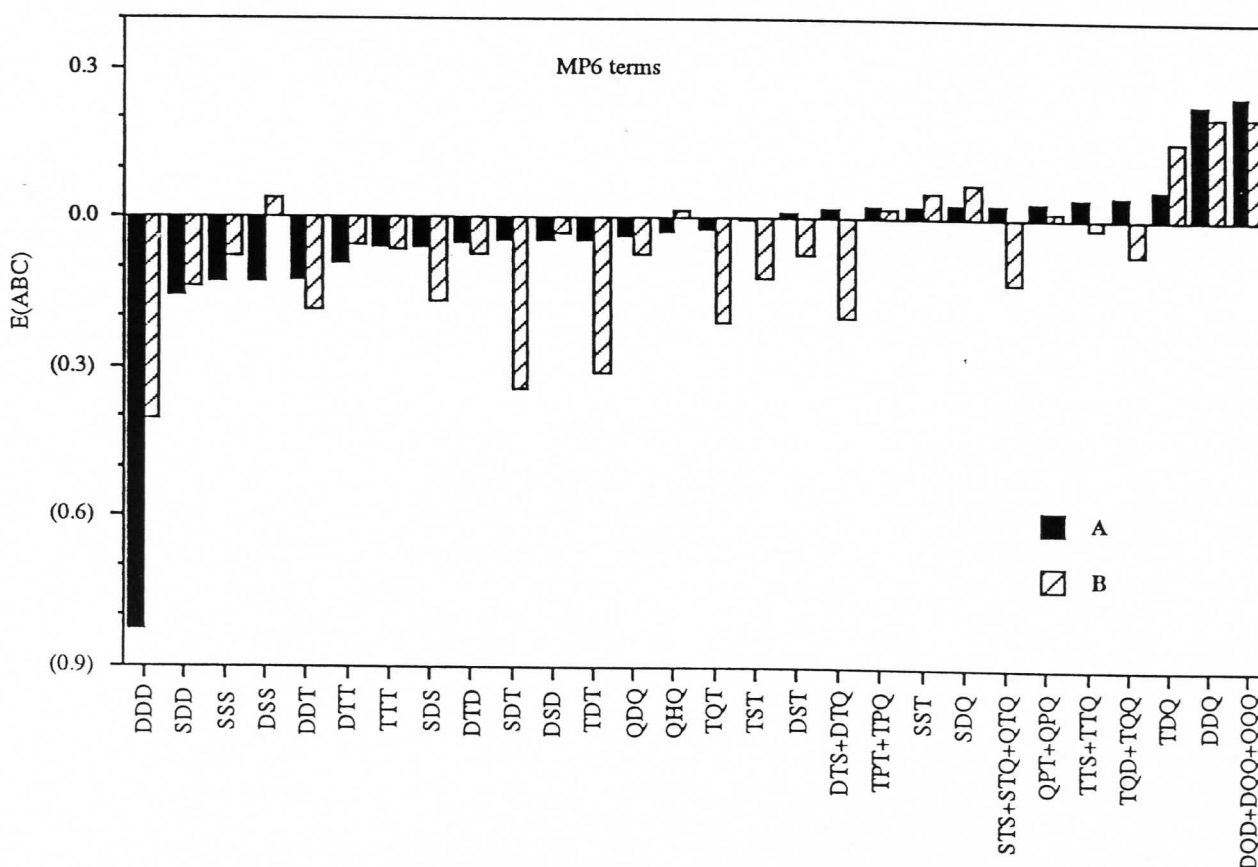

Figure 12 MP6 spectra for class A and class B molecules. Reproduced with permission from D. Cremer and Z. He, *J. Phys. Chem.*, 1996, **100**, 6173–6188. Copyright (1996) American Chemical Society

class B systems reveal that four-electron correlation effects become important in the case of electron clustering.[24,34] Apart from this, MP6 correlation effects are similar to MP5 correlation effects. For class A systems, pair effects dominate while for class B systems three- and four-electron correlation effects are of similar importance to pair correlation effects as is revealed by the corresponding MP6 spectra (Figure 12).

At MP7, the coupling between connected Q effects, disconnected P and H effects is included. At MP8, MP10, connected P, H, etc. are included and at the corresponding odd orders (MP9, MP11, etc.) a coupling between these effects. One can compare MP PT with a car that is fueled at even orders with new correlation effects but slowed down at odd orders by a coupling between these effects. This basic nature of MP theory has been brought into connection with the erratic convergence of the MP series and oscillations in the values of calculated molecular properties dependent upon the order p.[23,24,34]

3.4 MP Equilibrium Geometries

Since the mid-1970s, a vast amount of MP data on molecular properties has been collected. Several detailed summaries have been given in the literature[23,67,68] and, therefore, just some general aspects of MP properties are discussed here.

It is a general observation that *bond lengths* calculated at the HF level decrease with increasing size of the basis set. The same observation can be made at the MP2 level, except that all MP2 bond lengths are shifted to larger values (see Table 4). This is a result of the inclusion of left–right pair correlation effects at MP2. In the D excited configurations, orbitals are occupied that possess a nodal surface in the bonding region and, by this, reduce the bond density thus leading to a lengthening of the bond. Angular and in–out correlation effects contribute to this effect since they both lead to a transfer of negative charge from the regions closer to the nuclei (core and σ region) to outer regions. In this way the nuclei are deshielded and nuclear repulsion is increased, again causing a lengthening of the bond distance. These effects help to correct the well-known underestimation of bond lengths at the HF level provided the basis set is sufficiently large. HF calculations with small basis sets often lead to rather long bond distances and, then, MP2 increases differences between theory and experiment as is shown for the case of the H_2O

molecule in Table 4. However, as noted previously, MP or any other correlation corrected calculations with minimal or split valence basis sets are a waste of computer time since the use of an extended basis set is the first prerequisite of correlation studies. The dependence on the size of the basis set can be used to select that basis which due to a fortuitous cancelation of basis set truncation and correlation errors exactly reproduces the experimental bond length; of course it has always to be checked whether an experimental equilibrium (r_e) value is known at all.

There are also cases where pair correlation effects reduce rather than lengthen an interaction distance. This happens, e.g., in the case of nonclassical bonding, with the bonding in donor–acceptor complexes, H bonding or situations where electropositive elements participate in bonding. In all these cases, two electrons are excited into orbitals with bonding rather than antibonding character, which leads to an accumulation of negative charge in the bond region and, as a consequence, to shorter interaction distances. It also plays a role in the relatively strong charge transfer from a more electropositive to a more electronegative atom being reduced at the MP2 level, thus leading to a stronger shielding of the electropositive atom and a shorter bond length. Very strong effects are obtained in the case of donor–acceptor complexes. For example, the HF/6-31G(d) value for the BC distance in H_3BCO is 1.630 Å (compared to an experimental value of 1.540 Å), which is corrected at the MP2/6-31G(d) level to 1.55 Å due to the mixing in of bonding BC orbitals.[67]

One might expect that with increasing order of MP the lengthening of calculated bond distances continues, and that the FCI value is reproduced due to an asymptotic approach to both correlation and basis set limit, i.e., the superposition of bond lengthening due to the addition of higher and higher correlation effects and bond shortening due to extending the basis set more and more should lead to the correct r_e value. However, in practice this happens only in the minority of cases. Mostly, one observes oscillations in calculated geometrical parameters, which is demonstrated for carbonyl oxide, CH_2OO (1).[69]

In Table 5, MP bond lengths and bond angles of the heavy atom framework of CH_2OO are given together with the dipole moment where the latter provides an insight into the calculated charge distribution. HF and MP2 give two contradicting descriptions of the geometry of CH_2OO. The HF geometry corresponds to an aldehyde oxide that is best described by resonance formulas **1a** and **1b** (Scheme 1).

Table 4 HF and MP Geometries of Water

	HF		MP2	
Basis	R(OH) (Å)	HOH (deg)	R(OH) (Å)	HOH (deg)
STO-3G	0.990	100.0	1.014	97.2
3-21G	0.967	107.7	0.989	105.2
4-31G	0.951	111.2	0.976	109.1
6-31G(d)	0.947	105.5	0.969	104.1
DZ+P	0.944	106.6	0.963	104.4
6-31G(d,p)	0.943	105.9	0.961	104.1
6-311++G(d,p)	0.941	106.2	0.959	103.5
TZ+2P	0.941	106.1	0.958	104.2
Experimental			0.958	104.5

Table 5 MP Geometry and Dipole Moment μ (debye) of Carbonyl Oxide

Method/Basis	R(OO) (Å)	R(CO) (Å)	∠COO (deg)	μ (D)
HF/6-31G(d,p)	1.482	1.201	114.5	5.46
MP2/6-31G(d,p)	1.293	1.297	120.4	3.34
MP2/DZ+P	1.285	1.300	120.8	3.36
MP2/TZ+2P	1.297	1.282	119.8	3.70
MP3/6-31G(d,p)	1.338	1.252	118.7	4.44
MP4(SDQ)/6-31G(d,p)	1.329	1.274	119.2	4.04
MP4(SDTQ)/6-31G(d,p)	1.306	1.314	119.8	3.25
CCSD(T)/TZ+2P	1.355	1.276	117.0	3.97

(1a)   **(1b)**   **(1c)**
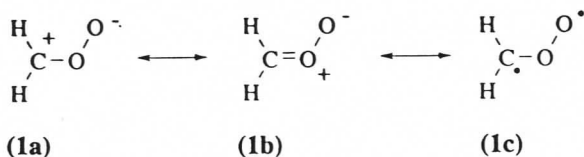
Scheme 1

The CO double bond of formaldehyde is largely maintained ($R(C=O) = 1.20$ Å) and the OO bond resembles a slightly elongated peroxide single bond ($r(O-O) = 1.45$ Å). The MP2 geometry, on the other hand, corresponds better to the biradical structure **1c** with two single π-electrons being formally localized at C and the terminal O atom while a π-electron pair is positioned at the central O atom. In this way, both the CO and the OO bond formally get about 50% π-bond character. Since typical values for CO and OO single and double bonds are: $R(CO) = 1.43, 1.20$ Å, $R(OO) = 1.45, 1.21$ Å, one can expect bond lengths of about 1.3 Å for both CO and OO in the case of **1c**. Exactly, this prediction is confirmed by the calculated MP2 geometry of **1** (see Table 5).[69]

Since the MP2 description of **1** was the best description available for some time, there was a tendency to attribute biradical rather than zwitterionic character to **1**. However, both the HF and the MP2 description are incorrect because HF overestimates the importance of polar and ionic structures while MP2 does the same with regard to biradical structures due to an exaggeration of left–right correlation. This is nicely reflected by the calculated dipole moment, which is rather large at the HF level (5.5 debye, Table 5) and relatively small at MP2 (3.3 debye, Table 1). MP3 slightly shifts the geometry in the direction of the HF values, thus indicating that pair correlation effects are exaggerated at MP2. But this trend is again reversed at the MP4 level where in particular the T contributions have a rather strong effect (Table 5). They lead to a considerable lengthening of the CO bond, which becomes longer than the OO bond. Comparison with CCSD(T) results,[69] which should be close to true values, reveals that MP4 exaggerates T effects and that the molecule possesses more zwitterionic character than suggested by MP4. Hence, in such a case none of the commonly used MP methods provides a satisfactory geometry even though results are qualitatively much better than HF results.

Trends in calculated MP bond angles couple with trends in calculated bond lengths as is shown for the HOH and the COO angle in Tables 4 and 5. Normally, larger bond lengths imply smaller bond angles, which can also be explained by the electrostatic model of charge distribution used to analyze trends in calculated bond lengths. For example, for H_2O or any other AH_n molecule, accumulation of charge in the nuclear region of A is accompanied by a short bond length. It also leads to relatively large positive charges at the H atoms. As a consequence, Coulomb repulsion between the H atoms becomes large, thus forcing the HAH angle to widen. This trend is interrupted when polarization functions are added to the basis. They allow for smaller bond angles and also lead to a better distribution of negative charge in the nonbonding region. Hence, the addition of polarization functions leads to both shorter bond lengths and smaller bond angles at the MP level. In general, changes in bond angles and even more in dihedral angles, dependent upon the order of MP PT and

the basis set applied, are much smaller than trends in bond lengths. For equilibrium geometries of molecules with normal single bonding a MP2 description is already rather reliable. Molecules with multiple, nonclassical or hypervalent bonding should be better described at the MP4 level since the T effects are important for a reasonable description of electron clustering as in the bonding region.

3.5 MP Energies

In chemistry, only relative energies are of relevance and, therefore, one might expect that correlation effects largely cancel out in energy differences needed to describe chemical reactions or individual molecules. Under certain circumstances this is the case while in other cases MP correlation corrections add a large correction to HF energy differences. One can distinguish between the following situations:

1. The energies of chemical species are compared that differ in the number of paired electrons. This happens in dissociation reactions, ionization or electron attachment processes, excitation processes, etc. In general, when radicals or biradicals are compared with closed-shell systems correlation effects are important. The larger the difference in the number of paired electrons the larger the correlation effect will be (e.g., $N \equiv N \rightarrow N(^4S) + N(^4S)$, three electron pairs are uncoupled). Of course, in all these cases, both dynamic and nondynamic correlation effects have to be considered while low-order MP methods can only cover dynamic correlation effects.

2. If the number of electron pairs for two chemical species (e.g., reactant and product) is equal, it will matter whether the space (MO) occupied by each electron pair is different in the two systems, e.g., expanded in one case, contracted in the other, delocalized or localized, more or less spherical, more or less crowded due to the vicinity of other electron pairs, etc. Significant differences in the distribution of electron pairs occur if one compares a TS of a pericyclic reaction with reactants or products (reaction barrier), a molecule with classical bonding with an isomer possessing nonclassical (delocalized) bonding (molecular stability), a donor–acceptor complex with its separated parts (complex binding energy), isoelectronic species such as carbocations and boranes, etc. In all these cases, dynamic electron correlation should play an important role.

3. With increasing number of electrons, differences in pair correlation energies and pair–pair couplings add up to a significant effect even though individual differences may be rather small. In these cases, it is no longer easy to predict whether correlation corrections should be similar or different for the species considered. Therefore, the rule of thumb is that molecules made up by electron rich atoms of the second or even higher periods should be calculated including at least pair correlation effects.

4. There is a small class of processes for which correlation effects on relative energies should cancel so that an HF description may be sufficient. These are conformational processes and electron pair conserving reactions such as *isodesmic reactions* or *homodesmotic reactions* involving just first row atoms provided effects described under point 2 are not significant.

Table 6 Comparison of MP Energy Differences (kcal mol^{-1}) Relative to the Corresponding FCI Value

		MP2	MP3	MP4	MP5	MP6	FCI
BH	$1.5r_e - r_e$	4.7	2.9	1.4	0.5	0.1	32.4
	$2.0r_e - r_e$	15.2	10.1	5.2	2.2	0.5	62.9
FH	$1.5r_e - r_e$	1.8	4.0	0.6	1.2	−0.1	56.8
	$2.0r_e - r_e$	10.4	13.7	3.4	4.8	−0.3	106.6
CH$_2$	$^1A_1 - {}^3B_1$	6.7	3.2	1.9	1.4	1.0	12.0

Clearly, correlation effects are large for the energy changes in a homolytic dissociation process (*homolytic bond cleavage*), in which one or more electron pairs are split. In Table 6, the energy increase is considered when the equilibrium bond length r_e of BH and FH, respectively, is extended to $1.5r_e$ and $2.0r_e$.[18] In each case, the FCI value is used as a reference and just the error in calculated MP energies is given. Clearly, low-order MP theory (MP2, MP3) is unable to describe this situation and errors become the larger the more the bond is stretched. In the case of BH, MP energies smoothly converge to the FCI value with increasing order p, while they oscillate in the case of FH. Reliable values (compared to the FCI result) are only provided by MP6 where for FH a slight overshooting of the FCI value can be observed. Results can be improved by using spin-projected UMP (PUMP, Table 2; see *Spin Contamination*). The singlet–triplet splitting of methylene is also sensitive to correlation effects since the singlet state possesses one electron pair more than the triplet state. Calculated MP splittings decrease only slowly from MP2 (error: 56%) to the FCI value (Table 6).[18]

It is well known that HF dissociation energies D_e strongly underestimate true values. For A–H bonds of AH$_n$ molecules, errors are already as large as 50 kcal mol^{-1} (Table 7).[67] MP2 reduces these errors to ≤ 10 kcal mol^{-1}. Additional, though rather small improvements of calculated D_e values are obtained at the MP3 and MP4 level so that residual errors are still in the 10 kcal mol^{-1} region (Table 7). This observation led Pople and co-workers[70] to add empirical corrections to calculated MP energy differences in all those cases in which the number of electron pairs is changed. They developed the idea that high-level MP correlation corrections and the effects of polarization or *diffuse functions* can be treated separately and combined with MP energy differences in an additive manner. This idea is the basis of the G methods (see *G2 Theory*), which lead to dissociation energies, ionization potentials, and electron affinities of chemical accuracy (errors: ≤ 1 kcal mol^{-1}).

Large reorganizations of electron pairs occur in the TS (relative to the electronic structure of reactants or products) of many chemical reactions. Therefore, the calculation of reliable reaction barriers often depends on a proper assessment of electron correlation effects. As an example, calculated MP reaction barriers for three pericyclic reactions, namely for the 1,5 sigmatropic H shift in (Z)-1,3-pentadiene, the electrocyclic ring opening of cyclobutene to butadiene, and the Diels–Alder reaction between butadiene and ethene, are given in Table 8.[71] For the three reactions, HF exaggerates the barrier by 10–20 kcal mol^{-1}. Pair correlation as described at the MP2 level leads to a major improvement of reaction barriers and in the case of the Diels–Alder reaction the experimental barrier is now underestimated by 7 kcal mol^{-1}. MP3 increases barriers in the direction of the HF values, thus accidentally approaching the experimental value in the case of the Diels–Alder reaction. At the MP4(SDQ) level, changes are relatively small compared to MP3 barriers. The best agreement between theory and experiment is obtained when T effects are included at the MP4 level. MP4(SDTQ) barriers differ from experimental values by ≤ 3 kcal mol^{-1} where it has to be considered that uncertainties in experimental values are as large as 2 kcal mol^{-1}.[71]

The observations made for pericyclic reactions are valid for many other reactions as well. Reliable TS energies can only be obtained at the MP4 level if T effects are included. However, a reasonable guess is already obtained at the MP2 level due to a fortuitous cancellation of errors. Important in this connection is that the TS geometry is calculated at the MP2 rather than the HF level. In most cases, it is rather difficult or even impossible to make predictions for higher order MP results since as shown by the data of Table 8 calculated barrier values oscillate strongly at low order.

MP correlation corrections are particularly important when determining *binding energies* of van der Waals molecules[72,73] (see *Intermolecular Interactions by Perturbation Theory*). These are held together by electrostatic, induced, dispersion

Table 7 Comparison of MP Dissociation Energies D_e (kcal mol^{-1}) with Experimental Values

		HF	MP2	MP3	MP4	exp
H$_2 \rightarrow$ H + H		85	101	105	106	109
CH $\rightarrow$ C + H	$^2\Pi$	55	73	75	76	84
	$^4\Sigma^-$	62	68	66	66	67
CH$_2 \rightarrow$ CH + H	$^3B_1$	101	109	108	107	106
	$^1A_1$	70	89	90	91	98
CH$_3 \rightarrow$ CH$_2$ + H		88	110	112	112	117
CH$_4 \rightarrow$ CH$_3$ + H		87	109	110	110	113
OH $\rightarrow$ O + H		67	96	96	96	107
OH$_2 \rightarrow$ OH + H		86	119	115	116	126
FH $\rightarrow$ F + H		93	131	127	128	141

Table 8 MP Reaction Barriers (kcal mol^{-1}) for some Pericyclic Reactions (6-31G(d) Basis)

Energy	Geometry	1,5 H shift	Cyclobutene opening	Diels–Alder
HF	HF	58.7	46.9	45.0
MP2	MP2	36.5	36.8	17.6
MP3	MP2	44.7	40.2	26.9[a]
MP4(SDQ)	MP2	46.1	39.8	29.0[a]
MP4(SDTQ)	MP2	41.1	36.6	21.9
Experimental		38.8 ± 2.2	34.5 ± 0.5	25.1 ± 2

[a] HF geometry

and exchange repulsion forces where the first three are stabilizing and the last destabilizing. In the case of van der Waals interactions between molecules with permanent multipole moments HF often overestimates binding energies because of its tendency to exaggerate bond polarities and atomic partial charges, thus yielding too large dipole moments. However, in the case of van der Waals complexes, which are stabilized just by induced and dispersion forces, HF mostly fails to predict a stable van der Waals complex at all while MP theory provides the simplest way to get to a reasonable description of the complex. Dispersion forces result from the interactions of temporary (rather than permanent) multipole moments of the two complex partners, which HF cannot describe because of its average electron interaction potential. MP2 includes the most important temporary dipole–dipole interactions (see Section 2.1.4) and, therefore, provides a reasonable account of complex binding energies and geometries of van der Waals complexes between nonpolar compounds.

MP correlation effects can be observed for reaction energies, in particular if different electronic structure situations are related to each other by the reaction. Examples are hydrogenation energies or in general reactions that relate multiple bonds to single bonds. MP2, MP3, and MP4 corrections normally are 2–5 kcal mol^{-1}, but can be as large as 10 kcal mol^{-1} if electronegative atoms are involved. An exception is the reaction $O = O + 2H_2O \rightarrow 2HO - OH$, where the MP2 correction is about 20 kcal mol^{-1} (HF reaction energy $\Delta E = 70$; MP2: 52; MP3: 50; MP4: 49; exp. 47 kcal mol^{-1}).[67] However, this is actually an example, for which the number of electron pairs changes by converting a triplet into a singlet molecule. Energy changes of the order of 2–10 kcal mol^{-1} are also observed when comparing the relative stability of carbocations of classical structure with those containing *nonclassical structure* or when calculating the stabilization energy of aromatic molecules (with delocalized π-systems) using as a reference a molecule with localized π-bonds. All these cases represent typical examples of changes in pair distributions and the pair–pair coupling effects as described under point 2.

In summary, one can say that MP2 calculations should be performed in almost all cases that require a reasonable account of relative energies. From case to case, one has to decide whether also MP4(SDQ) or MP4(SDTQ) calculations have to be carried out to get more reliable energy values. A serious disadvantage of MP corrected energy differences is that they oscillate with order p in many cases so that a reliable prediction of high-accuracy values is difficult.

3.6 MP Response Densities and Other One-electron Properties

Changes in the *electron density* distribution $\rho(r)$ nicely reflect trends in calculated one-electron properties due to the stepwise addition of different correlation effects within the MP series.[22,23] The total electron density distribution $\rho(r)$ at a point r_p is the response of the molecule to an external perturbation that corresponds to the Dirac delta operator $\delta(r_p - r)$.

$$\left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=0} = \langle \Psi | \delta(r_p - r) | \Psi \rangle = \rho(r_p). \quad (101)$$

When $\rho(r)$ is expanded in terms of basis functions used to calculate energy and wavefunction one obtains

$$\left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=0} = \rho(r) = \sum_{\mu\nu} D_{\mu\nu}^{res} \chi_\mu(r) \chi_\nu(r), \quad (102)$$

where $D_{\mu\nu}^{res}$ is an element of the response density matrix D^{res}, which, in the case of an MP calculation, can be decomposed into

$$D^{res} = D^{HF} + D^{corr} \quad (103)$$

indicating that D contains an HF and a correlation part. Accordingly, $\rho(r_p)$ is expressed as a sum of the HF density and a correlation correction

$$\rho(r)^{res,MP} = \rho(r)^{HF} + \rho(r)^{corr,MP} \quad (104)$$

One-electron properties calculated as energy derivatives are closely related to the response density. Provided that the basis set chosen is independent of the perturbation the corresponding one-electron property is given as the product of the response density matrix D^{res} with the corresponding property integrals.

$$O = \left.\frac{dE(\lambda)}{d\lambda}\right|_{\lambda=0} = \sum_{\mu\nu} D_{\mu\nu}^{res} \langle \chi_\mu | \hat{O} | \chi_\nu \rangle. \quad (105)$$

Typical MP correlation effects are reflected by the response density distribution as discussed for the case of the CS molecule.[23] In CS, one of the electron lone pairs of S can be shared between the two atoms thus establishing a semipolar bond beside the two normal bonds. This leads to charge transfer from S to C and relatively large partial charges at C and S contrary to what one might expect in view of the similar electronegativities of the two elements: $C^{\delta-} \equiv S^{\delta+}$ This is confirmed by the dipole moment, which was measured to be 1.98 debye.

HF theory predicts relatively small partial charges for C and S suggesting that there is no or only weak semipolar bonding. The calculated dipole moment of CS is just 1.77 debye (HF/MC-311G(2d)).[23] Obviously, HF underestimates the extent of semipolar bonding. Correlation corrections should lead to a charge transfer from S to C.

In Figure 13(a), the density distribution $\rho(r)^{corr,MP2} = \rho(r)^{res,MP2} - \rho(r)^{res,HF}$ of CS calculated with a VTZ + 2P basis set is given in the form of a contour line diagram. Solid (dashed) contour lines are in regions of positive (negative) correlation corrections to the response density. Left–right, angular, and in–out correlations included at the MP2 level lead to a transfer of π-electronic charge from S to C and a complex pattern of smaller changes involving both σ, core, and valence densities (Figure 13a). Charges at C and S are considerably increased as is reflected by a MP2 dipole moment of 2.31 debye that is 15% larger than the experimental dipole moment (Table 9). Left–right correlation has the strongest effect on the charge distribution, but the effects of angular and in–out correlation are also substantial.

The same features of $\rho(r)^{res}$ are found at the MP3, MP4(SDQ), MP4(SDTQ), and even higher correlation corrected levels. Qualitatively, there are no differences in the corresponding response densities which means that MP2 already includes the most important correlation corrections. However, the difference density $\rho^{res,MP3} - \rho^{res,MP2}$ shown in Figure 13(b) reveals that MP3 correlation corrections reduce MP2 effects, i.e., the MP2 response density is slightly changed back into the direction of the HF electron density distribution.
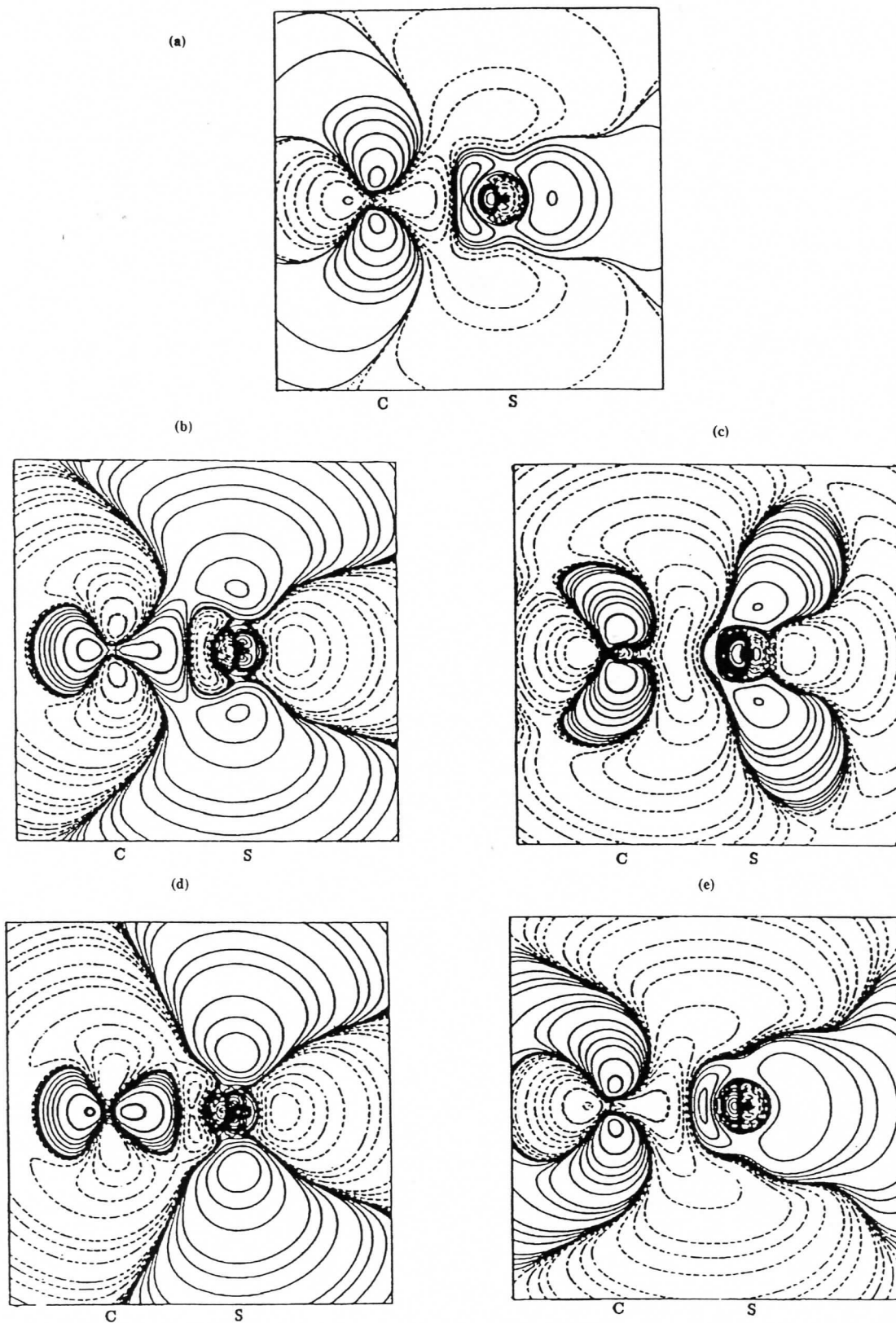
Figure 13 Difference electron density distributions (a) $\rho(r)^{\text{res,MP2}} - \rho(r)^{\text{res,HF}}$, (b) $\rho(r)^{\text{res,MP3}} - \rho(r)^{\text{res,MP2}}$, (c) $\rho(r)^{\text{res,MP4(SDQ)}} - \rho(r)^{\text{res,MP3}}$, (d) $\rho(r)^{\text{res,MP4(SDQ)}} - \rho(r)^{\text{res,MP2}}$, and (e) $\rho(r)^{\text{res,MP4(SDTQ)}} - \rho(r)^{\text{res,MP4(SDQ)}}$ of CS calculated with a VTZ + 2P basis. Solid (dashed) contour lines are in regions of positive (negative) difference densities. Reproduced with permission from J. Gauss and D. Cremer, *Adv. Quantum Chem.*, 1992, **23**, 205–299. Copyright (1992) Academic Press

Table 9 MP Bond Length, Charge, and Dipole Moment of CS (VTZ+2P Basis)

Method	$R(CS)$ (Å)	Charge at S (electron)	Dipole moment (debye)
HF	1.513	0.188	1.77
MP2	1.541	0.273	2.31
MP3	1.527	0.253	2.11
MP4(DQ)	1.529	0.249	2.11
MP4(SDQ)	1.542	0.239	2.06
MP4(SDTQ)	1.565	0.240	2.11
QCISD(T)	1.551	0.239	2.03

Changes comprise a π-electron transfer from C to S, transfer of σ-electrons from outer valence to inner valence space at C and vice versa at S, a transfer of σ-electronic charge from S to C and depopulation (population) of the lone-pair region at S (C). These changes lead to a decrease of the CS bond polarity and decreased *atomic charges* relative to MP2 (Table 9). Pair correlation effects included at MP2 are reduced by the coupling of pair correlations covered at MP3.

In Figure 13(c), the difference response density distribution $\rho^{\text{res,MP4(SDQ)}} - \rho^{\text{res,MP3}}$ of CS is given. Its general features are similar to those of the MP2 response density, i.e., MP4(SDQ) correlation corrections are in the same direction as MP2 correlation corrections. As a consequence, correlation corrections to charges, dipole moment, and other molecular properties are larger than those calculated at the MP3 level of theory. Apart from this, there are significant differences in the charge distribution at the MP4(SDQ) level. Both bonding and lone-pair regions are depopulated relative to the MP3 charge distribution. Charge concentrates in the C $2p\pi$ and S $2p\pi$ and $3p\pi$ region in such a way that electron repulsion is minimized (see Figure 13c).

The difference response density $\rho^{\text{res,MP4(SDQ)}} - \rho^{\text{res,MP2}}$ (Figure 13d) gives the changes relative to the MP2 density distribution and reveals that at MP4(SDQ) the charge transfer to the C $2p\pi$ orbitals is smaller than at MP2. Hence, the pattern of changes is similar to that obtained at the MP3 level where corrections due to S, D, and Q excitations at MP4 are between those obtained at MP2 and MP3. Figure 13(e) gives the changes in the response density distribution that are due to T excitations at MP4. They are in the same direction as those obtained from S, D, and Q excitations, i.e., they increase the charge transfer from the S to the C atom. A detailed analysis of calculated charges and dipole moments shows that the changes due to T effects are larger than those due to S, D, and Q excitations at the MP4 level thus proving the importance of T excitations for multiple bonded systems. Even higher order correlation corrections obtained with CC theory indicate that T effects at MP4 are somewhat exaggerated, which is corrected by TT coupling at the MP5 and higher levels.[23]

The changes in the response density distribution of CS are parallel to calculated changes in other one-electron properties of CS. Most properties oscillate dependent upon the order of PT applied where HF and MP2 results often represent the upper and lower bounds of computed values. Oscillations in calculated one-electron properties are observed in many cases (charges, dipole moments, quadrupole moments, electric field gradients, nuclear quadrupole moments, etc.)[22,23] and are largely independent of the basis set used. In general, one can draw the following conclusions:

1. The largest part of the correlation corrections to response properties is recovered at the MP2 level, but higher order effects are still considerable and cannot be neglected if accurate one-electron properties are needed.
2. Correlation corrections due to D excitations are exaggerated at the MP2 level. They are reduced at the MP3 and higher levels of PT where couplings between D excitations are considered.
3. Single excitations lead only to relatively small changes in calculated response properties.
4. The influence of T excitations at MP4 is relatively large, at least for molecules with multiple bonds. However, comparison with CC suggests that T effects are exaggerated at the MP4 level.
5. In many cases, oscillations of response property values are only slowly dampened out.

3.7 MP Second-Order Properties

In Figure 14, harmonic frequencies ω of H_2O calculated at different levels of MP theory with different basis sets are compared with experimental ones. Clearly, the theoretical ω values reflect a strong dependence on the computed equilibrium geometries. A short (long) bond length implies a large (small) value for the corresponding stretching frequency. A large (small) bond angle, which can be considered to be the result of a short (large) bond length, implies a small (large) value of the corresponding bending frequency.[23]

The harmonic frequency is proportional to the curvature of the potential surface at the equilibrium geometry in the direction of the corresponding internal coordinate. Therefore, on first sight it may be surprising that calculated frequencies depend directly on the theoretical values of the geometrical parameters. However, the potential surface in the direction of a bond distance AB (AH) becomes steeper if the AB (AH) distance is shortened and, hence, the corresponding bond strengthened. Accordingly, the stretching frequencies increase with a shortening of the bond. Widening of an angle ABC (HAH), on the other hand, decreases electrostatic repulsion between A and C (or the H atoms) so that the angle becomes softer and the bending frequency decreases. Figure 14 also reveals that MP4(SDQ)/TZ+2P is not sufficient to get accurate harmonic frequencies since calculated values are still too large. Higher order correlation effects have to be included to improve the accuracy of calculated values.

In Figure 15, theoretical and experimental infrared intensities of the three vibrational modes of H_2O are compared. Since there are not so many accurately determined infrared intensities available from experiment the comparison of calculated and measured infrared intensities is limited in the literature to just a few examples. The water example shows that agreement of MP data with experimental values is even poorer than in the case of the harmonic frequencies. HF intensities are too large by up to 50 km mol^{-1} and more. Stepwise inclusion of MP correlation effects leads to a continuous decrease of intensities. Similar trends are also observed for other molecules. However, dependence on method and basis set may change more strongly than observed for geometrical parameters and vibrational frequencies. In particular, the inclusion of diffuse basis functions is important in calculating reasonable MP intensities.

Infrared intensities are derived from dipole moment derivatives with regard to Cartesian coordinates. Assuming that
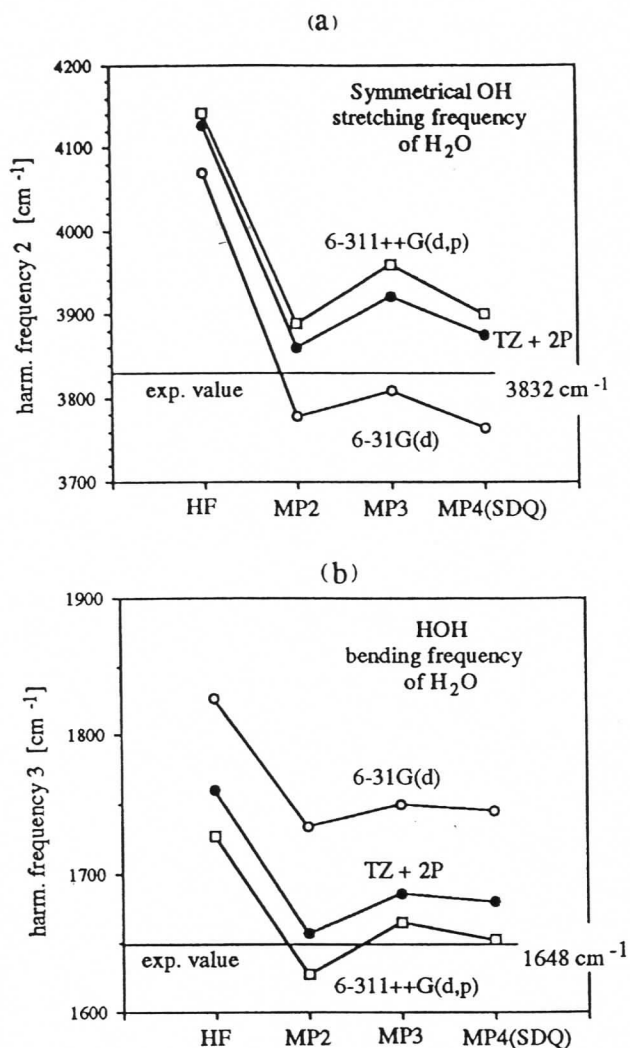
(a)

(b)

Figure 14 Dependence of calculated harmonic frequencies of water on method and basis set. (a) Symmetric OH stretching frequency, (b) HOH bending frequency. Reproduced with permission from J. Gauss and D. Cremer, *Adv. Quantum Chem.*, 1992, **23**, 205–299. Copyright (1992) Academic Press
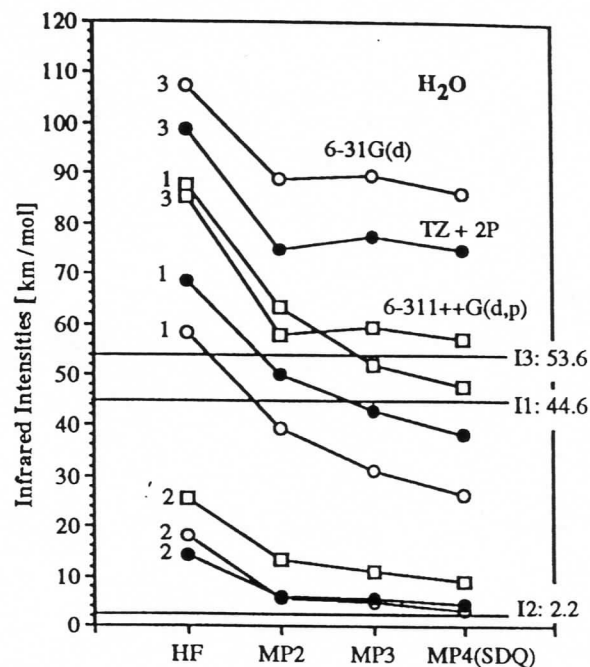

Figure 15 Dependence of calculated infrared intensities of water on method and basis set. Reproduced with permission from J. Gauss and D. Cremer, *Adv. Quantum Chem.*, 1992, **23**, 205–299. Copyright (1992) Academic Press

dipole moment derivatives change similarly to dipole moments with method and basis set, HF and MP intensities can be discussed. At the HF level, the OH bond polarity and, thereby, the molecular dipole moment are exaggerated, obviously causing also enlarged infrared intensities (Figure 15). Correlation effects reduce bond polarities and molecular dipole moment. The same is reflected by the computed infrared intensities. In the case of H_2O, the best values are obtained at the MP4(SDQ) level of theory with a VTZ+P basis set that includes diffuse functions.

Another important second-order property, which is considerably improved by MP correlation effects is the NMR chemical shift (see *NMR Chemical Shift Computation: Ab Initio* and *NMR Chemical Shift Computation: Structural Applications*). Calculations by Gauss[58] have shown that for ^{13}C shifts accurate values are already obtained at the GIAO-MP2 level. Further improvements are obtained by GIAO-MP3 and GIAO-MP4(SDQ) calculations. In the case of molecules with multiple bonds such as N_2, the inclusion of T effects

becomes important. Again, calculated values oscillate dependent upon the order of MP theory applied, however the GIAO-MP4(SDTQ) value agrees very well with experiment.[60]

4   CONCLUSIONS

Because MP2 is the correlation corrected *ab initio* method with (a) the best efficiency factor (determined by the ratio of accuracy and computational cost), (b) the largest applicability repertoire (see Table 2), and (c) the largest amount of reference data, it is and will also be in the future the standard *ab initio* method for getting a first insight into a chemical problem. It has replaced in this respect HF theory to a large extent although this statement depends somewhat on the size of the molecules considered. There is no indication that CCD or CCSD will replace MP2, which has certainly to do with the higher cost of these methods ($N_{iter}O(M^6)$) and the fact that CCD or CCSD are not much better than MP2 in many cases. On the other hand, one has to realize that in the way the use of density functional theory (DFT) is systematized and standardized there will be more work done with DFT than with MP2. However, it is a fact that DFT results are much more difficult to interpret and, therefore, we shall see in the near future work in which MP2 calculations may be done just for the sake of checking and analyzing DFT results.

In the past, there were few applications of MP3 and MP5 to chemical problems. These methods do not introduce new excitations and, therefore, most people have considered them as not attractive for practical use. Probably, they will only be applied in future studies if one wants to investigate the convergence behavior of the MP series. It remains to be asked whether MP4 will function also in the future as a method providing higher perhaps even sufficient accuracy for

a given chemical problem. Clearly, this role has been taken over by CCSD(T) theory and despite the fact that CCSD(T) calculations are somewhat more expensive there will probably be less and less work with MP4 since CCSD(T) provides much more reliable data. On the other hand, MP4(SDQ) is a cheap method ($O(M^6)$) to complement MP2 results in those cases in which T effects do not play an important role and, therefore, MP4 calculations may still be done in the future for reasons of comparison.

Probably, there will be little development work for getting to MP7 or even higher MP methods since on the one hand these methods are too expensive for routine calculations, on the other hand they are too difficult to be developed by traditional techniques. There will be more work to investigate the convergence of the MP series and in this connection MP6 will probably play an important role.

Contrary to SRS MP, further development work will have to be done in the area of MRS MP where the GVB-MP methods can only be considered as a first entry into this field. The repertoire associated with these methods is rather small for various reasons but at least in the case of GVB-MP2 one should see in the near future analytical derivatives, direct methods, etc. As soon as routinely applicable MRS MP programs become available, the use of MRS MP methods will considerably increase.

5 RELATED ARTICLES

Basis Sets: Correlation Consistent Sets; Complete Active Space Self-consistent Field (CASSCF) Second-order Perturbation Theory (CASPT2); Configuration Interaction; Coupled-cluster Theory; Density Functional Theory (DFT), Hartree–Fock (HF), and the Self-consistent Field; G2 Theory; Geometry Optimization: 1; Gradient Theory; Intermolecular Interactions by Perturbation Theory; Molecular Magnetic Properties; NMR Chemical Shift Computation: Ab Initio; NMR Chemical Shift Computation: Structural Applications; Self-consistent Reaction Field Methods; Spin Contamination.

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Monte Carlo

A method to propagate the positions of atoms or groups of atoms in a molecule or collection of molecules through conformational space using a Boltzmann sampling of phase space. See *Monte Carlo Quantum Methods for Electronic Structure; Monte Carlo Simulations for Complex Fluids;* and *Monte Carlo Simulations for Polymers*.

Monte Carlo Quantum Methods for Electronic Structure

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Abbreviations

DMC = diffusion Monte Carlo; GFMC = Green's function Monte Carlo; QMC = quantum Monte Carlo; VMC = variational Monte Carlo.

1 INTRODUCTION

As the name may imply, Monte Carlo methods employ random numbers to solve problems. The range of problems that may be treated by Monte Carlo is substantial; these include simulation of physical (and other) processes, integration of multi-dimensional integrals, solution of integral and linear operator equations, and applications in statistical mechanics.[1,2] The treatment of problems arising in the field of quantum mechanics using Monte Carlo is generally referred to as quantum Monte Carlo (QMC). In QMC, the Monte Carlo applications most often encountered are integration, simulation, and solution of an integral equation. Another approach, path integral Monte Carlo, is especially useful for the study of quantum mechanical systems at finite temperature; for a review, see Ref. 3. The focus of this contribution will be the application of QMC in *ab initio* quantum chemistry.

Since the 1960s, expansion and perturbative approaches, such as *Hartree–Fock* (HF), configuration interaction, many-body perturbation theory, and coupled cluster have dominated the field of *ab initio* quantum chemistry.[4] The range of systems that may be treated by these methods, and the accuracy, has grown tremendously over the last 30 years owing to increases in computational speed and *algorithm* efficiency. However, the accuracy of these methods is determined by the one-particle (basis set) and the many-particle (determinants or configuration