

## **Moller–Plesset perturbation theory with two-configurational reference wavefunction**

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**Summary.** The recently proposed consistent generalization of the Moller–Plesset (MP) perturbation theory for arbitrary open-shell and multiconfigurational reference states is formulated and described in detail for a simple two-configurational (TC) SCF wavefunction. The problem of non-diagonality of  $H^0$  is discussed. Dynamical correlation contributions to the energy, dissociation energy, and dipole moment of HF are analyzed in terms of different types of excitations.

**Key words:** Moller–Plesset perturbation theory – Two-configurational SCF wavefunction

### **1. Introduction**

It has been recognized that the many-body perturbation theory (MB PT) [1, 2] provides the most efficient treatment of dynamical electron correlation in molecules. Usually, the first few orders of MBPT are enough to recover the most significant part of the correlation energy. The efficiency of this approach arises from the consistent neglect of higher-order contributions which are present in configuration interaction (CI) and coupled cluster (CC) methods. The latter include some contributions through infinite order and usually require about 10 iterations for convergence if any DIIS-type of acceleration is used [3]. On the other hand, from the point of view of numerical effort, the perturbational approach up to the third order corresponds to one CI iteration. It makes second- and third-order perturbation theory roughly an order of magnitude more efficient than both CI and CC methods. For this reason the perturbation theory is applicable to much larger systems than more accurate CI and CC methods.

Applicability of the perturbation theory to the electron correlation problem has been known for a long time [4]. However, its acceptance was slow. Major objection against the use of perturbational approach resulted from the absence of the upper-bound property. According to the modern view, the upper-bound property is less important than the size consistency [2, 5, 6] or more properly size extensivity [7]. The latter is much easier to be achieved in perturbational methods than in variational ones. After it was realized, the perturbational

techniques became very popular and widely used, mainly due to the systematic studies of Bartlett and Silver [1] and Pople's group [2, 8].

The most important step in formulating a perturbational method is the proper choice of the zeroth-order Hamiltonian  $H^0$ . It determines the convergence of the perturbation expansion and degree of numerical complexity. Thus,  $H^0$  besides modeling the full Hamiltonian well, should be also a simple, uniquely defined one-electron-type operator. It is also very important to define  $H^0$  depending on the reference wavefunction  $\Psi^0$  alone, but not on the particular orbital representation of  $\Psi^0$ .

Arbitrariness in partitioning of the full Hamiltonian causes the problem that a number of  $H^0$  operators can be defined, leading to various versions of perturbational methods. Without any formal criteria for their performance, the only possible verification can be based on test calculations.

For the closed-shell systems the best results have been obtained with the Moller–Plesset (MP) partitioning [4]. In this approach the zeroth-order Hamiltonian is the sum of the one-electron Fock operators. All attempts to modify it have not been successful [9–12].

The MP perturbation theory can be formulated for both the restricted Hartree–Fock (RHF) closed-shell and unrestricted Hartree–Fock (UHF) wavefunctions [2, 13]. These two MP perturbational methods are often called RHF MP and UHF MP, respectively. Distinction between both methods is very important, since their behavior is significantly different [14–19]. In the case of the UHF MP method there is a spin contamination problem which reflects quasi-degeneracy of the reference state. Shortly, the UHF MP method allows to treat open-shell states but it does not solve the quasi-degeneracy problem. Moreover, the UHF MP method is much more expensive than the RHF MP because of approximately double number of the orbitals [20]. At the end, an additional computational effort is wasted, since most of the UHF orbitals are very well paired in corresponding orbitals [21].

The spin contamination problem in the UHF MP method may be partially solved by using projection techniques [22]. Very recently, the new promising approach has been proposed [23]. It is based on a certain spin-constraint within the UHF theory (SUHF) which introduces an additional parameter (Lagrange multiplier) responsible for the final spin expectation value. When this multiplier varies from zero to infinity the SUHF solution goes from the UHF to ROHF (restricted open-shell HF) wavefunction [23]. The MP perturbation theory may be formulated for the SUHF reference as well as for the UHF one. With a large value of the Lagrange multiplier it gives the possibility of approaching the ROHF MP theory [23]. The choice of a given value of the Lagrange multiplier is, however, arbitrary.

In the MP perturbation theory it is assumed that the Hartree–Fock wavefunction is a sufficiently good approximation to the exact wavefunction. If this condition is satisfied, the perturbational expansion converges rapidly and the second-order level already gives quite useful results. Otherwise, perturbation expansions converge very slowly or even not at all and lower-order approximations deliver rather unreliable predictions.

Unfortunately, there are a lot of cases where neither a restricted nor unrestricted single-determinant can represent the zeroth-order wavefunction and multiconfigurational (MC) reference is necessary. It may be due to near-degeneracy effects. However, this is not the only case. It should be emphasized that the multiconfigurational nature of the reference wavefunction does not necessarily

mean quasi-degeneracy; very often it follows simply from strong electron correlation effects or from the requirement of correct description of the dissociation process.

A general perturbation theory for the case of multireference states was formulated over 20 years ago [24] in order to solve quasi-degeneracy problems. Several possible formulations of that approach were proposed [25–29]. All of them are based on the concept of an effective Hamiltonian [30]. They are not equivalent to the Moller–Plesset perturbation theory for the closed-shell state. In spite of the extensive theoretical studies, applications of these methods develop slowly [31]. The major drawback is known as the intruder state problem [32].

Some years ago an attempt was made to formulate second-order perturbation theory for complete active space SCF (CAS SCF) wavefunctions [33]. However, it may be considered as an approximation to the full treatment mostly due to restricted first-order interacting space used there.

Recently, we have proposed a consistent way to generalize the Moller–Plesset perturbation theory to an arbitrary reference state [20]. The performance of our method has been demonstrated in several numerical applications with the zeroth-order wavefunction of a two-configuration (TC) type [20, 34]. This comprised, besides the traditional TC (equivalent to the generalized valence bond (GVB) with one correlated pair), the  $(2 \times 2)$  complete-active-space (CAS), the RHF doublet and the excited singlet states. The results obtained were very good in all cases. They are comparable to the TC-based CI (singles and doubles) results, at much lower computational cost. Similar performance of a modified version of our method has been recently reported by Murphy and Messmer [35].

In this paper, we would like to describe in detail the generalized Moller–Plesset (GMP) perturbation theory for the simplest MC SCF, i.e., for the TC SCF reference wavefunction. We would like to analyze the importance of the different excitations in the perturbation treatment as well as the problem of diagonality of the one-electron Fock operator. These considerations will be illustrated by numerical results for the HF molecule.

## 2. Theory

As mentioned above, the proper choice of the  $H^0$  operator is one of the crucial steps in formulating perturbation treatment of the correlation energy. We have proposed to construct this operator, in analogy to the closed-shell MP case, on the basis of the one-electron Fock-type operator:

$$f = h + j - k. \quad (1)$$

Here  $h$  denotes the bare nucleus Hamiltonian, and  $j$  and  $k$  are the Coulomb and exchange operators, respectively. For a reference wavefunction of the form:

$$\Psi^0 = \sum_K A_K \Phi_K \quad (2)$$

the  $j$  and  $k$  operators can be expressed in terms of the orbitals and CI coefficients:

$$j = \sum_K A_K^2 \sum_{k \in K} j_{kk} + \sum_{K,L} A_K A_L j_{kl}. \quad (3)$$

In the first term the summations go over all Slater determinants  $\Phi_K$  in the reference function and over all spin orbitals  $\phi_k$  occupied in each  $\Phi_K$ . The second term contains the sum over the pairs of determinants which differ by one spin orbital;  $\phi_l$  replacing  $\phi_k$ . The exchange operator  $k$  is defined in an analogous way<sup>1</sup>.

The elementary Coulomb and exchange operators are given as usual by:

$$\begin{aligned} j_{kl}\phi(1) &= \langle \phi_k(2) | r_{12}^{-1} | \phi_l(2) \rangle_2 \phi(1) \\ k_{kl}\phi(1) &= \langle \phi_k(2) | r_{12}^{-1} | \phi(2) \rangle_2 \phi_l(1). \end{aligned} \quad (4)$$

In a special case of the closed-shell reference function our  $f$  operator defined above becomes the ordinary Fock operator for these states. For this reason, one may consider  $f$  as a *generalized Fock* operator.

Two important features of the  $f$  operator should be noted here. First of all,  $f$  is determined by a reference wavefunction alone but is independent of its particular orbital representation. Secondly,  $f$  is not diagonal in the orbital space for the general MC SCF state.

Let us consider now a decomposition of the configuration space for the perturbed wavefunction. It is divided into a set of the spin-adapted, orthogonal non-, singly-, doubly-, triply-, etc. substituted subspaces. The non-substituted subspace consists of the reference wavefunction  $\Psi^0$  alone. Each  $n$ -substituted subspace is generated by acting on the *whole* reference function  $\Psi^0$  with all possible products of  $n$  excitation operators  $E_1 \dots E_i \dots E_n$  (where  $i$  denotes a pair of orbitals), and then it is orthogonalized to all lower subspaces. For example, the space of singles contains functions of the form  $E_{rs}\Psi^0$  orthogonalized to  $\Psi^0$ , doubles are given as  $E_{rs}E_{tu}\Psi^0$  orthogonalized to both  $\Psi^0$  and singles, etc. Note the *internally* contracted nature of the configuration state functions (CSF) constructed in that way. The internal contraction [37, 38] brings a large saving in the CI method with negligible loss of accuracy [39]. In the expansion for perturbed wavefunction it greatly reduces a number of terms, at the cost of higher complexity of the individual terms.

Finally, we would like to define the zeroth-order operator  $H^0$  in such a way that only double excitations will contribute to the first-order wavefunction, in analogy to the closed-shell MP PT. This can be achieved by appropriate projection of the  $n$ -electron generalized Fock operator:

$$F = \sum_{\text{electrons}} f(i) \quad (5)$$

on the set of all subspaces introduced above. This projection is given in the following form:

$$H^0 = P_0 F P_0 + P_s F P_s + P_d F P_d + \dots, \quad (6)$$

where  $P_0$ ,  $P_s$ ,  $P_d$ , etc. denote the projectors to the reference, singles, doubles, etc. subspaces. Once  $H^0$  is defined, the Rayleigh–Schrödinger perturbation theory is uniquely determined with the perturbation being  $V = H - H^0$ . Perturbation

<sup>1</sup> The definition of the Fock operator, in particular the exchange part of it, will be discussed in a forthcoming paper (J. A. van Lenthe, K. Wolinski, P. Pulay)

The Fock operator introduced here has previously been used for other purposes. See for example [36]

expressions for the first-, second- and third-order energies can be written as:

$$\begin{aligned} E^0 &= \langle \Psi^0 | H^0 | \Psi^0 \rangle \\ E^1 &= \langle \Psi^0 | V | \Psi^0 \rangle = E_r - E^0 \\ E^2 &= \langle \Psi^1 | H | \Psi^0 \rangle \\ E^3 &= \langle \Psi^1 | H - E_r | \Psi^1 \rangle + E^2 \end{aligned} \quad (7)$$

where  $E_r = \langle \Psi^0 | H | \Psi^0 \rangle$  is the reference energy. The coefficient vector for the first-order wavefunction is given by the matrix equation:

$$C = -(H^0 - E^0)^{-1} V \quad (8)$$

with  $(H^0 - E^0)_{ij} = \langle \Psi_i | H^0 - E^0 | \Psi_j \rangle$  and  $V_j = \langle \Psi_j | V | \Psi^0 \rangle$ . The functions  $\{\Psi_j\}$  belong only to the doubly-substituted subspace, if the reference is a CAS SCF function, or to the both singly- and doubly substituted subspaces for a general MC SCF reference state. Our method is also size-consistent [20, 34] for the size-consistent reference wavefunction, i.e., total energy of an ensemble of noninteracting subsystems is equal to the sum of individual subsystem energies, in each order of perturbation [34].

Perhaps, the most interesting feature of the *generalized Moller-Plesset* perturbation theory (GMP PT) described here is that the  $H^0$  operator is non-diagonal in the CSF basis set. This is of course the consequence of our Eq. (1) for the generalized Fock operator, which is not diagonal in the orbital space. Perturbation theory with non-diagonal zeroth-order Hamiltonian has not been regarded as practical. It was the major obstacle in formulating a perturbation theory for multiconfigurational reference state in analogy to the MP approach. In fact, even ordinary MP PT for the closed-shell wavefunction can be formulated in a space of noncanonical orbitals, with non-diagonal  $H^0$ . It has been shown for localized orbitals [40–42] as well as for infinitesimal perturbations [43] that noncanonical MP PT is only slightly more expensive than the ordinary canonical variant. An iterative determination of the  $C$  vector in (8) does not create any problems.

The general theory presented above is valid for any MC SCF reference state. It is convenient, however, to discuss various aspects of the theory in a possibly simple case. The simplest MC SCF wavefunction is a two-configuration (TC) one. Moreover, it is actually an important case since there are many molecules which can be described by a TC (GVB) wavefunction. Thus, the reference state considered now is:

$$\Psi^0 = A_1 \Phi_1 + A_2 \Phi_2 \quad (9)$$

where configurations  $\Phi_1$  and  $\Phi_2$  are given as:

$$\Phi_1 = |(i\bar{i} \bar{j}\bar{j} \dots) m \bar{m}\rangle, \quad \Phi_2 = |(i\bar{i} \bar{j}\bar{j} \dots) n \bar{n}\rangle.$$

Here and further in the text  $i, j, k, l, \dots$  denote the core (internal, doubly occupied) orbitals, and  $m, n$  the two active ones. The virtual (external) orbitals will be denoted by  $a, b, c, d, \dots$ . Note, that the reference state of Eq. (9) is strictly equivalent to the  $(2 \times 2)$  CAS SCF wavefunction since the latter may always be written as Eq. (9) by rotation of active orbitals [44].

The first-order interacting space contains only doubly-substituted functions obtained from Eq. (9) according to the procedure described above. After orthogonalizing all doubles of the form  $E_{rs} E_{tu} \Psi^0$  to  $\Psi^0$  and singles, the final set

of functions used in the expansion of the first-order wavefunction is as follows:  
internal substitutions

$$\text{type I} \quad \Psi_{ij}^{mm} = \left( \frac{m\bar{m}}{i\bar{j}} + \frac{\bar{m}m}{\bar{i}j} \right) \Phi_2$$

semi-internal substitutions

$$\text{type II} \quad \Psi_{+1, ij}^{am} = \frac{1}{2} \left( \frac{a\bar{m}}{i\bar{j}} + \frac{\bar{a}m}{\bar{i}j} + \frac{m\bar{a}}{i\bar{j}} + \frac{\bar{m}a}{\bar{i}j} \right) \Phi_2$$

$$\Psi_{-1, ij}^{am} = \frac{1}{2} \left( 2 \frac{am}{ij} + 2 \frac{\bar{a}\bar{m}}{\bar{i}\bar{j}} + \frac{a\bar{m}}{i\bar{j}} + \frac{\bar{a}m}{\bar{i}j} + \frac{m\bar{a}}{i\bar{j}} + \frac{\bar{m}a}{\bar{i}j} \right) \Phi_2$$

$$\Psi_{+1, ij}^{an} = \frac{1}{2} \left( \frac{a\bar{n}}{i\bar{j}} + \frac{\bar{a}n}{\bar{i}j} + \frac{n\bar{a}}{i\bar{j}} + \frac{\bar{n}a}{\bar{i}j} \right) \Phi_1$$

$$\Psi_{-1, ij}^{an} = \frac{1}{2} \left( 2 \frac{an}{ij} + 2 \frac{\bar{a}\bar{n}}{\bar{i}\bar{j}} + \frac{a\bar{n}}{i\bar{j}} + \frac{\bar{a}n}{\bar{i}j} + \frac{n\bar{a}}{i\bar{j}} + \frac{\bar{n}a}{\bar{i}j} \right) \Phi_1$$

$$\text{type III} \quad \Psi_{+1, im}^{an} = \frac{1}{2} \left( \frac{a\bar{n}}{i\bar{m}} + \frac{\bar{a}n}{\bar{i}m} + \frac{n\bar{a}}{i\bar{m}} + \frac{\bar{n}a}{\bar{i}m} \right) \Phi_1$$

$$\Psi_{-1, im}^{an} = \frac{1}{2} \left( 2 \frac{an}{im} + 2 \frac{\bar{a}\bar{n}}{\bar{i}\bar{m}} + \frac{a\bar{n}}{i\bar{m}} + \frac{\bar{a}n}{\bar{i}m} + \frac{n\bar{a}}{i\bar{m}} + \frac{\bar{n}a}{\bar{i}m} \right) \Phi_1$$

$$\text{type IV} \quad \Psi_{-, i}^a = A_2 \left( \frac{a}{i} + \frac{\bar{a}}{\bar{i}} \right) \Phi_1 - A_1 \left( \frac{a}{i} + \frac{\bar{a}}{\bar{i}} \right) \Phi_2$$

external substitutions

$$\text{type V} \quad \Psi_{mm}^{ab} = \left( \frac{a\bar{b}}{m\bar{m}} + \frac{\bar{a}b}{\bar{m}m} \right) \Phi_1$$

$$\text{type VI} \quad \Psi_{+1, ij}^{ab} = \frac{1}{2} \left( \frac{a\bar{b}}{i\bar{j}} + \frac{\bar{a}b}{\bar{i}j} + \frac{b\bar{a}}{i\bar{j}} + \frac{\bar{b}a}{\bar{i}j} \right) \Psi^0$$

$$\Psi_{-1, ij}^{ab} = \frac{1}{2} \left( 2 \frac{ab}{ij} + 2 \frac{\bar{a}\bar{b}}{\bar{i}\bar{j}} + \frac{a\bar{b}}{i\bar{j}} + \frac{\bar{a}b}{\bar{i}j} + \frac{b\bar{a}}{i\bar{j}} + \frac{\bar{b}a}{\bar{i}j} \right) \Psi^0$$

$$\text{type VII} \quad \Psi_{+1, im}^{ab} = \frac{1}{2} \left( \frac{a\bar{b}}{i\bar{m}} + \frac{\bar{a}b}{\bar{i}m} + \frac{b\bar{a}}{i\bar{m}} + \frac{\bar{b}a}{\bar{i}m} \right) \Phi_1$$

$$\Psi_{-1, im}^{ab} = \frac{1}{2} \left( 2 \frac{ab}{im} + 2 \frac{\bar{a}\bar{b}}{\bar{i}\bar{m}} + \frac{a\bar{b}}{i\bar{m}} + \frac{\bar{a}b}{\bar{i}m} + \frac{b\bar{a}}{i\bar{m}} + \frac{\bar{b}a}{\bar{i}m} \right) \Phi_1$$

$$\Psi_{+1, in}^{ab} = \frac{1}{2} \left( \frac{a\bar{b}}{i\bar{n}} + \frac{\bar{a}b}{\bar{i}n} + \frac{b\bar{a}}{i\bar{n}} + \frac{\bar{b}a}{\bar{i}n} \right) \Phi_2$$

$$\Psi_{-1, in}^{ab} = \frac{1}{2} \left( 2 \frac{ab}{in} + 2 \frac{\bar{a}\bar{b}}{\bar{i}\bar{n}} + \frac{a\bar{b}}{i\bar{n}} + \frac{\bar{a}b}{\bar{i}n} + \frac{b\bar{a}}{i\bar{n}} + \frac{\bar{b}a}{\bar{i}n} \right) \Phi_2$$

The expression  $\frac{t\bar{u}}{r\bar{s}}\Phi$  means that spin orbitals  $(r, \bar{s})$  in  $\Phi$  are replaced by spin orbitals  $(t, \bar{u})$ . The subscripts  $+1$  and  $-1$  denote the different spin coupling of the electron pair i.e., singlet and triplet coupling, respectively. The partition of the first-order interacting space into the internal, semi-internal and external substitutions has been introduced here, depending on the number of virtual orbitals involved in the excitations [33].

There is one type of excitations, namely type IV, which perhaps requires some explanation. These functions arise from the two doubles:

$$E_{mi}E_{am}\Psi^0 = -A_1E_{ai}\Phi_1 = -A_1\left(\begin{matrix} a \\ i \\ \bar{i} \end{matrix}\right)\Phi_1$$

and

$$E_{mi}E_{an}\Psi^0 = -A_2E_{ai}\Phi_1 = -A_2\left(\begin{matrix} a \\ i \\ \bar{i} \end{matrix}\right)\Phi_2$$

orthogonalization to the single substituted functions:

$$E_{ai}\Psi^0 = \Psi_+, \quad a_i = A_1\left(\begin{matrix} a \\ i \\ \bar{i} \end{matrix}\right)\Phi_1 + A_2\left(\begin{matrix} a \\ i \\ \bar{i} \end{matrix}\right)\Phi_2$$

yields the considered function of type IV. Note that the functions of type VI are the only ones which appear in the closed-shell MP PT.

### 3. Non-diagonality of the Fock operator

The GVB MP perturbation theory described above is based on the non-diagonal  $H^0$  operator and the first-order wavefunction must be determined iteratively in order to avoid solving a large system of equations. There is no problem with convergence and usually 6 steps are enough to reach the accuracy of  $10^{-6}$  for the coefficient vector  $C$  in Eq. (8). However, it would not be needed at all if only the diagonal terms of  $f$  were included in  $F$  defining  $H^0$ .

Truncation of the Fock operator to a diagonal form [33, 45, 46] is an attractive idea since it simplifies the whole procedure. However, the question about the importance of non-diagonal terms appears.

We have performed the calculations of the potential energy curve of the HF molecule with both a non-diagonal and diagonal  $f$ . The results are presented in Table 1. At a very short distance the non-diagonal Fock operator gives more correlation energy than the diagonal one. Around the minimum (0.917 Å) the second-order energies are almost the same in both cases, and then, at the larger H–F separations, the potential curve corresponding to the diagonal  $f$  lies below that with a full operator. The off-diagonal Fock elements shift the potential curve of HF to the shorter internuclear distances. This is, however, not a general trend. In the case of BH for instance, the energy obtained with a full  $f$  is always lower than the one with a diagonal approximation. Table 1 shows an artificial effect: the very flat maximum on the potential curve at the large distance when the diagonal Fock operator is used.

The influence of the off-diagonal elements of the Fock operator on the equilibrium bond length and dipole moment of HF is significant as it may be seen in Table 2. First of all there is quite a difference in the equilibrium bond lengths being 0.0072 Å for the larger 6-311+ +(3df, 3pd) basis set. It makes *Re*,

**Table 1.** Non-diagonality of the Fock operator in GVB MP2. Potential energy curves for the HF molecule with full and diagonal  $f^a$ 

$R$ (Å)	GVB energy (a.u.)	GVB MP2 energy full	diagonal
6-311 (d, p) basis set			
0.667	-99.93177807	-100.14600330	-100.14325738
0.717	-99.99477836	-100.20956460	-100.20741101
0.767	-100.03388549	-100.24906321	-100.24906328
0.817	-100.05634173	-100.27173588	-100.27173599
0.867	-100.06720080	-100.28263748	-100.28257239
0.917	-100.07002283	-100.28533104	-100.28596373
0.967	-100.06733920	-100.28235142	-100.28362387
1.017	-100.06096377	-100.27551596	-100.27734130
1.517	-99.95947865	-100.16218360	-100.16469639
2.017	-99.90904592	-100.09843786	-100.09953473
3.017	-99.89378538	-100.07744308	-100.07815476
4.017	-99.89325465	-100.07667768	-100.07739081
8.017	-99.89322848	-100.07663621	-100.07735318
15.017	-99.89322848	-100.07663616	-100.07735359
25.017	-99.89322848	-100.07663616	-100.07735366
35.017	-99.89322848	-100.07663615	-100.07735367
50.017	-99.89322848	-100.07663615	-100.07735367
6-311+ +(3df, 3pd) basis set			
0.667	-99.94354437	-100.21612070	-100.21205694
0.767	-100.04492715	-100.31829791	-100.31545132
0.817	-100.06729980	-100.34096106	-100.33887646
0.867	-100.07814983	-100.35198209	-100.35071010
0.917	-100.08100018	-100.35485409	-100.35439901
0.967	-100.07834675	-100.35205908	-100.35237530
1.017	-100.07196871	-100.34537590	-100.34638066
1.517	-99.96711296	-100.22838464	-100.23091479
2.017	-99.91375792	-100.15712164	-100.15822580
3.017	-99.89752825	-100.13182968	-100.13264120
4.017	-99.89694013	-100.13077695	-100.13160872
8.017	-99.89690159	-100.13068152	-100.13152066
15.017	-99.89690158	-100.13068107	-100.13152085
25.017	-99.89690158	-100.13068107	-100.13152094
35.017	-99.89690158	-100.13068107	-100.13152095
50.017	-99.89690158	-100.13068107	-100.13152096

<sup>a</sup> In all calculations the Pople's triple-zeta-type basis sets have been used (see J Chem Phys 80:3265 (1984)). All electrons in the HF molecule have been correlated

compared to the experimental value of 0.9168 Å, longer by 0.0047 Å for diagonal  $f$ , while with a full  $f$  it is too short only by 0.0025 Å. Thus, the error in  $R_e$  is almost twice as big and has the opposite sign if the Fock operator is truncated to a diagonal form. At the equilibrium geometries corresponding to a full and diagonal  $f$  the values of the dipole moment differ by about 0.030 Debye with both small and large basis sets. Again the larger basis set result is closer to the experimental value with a full  $f$  than with a diagonal one. With a large basis set at  $R_e = 0.9143$  Å the contribution from off-diagonal elements of  $f$  is equal to



**Table 2.** Non-diagonality of the Fock operator in GVB MP2. The equilibrium bond length ( $R_e$ ), dissociation energy ( $De$ ) and dipole moment ( $Dm$ ) of the HF molecule<sup>a</sup>

Method	$R_e$ (Å)	$De$ (kJ/mol)	$Dm$ (Debye)
6-311 (d, p) basis set			
GVB	0.9143	464.19	1.890
GVB MP2 (diag)	0.9184	547.71	1.874
GVB MP2 (full)	0.9127	547.99	1.903 (1.866) <sup>b</sup>
6-311+ +(3df, 3pd) basis set			
GVB	0.9147	483.37	1.823
GVB MP2 (diag)	0.9215	585.22	1.799
GVB MP2 (full)	0.9143	588.59	1.833 (1.789) <sup>b</sup>
experiment <sup>c</sup>	0.9168	590.8	1.819

<sup>a</sup> Dipole moment has been evaluated by numerical differentiation of the energy with respect to the external electric field

<sup>b</sup> Neglecting off-diagonal elements of the Fock operator

<sup>c</sup> From: Huber KP, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand Reinhold, NY

0.044 Debye. This significantly reduces the error from  $-0.30$  to  $+0.014$  Debye compared to the experimental value of 1.819 Debye. The dipole moment of HF as a function of the H-F separation for both a non-diagonal and diagonal  $f$  is shown in Table 3. In both cases the dynamical electron correlation shifts the maximum of these functions to the longer internuclear distances. At large distances, when there is essentially no interaction between the separated atoms, the use of a diagonal  $f$  leads to evidently wrong (too high) values of the dipole moment.

The dissociation energy of HF is only slightly affected by non-diagonality of  $f$ . However, the results in Table 2 show that the use of the full Fock operator is again preferable. An excellent agreement with experiment might be noted here: the dissociation energy obtained from GVB MP2/6-311+ +G(3df, 3pd) calculations is too low only by 2.2 kJ/mol (e.g.  $\sim 0.5$  kcal/mol). It should be emphasized, however, that even with very large basis sets, there is quite significant basis set superposition error in HF [47], which balances the remaining correlation error. The very good agreement between the GVB-MP2 and experimental values of the dissociation energy may be a result of error cancellation like in the ordinary MP PT [47].

#### 4. Correlation effects in terms of different excitations

In the earlier attempt to formulate MP PT for the CAS SCF wavefunction by Roos et al. [33] only one type of excitations has been included, namely the external ones. The results, however, were not very encouraging, especially for dissociation energies. It was pointed out [33] that the lack of semi-internal substitutions is responsible for this. That conclusion has been fully confirmed by Werner [48] who showed that these excitations were very important for correct description of a potential surface.

**Table 3.** Non-diagonality of the Fock operator in GVB MP2. The dipole moment of HF as a function of the internuclear distance (6-311G+ +(3df, 3pd) basis set)

$R$ (Å)	Dipole moment (Debye)		
	GVB	GVB MP2 full	GVB MP2 diag
0.767	1.618	1.599	1.577
0.817	1.690	1.677	1.646
0.867	1.760	1.757	1.718
0.917	1.826	1.837	1.792
0.967	1.886	1.918	1.870
1.017	1.939	1.999	1.952
1.117	2.017	2.154	2.121
1.317	2.018	2.385	2.401
1.417	1.927	2.424	2.461
1.517	1.779	2.386	2.435
1.617	1.587	2.265	2.316
1.717	1.371	2.069	2.114
2.017	0.755	1.278	1.300
3.017	0.056	0.088	0.136
4.017	0.008	0.009	0.079
5.017	0.003	0.003	0.090
7.017	0.001	0.001	0.124

In our perturbation approach all three types of excitations are included. We have performed the calculations for hydrogen fluoride which show how important they are for the dissociation energy and dipole moment. The results obtained with the small 6-311G(d, p) and large 6-311G+ +(3df, 3pd) basis sets are presented in Table 4.

As one could expect, the dynamical electron correlation energy is dominated by contribution from the external excitations. At the equilibrium geometry of HF for a given basis set, they constitute about 80% of the total MP2 energy, while the semi-internals contribute only ~20%. However, increasing the internuclear distance to infinity, the total contribution from the semi-internals decreases by more than half, while those from the externals only by about 6%. Finally, the difference  $E^2(R_{\infty}) - E^2(R_e)$ , i.e., the dynamical correlation part of the dissociation energy, contains twice as much contributions from the semi-internals as from the externals (in the larger basis set). Thus, the semi-internal excitations are essential for the dissociation process.

The dynamical electron correlation has only an insignificant effect on the dipole moment of HF. The value obtained at the GVB/6-311G+ +(3df, 3pd) level is very close to the experimental one (see Table 2). It is important, however, to realize that this small effect is a result of cancellation of different contributions with an opposite sign. Indeed, for the large basis set, the internals and semi-internals give the contribution of +0.120 Debye. On the other hand, the external excitations contribute as much as -0.130, giving the final result equal to only -0.010 Debye, as shown in Table 4. In this case, the reference dipole moment (from GVB) is equal to 1.823 Debye. The neglect of the semi-internal (and

**Table 4.** Dynamical electron correlation contributions from different excitations to the correlation energy, dissociation energy, and dipole moment. The HF molecule at the equilibrium geometry:  $R_e = 0.9127 \text{ \AA}$  for 6-311G(d, p),  $R_e = 0.9143 \text{ \AA}$  for 6-311G+ + (3df, 3pd)

	Dynamical electron correlation contributions			Total MP2
	Internal	Semi-internal	External	
correlation energy (in a.u.):				
6-311 (d, f)	-0.00085577 (0.4%)	-0.04559891 (21.2%)	-0.16887112 (78.4%)	-0.21532580 (100%)
6-311+ + (3df, 3pd)	-0.00081374 (0.3%)	-0.04984585 (18.2%)	-0.22319725 (81.5%)	-0.27385685 (100%)
dissociation energy (in kJ/mol):				
6-311 (d, p)	2.25 (2.7%)	70.22 (83.8%)	11.34 (13.5)	83.80 (100%)
6-311 (3df, 3pd)	2.14 (2.0%)	67.50 (64.2%)	35.58 (33.8)	105.22 (100%)
electronic dipole moment (in Debye):				
6-311 (d, p)	+0.009	+0.073	-0.095	-0.013
6-311+ + (3df, 3pd)	+0.009	+0.111	-0.130	-0.010

internal) contributions would increase the total dipole moment from 1.833 to 1.953 Debye, which is much too high compared to the experimental value of 1.819 Debye.

## 5. Discussion

This paper discusses the problem of non-diagonality of the Fock operator which is introduced in our perturbation theory for the MC SCF reference state. It has been shown that the off-diagonal elements of  $f$  are very important for the bond length and dipole moment of HF. In this case, an external perturbation (a change in a bond distance or an electric field) can rotate orbitals, moving some contributions from diagonal to off-diagonal terms.

Another problem considered in this paper concerned the importance of different excitations in the GVB-MP2 correlation treatment. It has been shown that the semi-internal excitations are essential for correct description of a potential surface. Indeed, their contributions to the dissociation energy of HF constitute over 60% of the total second-order correlation correction in the larger basis set limit. With a smaller basis set they are even more important.

Although the dipole moment of HF at the equilibrium geometry is not affected significantly by a dynamical correlation, all three kinds of excitations are still very important. That is because their quite significant contributions have the opposite sign and cancel each other, giving a very small final effect.

The results presented in Table 2 concern the equilibrium properties of the HF molecule obtained with two basis sets of very different quality. It is interesting, however, to examine the changes appearing in results when the quality of the basis set improves systematically. For this purpose we have performed a series of calculations with the different basis sets from 6-311G(d, p) to 6-311G+ + (3df, 3pd). The full, non-diagonal Fock operator has been used in the GVB MP2 method.

**Table 5.** Basis set dependence of the equilibrium bond lengths ( $R_e$ ) dissociation energies ( $D_e$ ) and dipole moment for HF in GVB MP2

Basis set	Method	Energy (a.u.)	$R_e$ (Å)	$D_e$ (kJ/mol)	$D_m$ (Debye)
6-311 (d, p)	GVB GVB MP2	-100.07003020 -100.28535273	0.9143 0.9127	464.19 547.99	1.890 1.903
6-311 (2d, p)	GVB GVB MP2	-100.07091487 -100.30844491	0.9160 0.9172	466.46 550.10	1.850 1.887
6-311 (2d, 2p)	GVB GVB MP2	-100.07295313 -100.31309303	0.9140 0.9137	471.81 562.31	1.804 1.801
6-311++ (d, p)	GVB GVB MP2	-100.07629289 -100.29678418	0.9156 0.9157	472.96 562.77	1.938 1.970
6-311++ (df, pd)	GVB GVB MP2	-100.07899968 -100.32558281	0.9155 0.9123	478.26 583.96	1.921 1.941
6-311++ (2df, pd)	GVB GVB MP2	-100.07923267 -100.34568161	0.9167 0.9175	478.80 579.05	1.900 1.951
6-311++ (2df, 2pd)	GVB GVB MP2	-100.08008997 -100.34770154	0.9155 0.9155	481.05 584.35	1.847 1.863
6-311++ (3df, 2pd)	GVB GVB MP2	-100.08067676 -100.35417727	0.9149 0.9148	482.50 586.79	1.828 1.851
6-311++ (3df, 3pd)	GVB GVB MP2	-100.08100585 -100.35486249	0.9147 0.9143	483.37 588.59	1.823 1.833

The results presented in Table 5 demonstrate an almost smooth convergence of the dissociation energy at both the GVB and GVB MP2 levels. In this case the dynamical correlation always improves the GVB results and for the largest basis set employed yields a very good final value.

In contrast, results for the bond length and dipole moment of HF already accurate at the GVB level, are slightly deteriorated by the second-order correlation even for the largest 6-311G++(3df, 3pd) basis set. The second-order dynamical correlation increases the dipole moment of HF which is already too high at the GVB level, while the value of the bond length oscillates.

Further extension of the basis set by addition of the fourth set of  $d$  functions on the fluorine atom brings an improvement in the GVB MP2 treatment. The bond length of HF changes from 0.9150 Å of the GVB value to 0.9153 Å of GVB MP2, and dipole moment from 1.810 (GVB) to 1.820 Debye (GVB-MP2). The latter agrees very well with the experimental value of 1.819 Debye.

It should be stressed, however, that both a dissociation energy and dipole moment are calculated here as two-point energy differences and the very good agreement between the GVB MP2 and experimental values follows from a cancellation of errors. The equilibrium bond length of HF, as a one-point energy calculation, is still affected by an error.

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