

## Multireference Møller–Plesset method

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A multireference Møller–Plesset method is derived. The state-specific nondynamical correlation is accounted for by the MCSCF theory and the transferable dynamical correlation is estimated by the Møller–Plesset perturbation theory. There is a very close parallel between the standard single reference Møller–Plesset theory and the present multireference version. The method has been implemented at the second-order for 2-configuration MCSCF wavefunctions in which only two electrons are correlated. Potential curves for H<sub>2</sub>, HF and F<sub>2</sub> molecules agree well with the full or near-full CI results.

### 1. Introduction

The accurate description of electron correlation has long been recognized as one of the central problems in quantum chemistry. Electron correlation effects are known to be important in, for example, the calculation of potential energy surfaces, the study of excitation processes and electron–molecule scattering. Although the energy associated with electron correlation is a small fraction, typically less than 1%, of the total energy of a molecule, it is of the same order of magnitude as most energies of physical and chemical interest.

It is clear that significant progress has been made in correlation problems in the last ten years. One is embarrassed by the generality of the problems involved and by the diversity of the techniques available for their solution. In view of the high degree of sophistication of some of the techniques, the tremendous computational difficulties involved in their implementation and their heartbreakingly slow convergence, one also feels that we may be doing the wrong kind of mathematics. Perhaps we should be more adventurous once in a while, concentrating a bit more on the physics.

The progress in the field is due to the introduction and development of a series of pair theories. The independent electron-pair approximation (IEPA) proposed by Sinanoğlu [1] consists of approximating the total correlation energy as a sum of pair contri-

butions, which are calculated independently. However, the approximation on which IEPA is based, neglect of the pair coupling elements was thought a severe approximation and we were led to the coupled electron pair approximation. The present activity in the field is largely concerned with improving the coupled electron-pair approximation in the form of the variational CI [2], many-body perturbation theory [3–5], cluster expansion theory [5–8] and other methods.

In this paper, we propose a reliable, yet simple and feasible treatment of the correlation problem. The method is related to the multireference (MR) Møller–Plesset (MP) theory, but is presented in a different philosophy. In contrast to CI, the use of MR techniques in many-body perturbation theory is far less developed. Although much work [9–16] is being done to adapt MR techniques to perturbation theory, only a few modest sized calculations have been carried out. We want to keep the spirit and the logic of the IEPA as long as possible. We want to simplify theory and not to complicate it. How can this be done?

Let us consider a perturbation theory in which to the second-order energy electron pairs decouple. Perturbation theory gives good results if the perturbation is *small* and, therefore, the perturbation series converges rapidly, so that only the first few orders to the energy need to be considered. Electron interactions were thought to be far from being a small

perturbation. It is rather uncertain whether the perturbation series converges at all and no a priori recipe is available prescribing the order at which one should stop to get a reliable answer. Because of this, perturbation methods were not widely accepted for the treatment of correlation effects. Systematic studies by the Pople group [17] and the availability of the GAUSSIAN code were instrumental in establishing the reliability of perturbation techniques. Now we can draw a conclusion from the gained experience that the performance of the perturbation theory depends critically on the choice of the zeroth-order Hamiltonian. It is also concluded that the convergence of the perturbation theory with MP partitioning, on the whole, is not so bad, but it is very poor for describing the nondynamical correlation. For the dynamical correlation decoupling of the first-order pairs has been proved to be a fairly good approximation.

The key idea is that traditional IEPA is not really bad, it breaks down when there exists strong coupling between electron pairs. We must remedy this by performing a multiconfigurational SCF (MCSCF) calculation only for strongly interacting electron pairs. Once the strongly interacting electron pairs are included in the MCSCF wavefunction, coupling of the remaining electron pairs is expected to become weak and they can be treated independently. This is a generalization of the EIPA concept. It must be stressed that the optimization of orbitals in the MCSCF scheme is essentially important in order to redefine the remaining electron pairs in the field generated by the MCSCF wavefunction.

In many chemical reactions involving polyatomic molecules only a few bonds are broken or created while the remainder suffer only minor distortions from equilibrium. In such a case only those bonds which suffer from large distortions require a more refined description. Consider the calculation of the potential curves. At, or near, the equilibrium configuration for the nuclei, the total wavefunction is dominated by the closed-shell Hartree-Fock function. In such a case, IEPA is useful for the study of the dynamical correlation and the convergence of the perturbation series is usually rapid. However, perturbation series either show very slow convergence or divergence at intermediate and large internuclear distances. This is due to the strong coupling between

singly and doubly excited configurations and also due to the (near) degeneracies. That is, the failure of the perturbation theory arises from the nondynamical correlation effects. The first-order MCSCF theory is required to remove the qualitative errors of the single configuration SCF theory which arise from (near) degeneracies.

The main message of this paper is that one can avoid complicated coupling between electron pairs if one starts with the first-order MCSCF function and get good results nevertheless.

In section 2 the general theoretical background is outlined. Some numerical results will be given in section 3. A summary is given in section 4.

## 2. Theoretical background

We start with the MCSCF wavefunctions with energies that can be expressed as

$$E = 2 \sum_i f_i h_{ii} + \sum_{ij} (a_{ij} J_{ij} - b_{ij} K_{ij}), \quad (1)$$

where the summation runs over  $n$  orbital basis functions  $\{\varphi_i\}$  in terms of which the wavefunction is described. Here the  $f_i$  are given by

$$2f_i = D_i^i, \quad (2)$$

where  $D_i^i$  are diagonal elements of the one-electron density matrix. The  $a_{ij}$  and  $b_{ij}$  are energy coefficients and  $J_{ij}$  and  $K_{ij}$  indicate the usual Coulomb and exchange energies, respectively. Requiring that the energy be stationary with respect to all orbital variations leads to the general variational condition

$$\sum_i \langle \delta \varphi_i | F_i^{\text{MCSCF}} | \varphi_i \rangle = 0, \quad (3)$$

where  $F_i^{\text{MCSCF}}$  is the generalized Fock operator

$$F_i^{\text{MCSCF}} = f_i h + \sum_j (a_{ij} J_j - b_{ij} K_j). \quad (4)$$

The energy can be written as

$$E = 2 \sum_i \langle \varphi_i | F_i^{\text{MCSCF}} | \varphi_i \rangle - \sum_{ij} (a_{ij} J_{ij} - b_{ij} K_{ij}). \quad (5)$$

Now let us consider the perturbation theory based on the MCSCF function. Many-body perturbation theory is useful only if the zeroth-order Hamiltonian  $H_0$  is a one-electron operator. Experience shows that,

for closed-shell systems, the best results are obtained with the MP partitioning, i.e. with the sum of one-electron Fock operators as  $H_0$  [18], although the  $1/Z$  partitioning scheme yields better perturbation results for the helium isoelectronic sequence [19]. A possible choice of the one-electron operator for the MR case is the generalized Fock operator given by eq. (4). However, one disadvantage of this choice is lack of the physical meaning of the operator, unlike the closed-shell Fock operator. A one-electron operator which is closely analogous to the closed-shell Fock operator can be defined for MCSCF wavefunctions as

$$F = h + \sum_j f_j (2J_j - K_j). \quad (6)$$

In order to remove the arbitrariness of the density weighing, we use the *natural orbitals*. That is, canonical MCSCF orbitals are transformed to the natural orbitals before perturbing. This definition corresponds to the electrostatic energy of an electron in the field generated by the reference wavefunction. In addition, its definition is unique and can be extended to the virtual space.  $F$  is not diagonal in a basis of orbitals. The one-electron operator in the sense of diagonal form can be redefined as

$$\hat{F} = \sum_\nu |\varphi_\nu\rangle \langle \varphi_\nu | F | \varphi_\nu \rangle \langle \varphi_\nu|. \quad (7)$$

The total energy is re-expressed in terms of  $F$  as

$$E = 2 \sum_i f_i \langle \varphi_i | F | \varphi_i \rangle - \sum_{ij} [(4f_i f_j - a_{ij}) J_{ij} - (2f_i f_j - b_{ij}) K_{ij}]. \quad (8)$$

We then have eigenfunctions  $\Phi_I$  and eigenvalues  $W_I$  of the zeroth order Hamiltonian  $H_0$ :

$$H_0 \Phi_I = W_I \Phi_I, \quad (9)$$

with

$$H_0 = \sum_I |\Phi_I\rangle \langle \Phi_I | \hat{F} | \Phi_I \rangle \langle \Phi_I|. \quad (10)$$

$\Phi_0$  is the MCSCF wavefunction with the eigenvalue

$$W_0 = 2 \sum_i f_i \langle \varphi_i | F | \varphi_i \rangle. \quad (11)$$

The sum in eq. (10) goes over all possible orthonormal configurations  $\{\Phi_i\}$  constructable from the occupied and virtual orbitals. The perturbation

is  $V = H - H_0$ . This choice of  $H_0$  in the Rayleigh-Schrödinger perturbation series guarantees size consistency if the reference wavefunction is size consistent. There is a very close parallel between the standard single reference MP theory and its MR version. The first-order wavefunction, for instance, contains only double substitutions. Singles cannot contribute due to the generalized Brillouin theorem [20]. Triples and higher substitutions are also excluded because any configurations having a non-zero matrix element with the reference configuration do not enter the first-order correction to the wavefunction. The correlation of two active *holes* with two active *particles* must be excluded to avoid overcounting since this effect is included in the reference function. When all  $f_i = 1$ , the theory is reduced to the standard single reference MP theory.

### 3. Some numerical results

We have implemented the second-order of the MR-MP perturbation theory for a two-configuration wavefunction in which one electron pair is correlated. The method is abbreviated as MR-MP2. The 2-configurational MR-MP2 is suitable for the description of the closed-shell ground state of a singly bonded molecule.

Results obtained for the potential curve of  $H_2$  with the TZp basis set [21] are given in table 1 and fig. 1. It is seen from table 1 and fig. 1 that MR-MP2 theory yields a potential curve which is very close to the full CI results. The predicted TZp bond length is only 0.0034 Å longer and the dissociation energy,  $D_e$ , 0.081 eV smaller than the full CI results. 2-configuration MCSCF (MCSCF-2) itself is quite poor near equilibrium. Its bond length is computed too long, overestimating the contribution of the dissociative configuration. Single reference MP2 is fairly good near the equilibrium but becomes poor at the intermediate bond-breaking region and it diverges at dissociation.

In table 2 we have summarized results for HF using the DZ basis set [21] at three geometries ( $r_e$ ,  $1.5r_e$ ,  $2r_e$ ). Results are compared with the full CI [22] to assess the reliability of the present method. The SCF description becomes quite poor as the bond is stretched. The single and double CI (SDCI) shows

Table 1

Potential curve, equilibrium distance and dissociation energy for H<sub>2</sub> with TZp basis <sup>a)</sup>. Energies ( $-E$ ) in hartree

$r$ ( $a_0$ )	SCF	MP2	2-Config. MCSCF	MR-MP2	Full CI
1.0	1.08319	1.110415 (80.3)	1.096577 (39.5)	1.113048 (88.1)	1.122025
1.2	1.123779	1.150942 (79.5)	1.139496 (46.0)	1.154414 (89.7)	1.157950
1.4	1.132595	1.160076 (78.9)	1.151096 (53.1)	1.164396 (91.3)	1.167438
1.6	1.125283	1.152761 (76.3)	1.147044 (60.4)	1.158719 (92.9)	1.161283
1.8	1.109740	1.137680 (74.0)	1.135268 (67.6)	1.145362 (94.4)	1.147481
2.0	1.090177	1.118834 (71.4)	1.120021 (74.3)	1.128623 (95.7)	1.130337
2.4	1.047281	1.078247 (65.4)	1.087624 (85.2)	1.093583 (97.8)	1.094617
3.0	0.986437	1.023107 (57.1)	1.047422 (94.9)	1.050359 (99.5)	1.050709
4.0	0.908691	0.960513 (50.0)	1.012668 (99.4)	1.013231 (100.0)	1.013255
6.0	0.821259	0.924424 (57.7)	1.000172 (100.0)	1.000184 (100.0)	1.000185
10.0	0.764081	1.013071 (105.7)	0.999620 (100.0)	0.999620 (100.0)	0.999620
100.0	0.717502	4.092631 (1096.0)	0.999619 (100.0)	0.999619 (100.0)	0.999619
$r_e$ (Å)	0.7458	0.7467	0.7664	0.7554	0.7521
$D_e$ (eV)	11.296	-	4.134	4.488	4.569

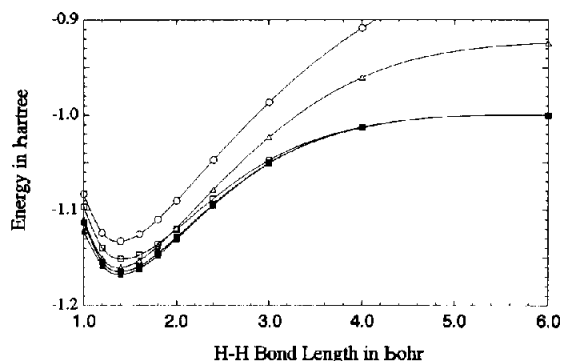
<sup>a)</sup> Values in parentheses are percentage of correlation energies recovered.

Fig. 1. SCF, MP2, MCSCF-2, MR-MP2 and full CI potential curves for H<sub>2</sub>. The various curves are identified as follows: (○) SCF; (△) MP2; (□) MCSCF-2; (■) MR-MP2; and (▲) full CI.

a substantial improvement over SCF, but still retains some of the bias of a poorer zeroth-order description of the SCF wavefunction at the stretched bonds. Note that the results at the single, double and triple CI (SDTCI) level are still inadequate since the energy contribution of quadruple excitations is rapidly increasing as the bond is broken. At the single, double, triple and quadruple CI (SDTQCI) level we have satisfactory results. However, the SDTQ configuration expansion is quite lengthy and does not represent an optimal approach for including higher excitations. The single reference MP shows oscillation with order of perturbation. This indicates that the

correlation in the HF molecule is not small enough to be treated as a perturbation. A single reference perturbation theory is very poor for the description of the bond breaking. However, MP4 results seem to agree fortuitously well with the full CI potential within the calculated region in the nuclear distance. The shortcomings of the perturbation theory will become clear as the bond length is increased. The MCSCF-2 ( $\sigma^2$  and  $\sigma^{*2}$ ) description is better than SCF, but overcorrects because it overestimates the importance of the dissociative configuration. In contrast, the present MR-MP2 potential is substantially better. The MR-MP2 recovers about 97–98% of the total correlation energy in a given basis set in every case. Of course the MR-MP2 results are less accurate than SDTQCI, but if one takes the computational efficiency into consideration, the MR-MP2 results are rather impressive. This provides strong support for the validity of the generalized IEPA.

Laidig et al. [23] performed comparison calculations of the potential curve of F<sub>2</sub> employing a variety of standard techniques such as CI, perturbation theory, coupled-cluster (CC) theory. We also computed the potential curve with MR-MP2. The basis set used was the DZp+ and the two 1s core orbitals were frozen. The first-order MCSCF includes  $3\sigma_g^2 \rightarrow 3\sigma_u^2$  configuration. Geometries and energies are displayed in table 3 and fig. 2. The dissociation energies ( $D_e$ ) and equilibrium distances ( $r_e$ ) are listed in

Table 2  
Total energies ( $-E$ ) for HF with DZ basis <sup>a)</sup>

Method	$r_e$	$1.5r_e$	$2.0r_e$
SCF	100.021973 (0.125231)	99.924625 (0.154816)	99.815206 (0.193470)
MP2	100.143586 (0.003618)	100.072175 (0.007266)	99.988151 (0.020525)
MP3	100.141344 (0.005860)	100.067094 (0.012347)	99.981786 (0.026890)
MP4	100.147557 (0.000353)	100.078787 (0.000654)	100.004938 (0.003738)
SDCI <sup>b)</sup>	100.141486 (0.005718)	100.069621 (0.009820)	99.990518 (0.018158)
SDTCI <sup>b)</sup>	100.142551 (0.004653)	100.071516 (0.007925)	99.995429 (0.013247)
SDTQCI <sup>b)</sup>	100.146995 (0.000209)	100.079085 (0.000356)	100.008046 (0.000630)
MCSCF2	100.046880 (0.100324)	99.980410 (0.099031)	99.920218 (0.088458)
MR-MP2	100.143568 (0.003636)	100.076833 (0.002608)	100.004153 (0.004523)
full CI <sup>b)</sup>	100.147204 (0.0)	100.079441 (0.0)	100.008676 (0.0)

<sup>a)</sup> Values in parentheses are relative to the full CI energy. <sup>b)</sup> Ref. [20].

Table 3  
Selected  $F_2$  energies as a function of internuclear separation with DZp+ basis <sup>a)</sup>. Energies ( $-E$ ) are in hartree

$r$ ( $a_0$ )	SCF	MCSCF-2	MCSCF-32 <sup>b)</sup>	MR-LCCM-10 <sup>b)</sup>	MR-MP2
2.0	198.59731	198.62488	198.67123	199.00589	198.98780 (95.6)
2.2	198.69660	198.73481	198.78288	199.11832	199.09952 (95.5)
2.4	198.73311	198.78529	198.83241	199.16887	199.14891 (95.4)
2.5	198.73743	198.79783	198.84357	199.18056	199.15992 (95.3)
2.6	198.73572	198.80510	198.84895	199.18646	199.16513 (95.3)
2.7	198.72973	198.80874	198.85032	199.18832	199.16630 (95.2)
2.8	198.72078	198.80997	198.84902	199.18746	199.16478 (95.1)
2.9	198.70985	198.80968	198.84601	199.18490	199.16157 (95.1)
3.0	198.69767	198.80846	198.84204	199.18137	199.15739 (95.0)
3.2	198.67145	198.80478	198.83308	199.17326	199.14803 (94.9)
3.5	198.63157	198.79906	198.82085	199.16210	199.13519 (95.0)
4.0	198.57185	198.79280	198.80818	199.15034	199.12170 (95.0)
5.0	198.48897	198.78932	198.80084	199.14413	199.11410 (95.4)
6.0	198.44328	198.78911	198.79986	199.14338	199.11333 (95.7)
100.0	198.34472	198.78930	198.79948	199.14347	199.11338 (96.2)

<sup>a)</sup> Values in parentheses are recovered correlation energies in percentage relative to MR-LCCM-10. <sup>b)</sup> Ref. [21].

table 4. In fig. 3 we draw potential curves for  $F_2$  computed by various methods shifted such that their respective dissociated energies are zero. Although full CI calculation is not available in this basis set, a linearized version of a complete multireference coupled-cluster singles and doubles (MR-LCCM) [24] is expected to be close to the full CI.

The SCF dissociation energy is over six times as large as the experimental values of 1.66 eV. This is due to the inability of the SCF to separate correctly into two neutral F at dissociation. The MCSCF-2

wavefunction, which includes the  $3\sigma_g^2 \rightarrow 3\sigma_u^2$  configuration, is found to be bound by 0.56 eV. The computed minima of SCF and MCSCF-2, 1.332 and 1.498 Å, respectively, are both quite far from the experimental values of 1.412 Å. The SDCI  $D_e$  is computed to be 4.5 eV. The SDCI well depth is still nearly three times too deep. The coupled-cluster singles and doubles (CCSD) [5], which is equivalent to our symmetry-adapted cluster (SAC) theory [8], provides a dissociation value of 2.4 eV which is still about 40% in error. The minimum value of SDCI is

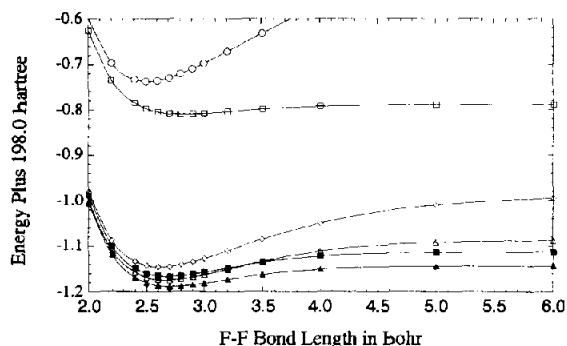


Fig. 2. SCF, MCSCF-2, SDCl, CCSD, MR-MP2 and MR-LCCM-10 potential curves for  $F_2$ . The various curves are identified as follows: (○) SCF; (□) MCSCF-2; (◇) SDCl; (△) CCSD; (■) MR-MP2; and (▲) MR-LCCM-10.

Table 4  
Equilibrium bond length and dissociation energy for  $F_2$

Method	$r_e$ (Å)	$D_e$ (eV)
SCF	1.3319	10.688
MCSCF-2	1.4979	0.564
MCSCF-10 <sup>a)</sup>	1.4824	0.669
MCSCF-32 <sup>a)</sup>	1.4256	1.384
SDCl <sup>a)</sup>	1.3852	4.491
CCSD <sup>a)</sup>	1.4102	2.362
MR-LCCM-10 <sup>a)</sup>	1.4350	1.221
MR-LCCM-32 <sup>a)</sup>	1.439	1.257
MR-MP2	1.4254	1.440
exp.	1.412	1.66

<sup>a)</sup> Ref [21].

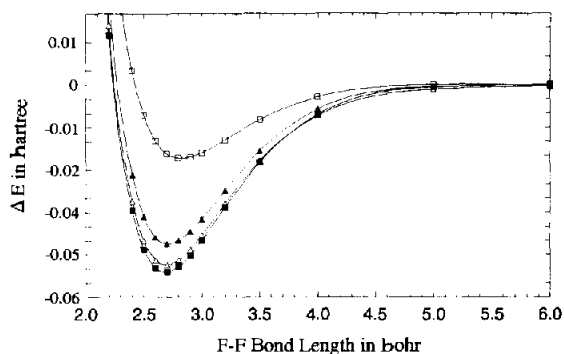


Fig. 3. MCSCF-2, MCSCF-32, MR-MP2 and MR-LCCM-10 potential curves for  $F_2$  shifted such that their respective dissociated energies are zero. The various curves are identified as follows: (□) MCSCF-2; (△) MCSCF-32; (■) MR-MP2; and (▲) MR-LCCM-10.

1.385 Å, which is within 0.03 Å of experiment while the CCSD value 1.410 Å is nearly identical with experiment. Thus, the single reference theory becomes poor when near degeneracies are present. However, in the absence of such degeneracies, CCSD (SAC) yields good energies. The single reference MP theory is also good within the region up to approximately 3.5 bohr in nuclear distance. However, beyond 4 bohr the perturbation series diverges due to the near degeneracy of the  $3\sigma_g$  and  $3\sigma_u$  orbital energies. Thus, none of these single reference based methods can describe all regions of the  $F_2$  potential curve to high accuracy.

The dissociation energies and equilibrium geometries have been improved in the MR based methods. The present MR-MP2 gives  $D_e = 1.44$  eV and  $r_e = 1.426$  Å. The  $D_e$  is computed only 13% in error and  $r_e$  is within 0.015 Å of experiment. It appears that there are no serious defects in the overall shape of the MR-MP2 curve. Note that the computed  $D_e$  and  $r_e$  are very close to those of 32-configurational MCSCF (MCSCF-32) (see fig. 3). The main differences between the two curves are in their absolute energies. The MR-MP2 curve is much lower in energy along its entire length than the analogous MCSCF-32 curve. The MR-MP2 recovers about 95–96% of the 10-configurational MCSCF based MR-LCCM (MR-LCCM-10) correlation energy at all geometries. The remaining errors will be recovered by the addition of higher excitations to MR-MP2 as in the third-order MP method. The MR-MP3 must substantially improve the shape of the potential curve in the short-range and equilibrium regions. Improvement may also be possible by extending the reference space.

#### 4. Summary

A new derivation of the MR-MP theory has been presented which is based upon applying the generalized IEPA to an MCSCF reference function. The MR-MP method is designed to compete directly against the traditional highly correlated methods. The theory retains the attractive features of the single reference MP theory. The method can be implemented in an efficient and straightforward manner via modification of the existing MP program. Taken as a

whole, the 2-configurational MCSCF based MR-MP2 results were shown to compare favorably with those of the highly correlated methods for the description of a single bond breaking.

The present approach is very powerful as a reliable method for the computation of correlation energy where errors of the order of a few percent are acceptable. The MR-MP2 gives good results and, therefore, the perturbation series are expected to converge rapidly, so that only the next few orders of perturbation to the energy need to be considered to recover the difference between MR-MP2 and full CI results. Implementation for general MCSCF, open-shell and excited-state wavefunctions is in progress.

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