

Letter

Multireference perturbation CI III. Fast evaluation of the one-particle density matrix

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Abstract. Within the frame of multireference perturbation configuration interaction we have developed a fast algorithm, based on diagrammatic techniques, for the calculation of the first-order correction to the one-particle density matrix. As an example of an application we have chosen the evaluation of the dipole moment of the CO molecule, where utilization of the first-order density is shown to corroborate the variational calculation.

Key words: Multireference configuration interaction – Perturbation configuration interaction

1 Introduction

Multireference perturbation configuration interaction (CI) methods have become quite common in quantum chemistry over the years since the pioneering work of many researchers in the early 1970s [1, 2]. Basically such methods rely on a good zero-order description carried out variationally at the level of a CI or a multiconfiguration self-consistent field (MC-SCF) calculation, followed by perturbation treatment usually truncated to the second-order in energy. The choice of zero-order variational space is usually performed either on the basis of a predefined excitation level, such as singles and doubles CI (SDCI) [3], or on the basis of the choice of a complete active space (CAS-SCF) [4] or of a selection procedure to build up the determinant space [2]. In this last case our group has been active recently in the implementation of fast diagrammatic techniques for the evaluation of the perturbational contribution to the energy [5, 6] as well as in devising new techniques for a better selection procedure and extrapolation to large determinantal spaces [7, 8]. Relatively little attention has been

devoted to the setting up of fast codes for the evaluation of the one-particle density matrices calculated to the first-order of perturbation theory. Such matrices are essential tools for the evaluation of one-electron state and transition properties as well as for the determination of well-approximated natural orbitals (NOs) [9]. Since the variational spaces currently in use in perturbation CI can be of considerable size, reaching some tens of thousands of determinants, the question of resorting to fast techniques for the evaluation of the density matrices is acquiring relevance. It is the purpose of this note to expose the main lines which have led us to efficient implementation, based on diagrammatic techniques, of the first-order perturbation evaluation of the one-particle density matrices.

The rest of this paper will be devoted to the description of the calculation methodology that we have adopted and to the illustration of an example calculation relating to the CO molecule.

2. Method

The basic definitions for the one-particle density matrices between electronic states Ψ_m and Ψ_n can be summarized by the following equation

$$\begin{aligned} {}^{mn}\rho(1; 1') &= N \int \Psi_m(1, 2, \dots, N) \Psi_n^*(1', 2, \dots, N) d\tau_2 \dots d\tau_n \\ &= \sum_{ij} {}^{mn}\rho_{ij} \psi_i(1) \psi_j^*(1'), \end{aligned} \quad (1)$$

where the ψ_i 's are a complete set of orthonormal spin-orbitals. From the definition we have the hermitian property

$${}^{mn}\rho_{ij} = {}^{nm}\rho_{ji}^* \quad (2)$$

If the annihilation (creation) operators associated with the ψ_i 's are indicated by a_i (a_i^\dagger), the quantities ${}^{mn}\rho_{ij}$ are given by

$${}^{mn}\rho_{ij} = \langle \Psi_n | a_j^\dagger a_i | \Psi_m \rangle \quad (3)$$

If the wavefunctions for states m and n are expanded on the determinant space $\{|M\rangle\}$ built on the spin-orbitals ψ_i 's, i.e.,

$$\Psi_m = \sum_M C_M^m |M\rangle \quad (4)$$

and analogously for Ψ_n , we obtain the formula

$${}^{mn}\rho_{ij} = \langle \Psi_n | a_j^\dagger a_i | \Psi_m \rangle = \sum_{M,N} C_M^m C_N^{*n} \langle N | a_j^\dagger a_i | M \rangle \quad (5)$$

The case we are interested in concerns wavefunctions which consist of a first component given by a variational expansion such as in Eq. (4) and of a first-order perturbational correction:

$$\Psi_m = \Psi_m^{(0)} + \Psi_m^{(1)}.$$

The density matrix including first-order will accordingly consist of two terms

$${}^{mn}\rho_{ij} = {}^{mn}\rho_{ij}^{(0)} + {}^{mn}\rho_{ij}^{(1)},$$

with ${}^{mn}\rho_{ij}^{(0)}$ identical to the expression in Eq. (5) and the first-order contribution given by

$${}^{mn}\rho_{ij}^{(1)} = \langle \Psi_n^{(1)} | a_j^\dagger a_i | \Psi_m^{(0)} \rangle + \langle \Psi_n^{(0)} | a_j^\dagger a_i | \Psi_m^{(1)} \rangle. \quad (6)$$

(We recall that no contribution due to the normalization of the wavefunction shows up at first-order.) The first-order correction to the wavefunction is given by

$$\Psi_m^{(1)} = \sum_{K \notin \mathcal{S}} |K\rangle \frac{\langle K | \hat{\mathcal{H}} | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_K^{(0)}}, \quad (7)$$

where \mathcal{S} denotes the set of determinants used in the expansion of $\Psi_m^{(0)}$, and $E_m^{(0)}$ and $E_K^{(0)}$ designate the zero-order energies associated with $\Psi_m^{(0)}$ and $|K\rangle$; such energies derive from the choice of the zero-order Hamiltonian which we have imposed to be either of Møller–Plesset baricentric-type [2, 10] or Epstein–Nesbet-type [11, 12]; for further details on the zero-order Hamiltonian the reader is referred to Ref. [6] and to the references quoted therein.

The explicit formula for the first-order correction to the density matrices is easily derived as:

$${}^{mn}\rho_{ij}^{(1)} = \sum_{K \notin \mathcal{S}} \frac{\langle \Psi_n^{(0)} | \hat{\mathcal{H}} | K \rangle \langle K | a_j^\dagger a_i | \Psi_m^{(0)} \rangle}{E_n^{(0)} - E_K^{(0)}} + \sum_{K \notin \mathcal{S}} \frac{\langle \Psi_n^{(0)} | a_j^\dagger a_i | K \rangle \langle K | \hat{\mathcal{H}} | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_K^{(0)}}. \quad (8)$$

From this formula it can immediately be seen that the diagonal elements ${}^{mn}\rho_{ii}^{(1)}$ vanish. Since the zero-order wavefunctions are of multireference-type, the two terms of the preceding equation can be written as:

$$\sum_{K \notin \mathcal{S}} \frac{\langle \Psi_n^{(0)} | \hat{\mathcal{H}} | K \rangle \langle K | a_j^\dagger a_i | \Psi_m^{(0)} \rangle}{E_n^{(0)} - E_K^{(0)}} = \sum_{M,N \in \mathcal{S}} C_M^m C_N^{*n} \sum_{K \notin \mathcal{S}} \frac{\langle N | \hat{\mathcal{H}} | K \rangle \langle K | a_j^\dagger a_i | M \rangle}{E_n^{(0)} - E_K^{(0)}}, \quad (9)$$

$$\sum_{K \notin \mathcal{S}} \frac{\langle \Psi_n^{(0)} | a_j^\dagger a_i | K \rangle \langle K | \hat{\mathcal{H}} | \Psi_m^{(0)} \rangle}{E_m^{(0)} - E_K^{(0)}} = \sum_{M,N \in \mathcal{S}} C_M^m C_N^{*n} \sum_{K \notin \mathcal{S}} \frac{\langle N | a_j^\dagger a_i | K \rangle \langle K | \hat{\mathcal{H}} | M \rangle}{E_m^{(0)} - E_K^{(0)}}. \quad (10)$$

The summation over K can be efficiently carried out using diagrammatic techniques following the same lines as adopted in the evaluation of the second-order correction to the energy [5]. In the summations over K in Eqs. (9) and (10), determinant $|M\rangle$ is assumed to be a provisional vacuum state, thus leading to the first-order diagrams shown in Fig. 1. We have adopted the antisymmetrized diagrams of Brandow [13], indicating with X the one-particle interaction and with a small square the density matrix operator $a_a^\dagger a_i$. The “diamond” symbols which are present in part of the diagrams represent the excitations which define determinant $|N\rangle$ with respect to $|M\rangle$ in Eqs. (9) and (10). For example, the formula corresponding to the first diagram of Fig. 1 gives the contribution $F_{ai}/(E_m^{(0)} - E_K^{(0)})$. Since the definition of the Fock matrix is referred

to determinant $|M\rangle$ which is assumed to be a provisional vacuum, a redefinition of particles and holes is necessary for each occurrence of $|M\rangle$. Such an operation is very quickly done by adding/subtracting the two electron contributions related to the particles/holes defining $|M\rangle$ with respect to the true Fermi vacuum

$$F_{rs} \leftarrow F_{rs} + \sum_{p \in M} \langle pr || ps \rangle - \sum_{h \in M} \langle hr || hs \rangle. \quad (11)$$

The sign of each diagram is given by the usual $(-1)^{h+l}$ rule with h and l designating the number of hole lines and loops, respectively. The denominators which are implied in the diagrams, $(E_m^{(0)} - E_K^{(0)})$, can always be expressed in terms of quantities depending only on the spin-orbital labels of the holes and particles defining determinant $|K\rangle$ with respect to $|M\rangle$. In the Møller–Plesset definition of the zero-order Hamiltonian, the denominators are simply formulated in terms of suitable orbital energies whereas in the Epstein–Nesbet case one needs a somewhat more laborious expression; so, for instance, in the case of a double excitation with respect to $|M\rangle$ we have for the energy of $|K\rangle$

$$E_K^{(0)} = \langle M | \hat{\mathcal{H}} | M \rangle + e'_a + e'_b - e'_i - e'_j + \langle ij || ij \rangle + \langle ab || ab \rangle - \langle ia || ia \rangle - \langle ib || ib \rangle - \langle ja || ja \rangle - \langle jb || jb \rangle$$

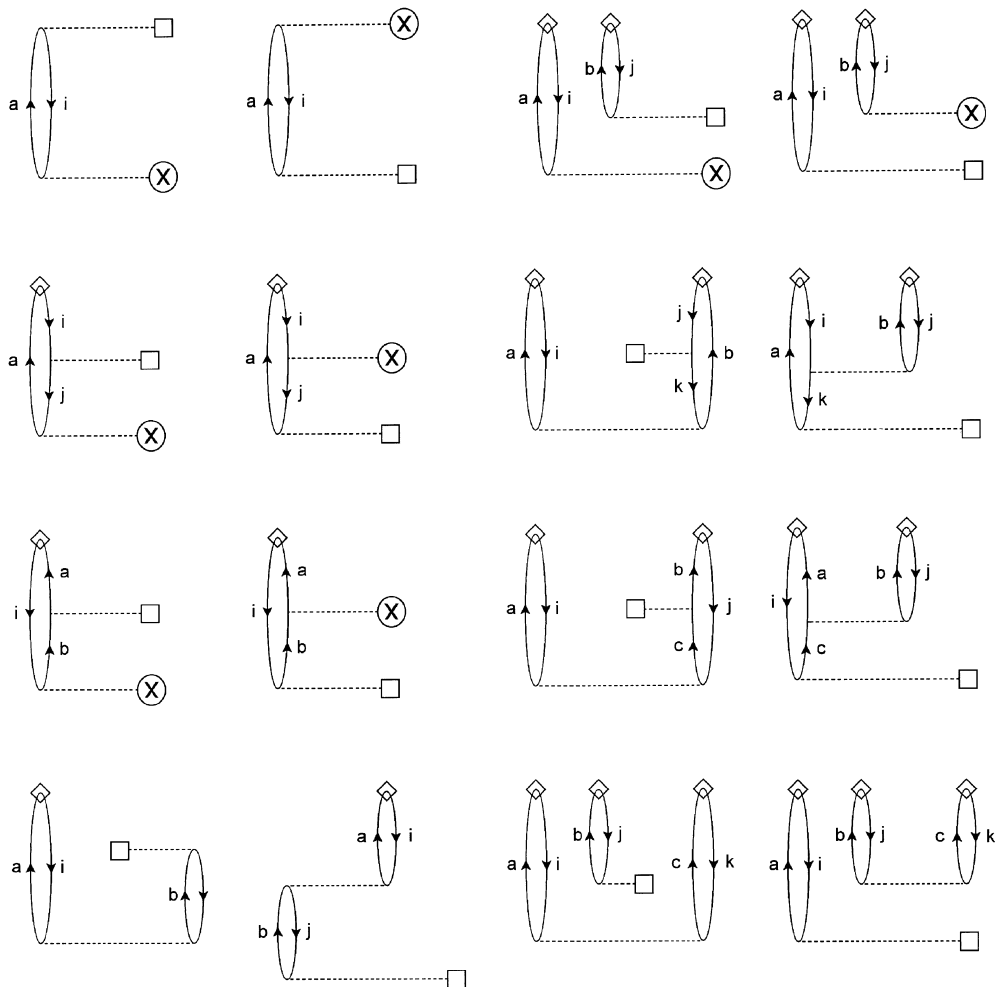
where the orbital energies e' are referred to the Fock operator defined with respect to the $|M\rangle$ determinant and where we have adopted the antisymmetrized notation for the bielectronic integrals ($\langle rs || tu \rangle = \langle rs | tu \rangle - \langle rs | ut \rangle$).

3 Test case: the CO dipole

As a test case we have considered the calculation of the electric dipole (μ) of the CO molecule. A large amount of work has been done on this system since the Hartree–Fock (HF) calculation of Nesbet [14] (for a recent review see Ref. [15]). It is well-known that for correct estimation of μ a good-quality one-electron basis set and a high-level correlation treatment are needed. For these reasons we have chosen this system as a test case. As we will see, the new diagrammatic implementation will allow us to use variational spaces with dimensions up to 100,000 determinants with reasonable processing time (all the calculations were performed on a 300 MHz Pentium II PC). The speed-up gained by the diagrammatic implementation increases with the dimension of the \mathcal{S} space and the molecular basis set. In the case of the CO molecule with spaces of a few thousand determinants in the extended basis set (see later) we observe an increase of several orders of magnitude in the efficiency ratio. In the most demanding calculation, the processing time is around one hour with the new method, whereas it would not even be feasible with the traditional code based on the explicit generation of perturbation determinants. With larger molecular systems the efficiency gain would improve further as in the case of the application of the diagrammatic techniques to the energy [5, 6].

The method proposed in this paper is obviously applicable to all the cases which can be dealt with by the energy diagrammatic technique, representing just a small fraction of the latter in terms of computation time. The diagrammatic technique for the energy has been widely applied to medium-sized molecules; we shall limit ourselves to citing just a couple of the calculations carried out in our laboratory, referring to sulfur-containing molecules and azobenzenes [16, 17].

Fig. 1. First-order diagrams involved in the calculation of ${}^{mn}\rho_{ia}^{(1)}$. The Fock operator defined with respect to determinant $|M\rangle$ (vacuum state) is represented by the symbol X in a circle, while the interaction due to the density matrix operator $a_a^+ a_i$ is represented by a square. The diamonds indicate the degree of excitation of $|N\rangle$ with respect to $|M\rangle$: no diamonds $\rightarrow |N\rangle = |M\rangle$, diagonal contribution; one diamond $\rightarrow |N\rangle$ is a single excitation with respect to $|M\rangle$, etc. The orbitals involved in the excitation are indicated by the lines going into and out from the diamonds. The sign of each diagram is given by the usual $(-1)^{h+l}$ rule with h and l designating the number of hole lines and loops, respectively



Let us note that when a multireference perturbation CI method is used, the electric dipole is usually calculated as the first-order derivative of the energy with respect to the electric field (μ_F), rather than as the expectation value of the perturbation corrected wavefunction (μ_{wf}) as in our case. The two approaches can give rather different results: in the case of HF + MP2, the first-order correction to μ vanishes in our approach due to the Brillouin theorem, while the correction to μ_{HF} is in general non-zero using the energy derivative. In the evaluation of $\rho^{(1)}$ (see Eqs. 9 and 10) only single excitations with respect to \mathcal{S} have to be taken into account, while in energy derivatives double excitations also contribute. On the other hand the calculation of $\rho^{(1)}$ is faster than the calculation of the second-order correction to the energy (needed for energy derivatives) and allows calculation of all the one-electron properties of interest.

We have used two different one-electron basis sets: the 6-31G* basis of Binkley et al.[18], which is usually assumed to provide acceptable requisites for the treatment of electron correlation, and the one designated “basis III” in Ref. [19] (designated hereafter “extended basis”) as an example of a large and more flexible basis. This extended basis consists of the (13s,8p) primitive set of van Duijneveldt [20] contracted to [8s,5p] with a set of four d functions and a set of f functions added to each atom (see Ref. [19] for more details). The two basis sets

contain 28 and 100 functions respectively (spherical harmonics are used for d and f functions). All the calculations were performed at the experimental equilibrium geometry ($R_e = 2.1322a_0$ [21]). The molecular orbitals are the natural orbitals of a CAS-SCF wavefunction (CAS-NOs). The CAS-CI space is obtained by sharing the eight valence electrons among the ten valence orbitals, and consists of 328 configuration state functions. The \mathcal{S} spaces are selected following the strategy reported in Ref. [2, 8] starting from a closed-shell determinant.

For comparison we have computed μ also using the energy derivative technique, resorting to a finite difference approach with two uniform electric fields (F) of ± 0.001 a.u., according to the following formula:

$$\mu_F = -\frac{\partial E}{\partial F} = -\frac{E(F_+) - E(F_-)}{F_+ - F_-} + O(|F|^3) \quad (12)$$

In order to verify that with a field intensity of 0.001 a.u. the second-order terms (contribution of polarizability to dipole) are negligible, we have compared μ_{wf} and μ_F at the CAS-SCF level. Indeed, as the CAS-SCF wavefunction is fully optimized with respect to orbital and coefficient rotations, the two approaches must give the same result if the second-order terms are negligible. A comparison shows that for both basis sets our field

Table 1. Convergence behaviour of energy and μ with respect to the dimension of \mathcal{S} ($\#\mathcal{S}$) for CO using two different basis sets. For comparison we also report the results obtained using energy derivatives with respect to the electric field (μ_F , see text). The

$\#\mathcal{S}$	Energy				μ_{wf}			μ_F	
	var	EN	MPB	var	EN	MPB	var	EN	MPB
6-31G* basis set, CAS-NOs (see text)									
1	-112.732930	-113.030467	-113.148445	-0.04693	0.16008	0.08395	0.12884	-0.14510	-0.40668
115	-112.907675	-113.015560	-113.032814	-0.10385	-0.09077	-0.09592	-0.03421	-0.04574	-0.04872
1395	-113.001394	-113.028814	-113.032984	-0.08216	-0.05911	-0.05968	-0.03307	-0.04359	-0.04500
10204	-113.022411	-113.031962	-113.033531	-0.05184	-0.04385	-0.04399	-0.03838	-0.03942	-0.03983
40317	-113.027609	-113.032790	-113.033610	-0.04107	-0.03942	-0.03970	-0.04001	-0.03820	-0.03804
62002	-113.028691	-113.032969	-113.033642	-0.03982	-0.03841	-0.03863	-0.04001	-0.03803	-0.03783
extended basis, CAS-NOs (see text)									
16	-112.899997	-113.145616	-113.180642	-0.12980	-0.14853	-0.14821	0.10379	-0.16560	-0.44842
153	-112.942192	-113.152229	-113.173163	-0.14246	-0.13950	-0.14268	0.00238	-0.08157	-0.08684
613	-112.987494	-113.157600	-113.170954	-0.13167	-0.11184	-0.11527	-0.11029	-0.08020	-0.06696
13705	-113.124456	-113.170931	-113.173979	-0.06956	-0.06050	-0.06027	-0.06773	-0.08082	-0.08170
35857	-113.145299	-113.172797	-113.174839	-0.06636	-0.06147	-0.06208	-0.05799	-0.07130	-0.07362
86179	-113.154312	-113.173694	-113.175107	-0.06744	-0.06538	-0.06588	-0.06316	-0.07108	-0.06911

intensity is correct: 6-31G* basis $\rightarrow \mu_{wf} = -0.10915$, $\mu_F = -0.10914$; extended basis $\rightarrow \mu_{wf} = -0.13549$, $\mu_F = -0.13548$ (dipole in a.u.).

Inspection of Table 1 shows that for the 6-31G* basis the iterative process leading to the improvement of the \mathcal{S} space reaches a satisfactory degree of convergence both for the energy and for the dipole moment; the Møller–Plesset and Epstein–Nesbet results are close to each other and the finite-difference values for the dipole are in very good accordance with those calculated with the density matrix. With this relatively small basis set the perturbation results can be safely judged as close to the full CI limit, as can be seen from the agreement between the two perturbation partitions, both for the energy and for the dipole moment.

Similar remarks can also be made for the extended basis results where, due to the much larger dimension of the orbital basis, convergence in the energy and in the dipole is more difficult to obtain. In both bases the first-order correction to the one-particle density matrix improves the zero-order results but not enough to affect the convergence behaviour and to allow the use of \mathcal{S} spaces of small dimension. As to the accordance with experiment of the results obtained with the two basis sets, neither the 6-31G* basis nor the extended basis seems to be able to correctly describe the electric dipole. The absolute difference from the experimental value is actually very small in magnitude (≈ 0.01 a.u. for the 6-31G* basis and ≈ 0.02 a.u. for the extended basis), but further work is needed to study the convergence behaviour of μ with respect to the basis set. Ernzerhof et al. [23] have also compared μ_{wf} and μ_F for the CO molecule using MRSDCI and averaged coupled pair functional methods and have shown that the nature of the MOs is crucial for the efficient convergence of both procedures.

From Figs. 2 and 3 the results obtained with the finite-difference approach (μ_F) appear to be somewhat more stable with respect to μ_{wf} . This is not surprising if one considers the important role played by double excitations from the \mathcal{S} space. The first-order density

behaviour of μ is also presented in Figs. 2 and 3: here we report only a selection of calculations. EN represents the use of an Epstein–Nesbet type Hamiltonian, while MPB represents a Møller–Plesset baricentric-type Hamiltonian. Energies and electric dipoles in a.u.

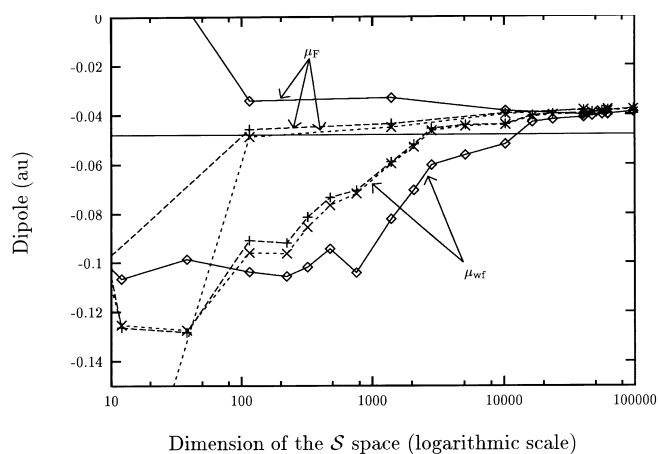


Fig. 2. Convergence behaviour of μ with respect to the dimension of \mathcal{S} using the 6-31G* basis. *Diamonds* \rightarrow zero-order, “+” \rightarrow first-order Møller–Plesset baricentric, “ \times ” \rightarrow first-order Epstein–Nesbet. The horizontal full line represents the experimental value of μ (-0.0484 a.u. [22])

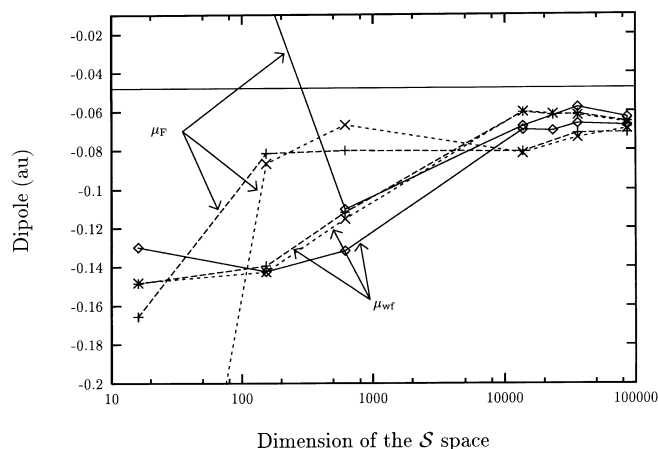


Fig. 3. The same as in Fig. 2, but using the extended basis

matrix only implies single excitations from \mathcal{S} and such contributions are usually small with respect to those of double excitations which on the contrary contribute to $\rho^{(2)}$. We are planning to implement the calculation of $\rho^{(2)}$ to verify this statement.

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