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Second-Order Møller−Plesset Analytical Derivatives for the Polarizable Continuum Model Using the Relaxed Density Approach

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We present a method for evaluating second-order Moller−Plesset (MP2) energy and gradients for solvated molecules described within the polarizable continuum model (PCM). The explicit inclusion of solvent effects into the evaluation of the relaxed MP2 density through the *Z*-vector technique is reported and analyzed. Applications to some one-electron response properties (dipoles, electrostatic molecular potentials, electric field gradients) as well as nuclear gradients are presented.

1. Introduction

In the past years, many important developments have made continuum solvation models the most versatile methods to include solvent effects into semiempirical and ab initio quantum chemistry.[1] In particular, large effort has been devoted to extend such models to quantum mechanical (QM) techniques of increasing accuracy. In this way, models originally limited to work at the Hartree−Fock (HF) level, can be now used in many post-SCF calculations. This computational extension has been accompanied by a reformulation of the various QM theories so as to include the specificities of the solvation model. Such requirement is particular pressing for those models in which an effective Hamiltonian (EH) is introduced. In this case, the solvent effects are added to the Hamiltonian $\hat{H}^0$ of the isolated molecule through a reaction potential operator depending on the solute wave function, $\hat{V}_R(\Psi)$; the resulting Schrödinger equation becomes nonlinear; namely, one obtains

$$[\hat{H}^0 + \hat{V}_R(\Psi)]\Psi = E\Psi \qquad (1)$$

In addition to a nonlinear character, the inclusion of the solvent also leads to define a new energy functional, the free energy G, to which the variation principle has to be applied. The difference between the eigenvalue E and the functional G is related to the work spent by the solute subsystem to distort the charge distribution of the solvent (polarization work), and thus the free energy expression is

$$G = \langle\Psi|\hat{H}^0 + {}^1/_2\hat{V}_R(\Psi)|\Psi\rangle \qquad (2)$$

The factor $^1/_2$ in eq 2 reflects the linearity in the polarization of the environment.

The recent evolution of EH methods is leading to very efficient computational codes, which reduce the complexity of the QM calculations in solution to that of the corresponding calculations in vacuo. There is of course the need of having efficient coupling between the two components, solvation and molecular QM description, and of using definitions of the interaction potential faithful and suitable for application at the various levels of the QM theory. In our opinion, the polarizable continuum model (PCM) we have developed in the past years[2,3] satisfies both requirements. With respect to other similar methods, the PCM has the great advantage of describing the solute potential field polarizing the solvent in an exact form, i.e., without the help of approximated and/or truncated expressions as those given in terms of multipole series. In addition, no restrictions have to be imposed on the form of the cavity enveloping the solute when immersed in the continuum dielectric medium. This can be in fact well modeled on the real geometry of the molecular system.

The PCM model has been largely modified over the past few years; in particular, two fundamental aspects have been completely revised: the technique exploited to solve the nonlinear QM problem[3] and the formulation of the basic system giving the expression of the electrostatic portion of the reaction potential $\hat{V}_R(\Psi)$. The latter revision has led to define a new and more general solvation model known as integral equation formalism (IEF-PCM).[4] In addition, many important extensions allowing the calculation of analytical derivatives of the free energy with respect to various parameters[5] (nuclear coordinates,[6,7] electric and magnetic fields,[8−10] etc.) and of the related molecular properties (vibrational frequencies, (hyper)polarizabilities, nuclear shieldings, etc.) have been realized. Here we present a different kind of extension related to the previously quoted efforts toward more accurate QM descriptions which take into account the effects of electron correlation in the solvation process. We recall that the solvent effects will be limited to the electrostatic contribution only; other interactions, of repulsive, dispersive, and steric nature, are completely neglected here; the latter are usually introduced into solvation models through techniques independent on the QM description of the system, for example by exploiting semiempirical expressions, and thus they have not to be taken into account in the QM reformulation of the model. Actually, examples of QM description of repulsion and dispersion effects have been recently formulated[11] in our group and introduced in the PCM effective

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Hamiltonian; here, however, we do not present any correlated correction to these contributions.

Electron correlation is more commonly introduced into solvent EH techniques using MCSCF and DFT methods. Both are implemented in recent and less recent versions of PCM,[12] and there are also numerous examples for other solvent EH procedures.[13,14] However, the perspective of treating solute electron correlation via perturbation theory approaches is tempting especially to enlarge the set of options to users asking for methods requiring reasonable computational costs.

Perturbation theory within solvation schemes has been originally considered by Tapia and Goscinski[15] at the CNDO level. An ab initio version of the Møller−Plesset perturbation theory was introduced years ago by Olivares et al.[16] following some intuitive considerations based on the fact that the electron correlation which modifies both the HF solute charge distribution and the solvent reaction potential depending on it can be back-modified by the solvent. To decouple these combined effects the authors introduced three alternative schemes: (1) the noniterative "energy-only" scheme (PTE), where the solvated HF orbitals are used to calculate MP*n* correlation correction; (2) the density-only scheme (PTD) where the vacuum MP*n* density matrix is used to evaluate reaction field; and (3) the iterative (PTED) scheme, where the correlated electronic density is used to make the reaction field self-consistent. As concerns the last scheme, some further comments are required.

The PTED scheme leading to a comprehensive description of the effects separately considered by PTD and PTE is rather cumbersome and not suited for the calculation of analytical derivatives, even at the lowest order of the MP perturbation theory. In addition, in an elegant theoretical paper Angyan[17] stressed that a rigorous application of the perturbation theory, in which the *n*th-order correction to the energy is based on the $(n - 1)$th-order density, the correct MP2 solute−solvent energy has to be calculated with the solvent reaction field due to the Hartree−Fock electron density.

In the following section we present a computational method, called PCM-MP2, in which no iterative procedures involving the electronic density corrected to second order, as those exploited in the PTED scheme, are introduced. As a consequence, the PCM-MP2 method has a structure which makes the analytical calculation of energy derivatives relatively easy. The central focus of the theory is then shifted to the evaluation of the relaxed MP2 density which is obtained within the *Z*-vector technique of Handy and Schaefer.[18] Such method is reformulated in section 3 so as to take into account solvent effects in the resulting coupled perturbed Hartree−Fock expression. As concerns MP2 gradients, further refinements arising from the derivatives of the primitive basis functions and from the derivative of the SCF orthogonality condition have been added still including the solvent contributions. Numerical applications to one-electron properties and to gradients are given in section 4. We remark that the examples we present are closed-shell molecules; but, in principle, the theory we have formulated can be extended to open-shell energies and gradients.

2. Basic Formulation of PCM-MP2 Free Energy

At the MP2 level, the free energy of the solvated system can be expressed as

$$\mathcal{G}^{\mathrm{MP2}} = \mathcal{G}^{\mathrm{HF}} + \mathcal{G}^{(2)} \tag{3}$$

where $\mathcal{G}^{\mathrm{HF}}$ is the Hartree−Fock (HF) contribution and $\mathcal{G}^{(2)}$ is the MP2 correction.

In a *N*-electron system described in terms of a single determinant with spin−orbitals expanded on a set of atomic orbitals (AO) $\{\chi_\mu, \chi_\nu, ...\}$, the HF free energy $\mathcal{G}^{\mathrm{HF}}$ is written as

$$\mathcal{G}^{\mathrm{HF}} = \sum_{\mu\nu} P^{\mathrm{HF}}_{\mu\nu}(h_{\mu\nu} + j_{\mu\nu}) + {}^{1}/_{2} \sum_{\mu\nu\lambda\sigma} P^{\mathrm{HF}}_{\mu\nu} P^{\mathrm{HF}}_{\lambda\sigma}[\langle\mu\lambda||\nu\sigma\rangle + \mathcal{B}_{\mu\nu,\lambda\sigma}] + \tilde{V}_{\mathrm{NN}} \tag{4}$$

where $h_{\mu\nu}$ are the matrix elements, in the AO basis, of the one-electron core operator and $\langle\mu\lambda||\nu\sigma\rangle$ are the antisymmetrized combination of regular two-electron repulsion integrals (ERIs).

The presence of solvent operators in the effective Hamiltonian is reflected here in the $j_{\mu\nu}$ and $\mathcal{B}_{\mu\nu,\lambda\sigma}$ integrals which describe the solute−solvent interactions within the PCM model; in particular, the former contain the term due to the nuclei-induced component of the solvent reaction field while the latter represent the electron-induced counterpart. In the PCM framework the solvent field is described in terms of "apparent" charges (in the following indicated as q) placed at the center of small regions (called tesserae) covering the surface of the cavity containing the molecular solute. In this framework both $j_{\mu\nu}$ and $\mathcal{B}_{\mu\nu,\lambda\sigma}$ are expressed in terms of products of these apparent or "induced" charges with the electrostatic potential due to the solute charge distribution. The detailed expressions defining the apparent charges as well as their interaction matrices can be found in ref 3 for the basic version of the model and in ref 4 for the last reformulation known as IEF-PCM. In the last term of eq 4, $\tilde{V}_{\mathrm{NN}}$ we include both solute nuclear repulsion and solute−solvent nuclear interaction.

The elements $P^{\mathrm{HF}}_{\mu\nu}$ of the HF density matrix are defined as

$$P^{\mathrm{HF}}_{\mu\nu} = \sum_{i}^{N} c_{\mu i} c_{\nu i} \tag{5}$$

where $c_{\mu i}$ are the expansion coefficients of molecular spin−orbitals. They are obtained by solving the corresponding HF equations:

$$\sum_{\nu} (\tilde{F}_{\mu\nu} - \epsilon_p S_{\mu\nu}) c_{\nu p} = 0 \tag{6}$$

where the elements $\tilde{F}_{\mu\nu}$ of the Fock matrix, namely

$$\tilde{F}_{\mu\nu} = (h_{\mu\nu} + j_{\mu\nu}) + G_{\mu\nu}(P^{\mathrm{HF}}) + X_{\mu\nu}(P^{\mathrm{HF}}) \tag{7}$$

contain the solvent effects in the already introduced matrix j and in the solvent-equivalent of the in vacuo two-electron matrix G; that is, we have

$$G_{\mu\nu} = \sum_{\lambda\sigma} P^{\mathrm{HF}}_{\lambda\sigma} \langle\mu\lambda||\nu\sigma\rangle \tag{8}$$

$$X_{\mu\nu} = \sum_{\lambda\sigma} P^{\mathrm{HF}}_{\lambda\sigma} \mathcal{B}_{\mu\nu,\lambda\sigma} \tag{9}$$

In eq 6 $S_{\mu\nu}$ are the elements of the overlap matrix in the AO basis and ϵ_p the energy of the *p*th spin−orbital. In the following the spin−orbitals obtained from eq 6 will be indicated as *i*, *j*, ... if occupied, *a*, *b*, ... if virtual, and *p*, *q*, ... when referring to general molecular orbitals.

The MP2 correlated contribution to the free energy thus becomes[16,17]

$$\mathcal{G}^{(2)} = {}^{1}/_{4} \sum_{ijab} t^{ab}_{ij} \langle ij||ab\rangle \tag{10}$$

where the double excitation amplitudes are given by

$$t_{ij}^{ab} = \langle ij||ab\rangle/(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \quad (11)$$

From eqs 3−11 it follows that solvent effects do not change the basic formalism leading to the final MP2 expression but they act at each step introducing new operators (and the related matrices) which modify all the involved quantities (MO coefficients, orbital energies, etc.) with respect to the parallel calculation for the isolated system.

3. Relaxed Density and Analytical PCM-MP2 Derivatives

Let us now consider the problem of determining the analytical first derivative of the PCM-MP2 free energy (3), namely

$$\mathsf{G}^{\mathrm{MP2},x} = \mathsf{G}^{\mathrm{HF},x} + \mathsf{G}^{(2),x} \quad (12)$$

We recall that the basis for much of the following work is represented by the key conceptual developments in analytical derivative theory for conventional, unsolvated calculations given in the articles we have collected in ref 19 and in those we shall explicitly quote below.

The basic theory of analytical PCM-HF free energy derivatives, $\mathsf{G}^{\mathrm{HF},x}$, has been formulated in previous papers;[5,6] here it is worth exploiting the following expression

$$\mathsf{G}^{\mathrm{HF},x} = \sum_{\mu\nu} P_{\mu\nu}^{\mathrm{HF}}(h_{\mu\nu}^x + j_{\mu\nu}^x) + {}^1/_2 \sum_{\mu\nu\lambda\sigma} P_{\mu\nu}^{\mathrm{HF}} P_{\lambda\sigma}^{\mathrm{HF}} [\langle\mu\lambda||\nu\sigma\rangle^x + \mathsf{B}_{\mu\nu,\lambda\sigma}^x] - \sum_{\mu\nu} S_{\mu\nu}^x W_{\mu\nu}^{\mathrm{HF}} + \tilde{V}_{\mathrm{NN}}{}^x \quad (13)$$

where we have used a contracted notation indicating the first derivative of any function A as $A^x = \partial A/\partial x$ and with $W_{\mu\nu}^{\mathrm{HF}}$ the elements of the matrix $W^{\mathrm{HF}} = P^{\mathrm{HF}}\tilde{F}P^{\mathrm{HF}}$. In the expression above, it does not compare any derivative of the density matrix P^{HF}.

By direct differentiation of the correction term $\mathsf{G}^{(2)}$ we arrive at the following expression, in which we have exploited the symmetry properties implicitly contained in eq 10:

$$\mathsf{G}^{(2),x} = {}^1/_2[\sum_{ijab} t_{ij}^{ab}\langle i^x j||ab\rangle + \sum_{ijab} t_{ij}^{ab}\langle ij^x||ab\rangle + \sum_{ijab} t_{ij}^{ab}\langle ij||a^x b\rangle + \sum_{ijab} t_{ij}^{ab}\langle ij||ab^x\rangle] - {}^1/_4 \sum_{ijab} t_{ij}^{ab} t_{ij}^{ab}(\epsilon_i^x + \epsilon_j^x - \epsilon_a^x - \epsilon_b^x) \quad (14)$$

In eq 14, first derivatives of both spin−orbitals and related orbital energies appear. These can be obtained by exploiting the coupled perturbed Hartree−Fock (CPHF) theory for solvated systems we have recently developed.[7−9]

The derivatives of the molecular orbitals (MO) can be expressed as[20]

$$|a^x\rangle = \sum_{f\neq a}^{\mathrm{vac}} U_{fa}^x|f\rangle + \sum_{k}^{\mathrm{occ}} U_{ka}^x|k\rangle + \sum_{\mu} c_{\mu a}|\mu^x\rangle \quad (15)$$

$$|i^x\rangle = \sum_{f}^{\mathrm{vac}} U_{fi}^x|f\rangle + \sum_{k\neq i}^{\mathrm{occ}} U_{ki}^x|k\rangle + \sum_{\mu} c_{\mu i}|\mu^x\rangle \quad (16)$$

where U_{pq}^x are the CPHF coefficients and $|\mu^x\rangle$ the derivatives of the AO basis functions.

The elements of the unknown matrix U^x can be obtained from the following equations:

$$U_{ai}^x = \sum_{bj} (\tilde{A}^{-1})_{ai,bj} \frac{\tilde{Q}_{bj}^x}{\epsilon_j - \epsilon_b} \quad (17)$$

$$U_{fa}^x = -\frac{1}{\epsilon_f - \epsilon_a}[\tilde{Q}_{fa}^x + \sum_{gm} U_{gm}^x(\langle fm||ag\rangle + \langle fg||am\rangle + 2\mathsf{B}_{gm,fa})] \quad (18)$$

$$U_{ki}^x = -\frac{1}{\epsilon_k - \epsilon_i}[\tilde{Q}_{ki}^x + \sum_{gm} U_{gm}^x(\langle km||ig\rangle + \langle kg||im\rangle + 2\mathsf{B}_{gm,ki})] \quad (19)$$

$$U_{pq}^x + (U_{qp}^x)^* + S_{pq}^x = 0 \quad (20)$$

where

$$\tilde{A}_{ai,bj} = \delta_{ab,ij} + \frac{\langle ab||ij\rangle + \langle aj||ib\rangle + 2\mathsf{B}_{ai,bj}}{\epsilon_a - \epsilon_i} \quad (21)$$

with

$$\tilde{Q}_{pq}^x = [h_{pq}^x + j_{pq}^x] - S_{pq}^x\epsilon_q - \sum_{kl} S_{kl}^x[\langle pl||qk\rangle + \mathsf{B}_{pq,kl}] + \sum_{\mu\nu\lambda\sigma} (c_{\mu p})^* c_{\nu q} P_{\lambda\sigma}[\langle\mu\lambda||\nu\sigma\rangle^x + \mathsf{B}_{\mu\nu,\lambda\sigma}^x] \quad (22)$$

$$h_{pq}^x + j_{pq}^x = \sum_{\mu\nu}[(c_{\mu p})^* c_{\nu q}(h_{\mu\nu}^x + j_{\mu\nu}^x)] \quad (23)$$

$$S_{pq}^x = \sum_{\mu\nu}(c_{\mu p})^* c_{\nu q} S_{\mu\nu}^x \quad (24)$$

while the orbital energy derivatives are given by

$$\epsilon_p^x = \tilde{Q}_{pp}^x + \sum_{gm} U_{gm}^x(\langle pm||pg\rangle + \langle pg||pm\rangle + 2\mathsf{B}_{gm,pp}) \quad (25)$$

Introducing eqs 15−24 into eq 14, we obtain, through simple algebra, the first derivative of the PCM-MP2 free energy correction as

$$G^{(2),x} = \sum_{ij} P_{ij}^{(2)}\tilde{Q}_{ij}^x + \sum_{ab} P_{ab}^{(2)}\tilde{Q}_{ab}^x + 2\sum_{ai}\tilde{L}U_{aiai}^x + \sum_{ij} I_{ij}S_{ij}^x + \sum_{ab} I_{ab}S_{ab}^x + 2\sum_{ai} I_{ai}S_{ai}^x + \sum_{\mu\nu\rho\sigma}\langle\mu\nu|\rho\sigma\rangle^x\Gamma(\mu\nu\rho\sigma) \quad (26)$$

where $P_{ij}^{(2)}$ and $P_{ab}^{(2)}$ are the elements of the occupied−occupied (o−o), and virtual−virtual (v−v) blocks of the relaxed MP2 density matrix, respectively:

$$P_{ij}^{(2)} = -{}^1/_2 \sum_{kab} t_{ik}^{ab} t_{jk}^{ab} \quad (27)$$

$$P_{ab}^{(2)} = {}^1/_2 \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc} \quad (28)$$

The Lagrangian elements $\tilde{L}_{ai}$ when computed within the PCM-MP2 framework become

$$\tilde{L}_{ai} = \sum_{jk} P^{(2)}_{kj}(\langle ki||ja\rangle + \mathsf{B}_{kj,ai}) + \sum_{bc} P^{(2)}_{bc}(\langle bi||ca\rangle + \mathsf{B}_{bc,ai}) + I_{ai} + {}^1/_2 \sum_{jbc} t^{bc}_{ij}\langle cb||aj\rangle \quad (29)$$

while I_{ij}, I_{ab}, and I_{ai} are defined exactly as in vacuo, with

$$I_{ij} = -{}^1/_2 \sum_{kab} t^{ab}_{ik}\langle jk||ab\rangle \quad (30)$$

$$I_{ab} = -{}^1/_2 \sum_{ijc} t^{ac}_{ij}\langle bc||ij\rangle \quad (31)$$

$$I_{ai} = -{}^1/_2 \sum_{jkb} t^{ab}_{kj}\langle ib||kj\rangle \quad (32)$$

The last term of eq 26 collects the AO derivative part where we define $\Gamma(\mu\nu\rho\sigma)$ as

$$\Gamma(\mu\nu\rho\sigma) = 2 \sum_{i>j,a>b} t^{ab}_{ij}(c_{\rho a}c_{\sigma b} - c_{\rho b}c_{\sigma a})c_{\mu i}c_{\nu j} \quad (33)$$

The presence of U^x_{ai} in the third term of eq 26 should require the solution of as many PCM-CPHF equations as the perturbative parameters. However, by exploiting the *Z*-vector method[18] it is possible to reduce the problem to a single PCM-CPHF equation which is independent on the perturbation. In fact, the third term of eq 26 can be expressed in the equivalent form

$$2\sum_{ai} \tilde{L}_{ai} U^x_{ai} = 2\sum_{ai} \tilde{L}_{ai} \sum_{bj} (\tilde{A}^{-1})_{ai,bj} \frac{\tilde{Q}^x_{bj}}{\epsilon_j - \epsilon_b} = 2\sum_{bj} P^{(2)}_{bj}\tilde{Q}^x_{bj} \quad (34)$$

where the virtual−occupied (v−o) block of the relaxed density matrix is the solution of the following perturbation-independent linear PCM-CPHF equation:

$$\sum_{bj} P^{(2)}_{bj}(\epsilon_j - \epsilon_b)\tilde{A}_{bj,ai} = \tilde{L}_{ai} \quad (35)$$

At the best of our knowledge eq 35 represents the first complete generalization to solvation methods (here applied to PCM approach) of the *Z*-vector equation. Olivares et al.[16] have proposed a version of eq 29 in which no solvation terms are included either in $\tilde{A}_{bj,ai}$ or in $\tilde{L}_{ai}$, while in the alternative formulation of Willets and Rice[21] the simpler model they use for the solvent reaction field seems to affect $\tilde{A}$ but not the Lagrangian $\tilde{L}$.

Introducing eq 34 into eq 26, we obtain the following expression for $\mathsf{G}^{(2),x}$

$$\mathsf{G}^{(2),x} = \sum_{ij} P^{(2)}_{ij}\tilde{Q}^x_{ij} + \sum_{ab} P^{(2)}_{ab}\tilde{Q}^x_{ab} + 2\sum_{ai} P^{(2)}_{ai}\tilde{Q}^x_{ai} + \sum_{ij} I_{ij}S^x_{ij} + \sum_{ab} I_{ab}S^x_{ab} + 2\sum_{ai} I_{ai}S^x_{ai} + \sum_{\mu\nu\rho\sigma}\langle\mu\nu|\rho\sigma\rangle^x\Gamma(\mu\nu\rho\sigma) \quad (36)$$

Adding eq 36 to the HF counterpart (13), the final expression for the first derivative of the PCM-MP2 free energy becomes

$$\mathsf{G}^{\mathrm{MP2},x} = \sum_{\mu\nu\rho\sigma} \Gamma^{\mathrm{MP2}}_{\mu\nu\rho\sigma}\langle\mu\nu||\rho\sigma\rangle^x + \sum_{\mu\nu} P^{\mathrm{MP2}}_{\mu\nu} h^x_{\mu\nu} - \sum_{\mu\nu} S^x_{\mu\nu} W^{\mathrm{MP2}}_{\mu\nu} + V^x_{\mathrm{NN}} + \sum_{\mu\nu} P^{(2)}_{\mu\nu}[j^x_{\mu\nu} + X^x_{\mu\nu}(P^{\mathrm{HF}})] + \sum_{\mu\nu} P^{\mathrm{HF}}_{\mu\nu}[j^x_{\mu\nu} + {}^1/_2 X^x_{\mu\nu}(P^{\mathrm{HF}})] \quad (37)$$

where $X^x_{\mu\nu}(P^{\mathrm{HF}}) = \sum_{\lambda\sigma} P^{\mathrm{HF}}_{\lambda\sigma}\mathsf{B}^x_{\mu\nu,\lambda\sigma}$.

The effective second-order density P^{MP2} and the energy-weighted density W^{MP2} are

$$P^{\mathrm{MP2}}_{\mu\nu} = P^{\mathrm{HF}}_{\mu\nu} + P^{(2)}_{\mu\nu} \quad (38)$$

$$W^{\mathrm{MP2}}_{\mu\nu} = W^{\mathrm{HF}}_{\mu\nu} + W^{(2)}_{\mu\nu} \quad (39)$$

where the second-order correction to the density and the energy-weighted density matrices are obtained by back-transforming the MO equivalents in the AO basis:

$$P^{(2)}_{\mu\nu} = \sum_{pq} (c_{\mu p})^* c_{\nu q} P^{(2)}_{pq} \quad (40)$$

$$W^{(2)}_{\mu\nu} = \sum_{pq} (c_{\mu p})^* c_{\nu q} W^{(2)}_{pq} \quad (41)$$

with

$$W^{(2)}_{ij} = {}^1/_2 \sum_{kab} t^{ab}_{jk}\langle ki||ab\rangle - \epsilon_i P^{(2)}_{ij} - \sum_{pq} P^{(2)}_{pq}[\langle ip||jq\rangle + \mathsf{B}_{ij,pq}] \quad (42)$$

$$W^{(2)}_{ab} = {}^1/_2 \sum_{ijc} t^{bc}_{ij}\langle ij||ca\rangle - \epsilon_a P^{(2)}_{ab} \quad (43)$$

$$W^{(2)}_{ai} = {}^1/_2 \sum_{jkb} t^{ba}_{jk}\langle jk||ib\rangle - \epsilon_i P^{(2)}_{ai} \quad (44)$$

The two-particle density matrix elements $\Gamma^{\mathrm{MP2}}_{\mu\nu\rho\sigma}$ introduced in eq 37 may be separated into two terms that are regarded as separable and nonseparable, namely

$$\Gamma^{\mathrm{MP2}}_{\mu\nu\lambda\rho} = \Gamma^{\mathrm{S}}_{\mu\nu\lambda\rho} + \Gamma^{\mathrm{NS}}_{\mu\nu\lambda\rho} \quad (45)$$

$$\Gamma^{\mathrm{S}}_{\mu\nu\lambda\rho} = {}^1/_2(P^{\mathrm{HF}}_{\mu\nu} + 2P^{(2)}_{\mu\nu})P^{\mathrm{HF}}_{\lambda\rho} - {}^1/_2(P^{\mathrm{HF}}_{\mu\rho} + 2P^{(2)}_{\mu\rho})P^{\mathrm{HF}}_{\lambda\nu} \quad (46)$$

$$\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\rho} = 2 \sum_{i>j,a>b} t^{ab}_{ij} c_{\mu i}c_{\lambda j}c_{\nu a}c_{\rho b} \quad (47)$$

The separable part (46) is similar in form to the expression of HF two-particle density matrix, while the nonseparable part (47) is a back-transformation of t^{ab}_{ij} from MO to AO basis.

4. One-Electron Properties and Nuclear Gradients

The Hellman−Feynman theorem assures that for solvated systems described within continuum model[17,22,23] the one-electron properties related to exact eigenfunctions can be determined both as expectation values of the related one-electron operator $\mathsf{M} = \sum_i m(i)$ and as first derivatives of the free energy, G^{λ}, with respect to the parameter λ defining the intensity of the perturbation, namely $\lambda\mathsf{M}$ and

$$\langle\Psi|\mathsf{M}|\Psi\rangle = \frac{\partial\mathsf{G}}{\partial\lambda} = \left\langle\Psi\left|\frac{\partial H'}{\partial\lambda}\right|\Psi\right\rangle \quad (48)$$

where H' is the linear component of the molecular Hamiltonian.

The equivalence between the two alternative methods applies also for HF or MCSCF approximated wave functions which exploit orbital expansions on basis functions not depending on λ.[20] When the wave function is approximated with many-body methods as the coupled-cluster (CC) or the MP*n* theories, Helmann−Feynman theorem is not fulfilled and the two methods to calculate first-order properties are no longer equivalent. In the latter cases, also for solvated systems, exactly as for isolated molecules,[24] the derivative method gives a more direct way toward higher-order response properties.

4.1. One-Electron Properties. If we consider as derivative parameter the factor defining the intensity of the perturbation λM and we assume that the basis functions are independent of the perturbation, the MP2 energy derivative (37) has to be limited to the MO derivative part. Indeed, the equation reduces to the first three terms only since the elements of S^x are zero; the resulting expression for the one-electron property connected to M thus becomes

$$M^{\mathrm{MP2}} = \sum_{\mu\nu} P_{\mu\nu}^{\mathrm{MP2}} m_{\mu\nu} \tag{49}$$

where $P_{\mu\nu}^{\mathrm{MP2}}$ are the second-order density matrix elements (see eq 38) and $m_{\mu\nu} = \langle \mu | m | \nu \rangle$.

From the analysis above it should be clear that the relaxed MP2 density is itself a one-electron property defined as the free energy derivative when the perturbation is the delta-function.

4.2. Nuclear Gradients. PCM-MP2 nuclear gradients can be directly obtained from eq 37 considering the 3N Cartesian coordinates of solute nuclei as derivative parameters. The derivatives of solvent-induced matrices, $j_{\mu\nu}^x$ and $X_{\mu\nu}^x$, can be calculated by exploiting the formalism we have recently formulated leading to the following expressions:[6]

$$j_{\mu\nu}^x = D_{\mu\nu}^{Ne} + D_{\mu\nu}^{eN} + \tau_{\mu\nu}^{Ne} + \tau_{\mu\nu}^{eN} \tag{50}$$

$$D_{\mu\nu}^{Ne} = -\sum_i V^{N,x}(i) q_{\mu\nu}(i) \tag{51}$$

$$D_{\mu\nu}^{eN} = -\sum_i V_{\mu\nu}^x(i) q^N(i) \tag{52}$$

$$\tau_{\mu\nu}^{eN} + \tau_{\mu\nu}^{Ne} = -\frac{4\pi\epsilon}{\epsilon - 1}\sum_i q_{\mu\nu}(i) q^N(i) \left(\frac{U_\Gamma^x(i)}{a_i} \right) \tag{53}$$

and

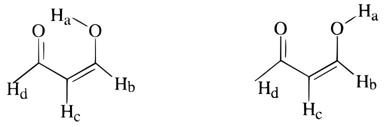
$$^1/_2 X_{\mu\nu}^x = D_{\mu\nu}^{ee} + \tau_{\mu\nu}^{ee} \tag{54}$$

$$D_{\mu\nu}^{ee} = -\sum_i V_{\mu\nu}^x(i) q^e(i) \tag{55}$$

$$\tau_{\mu\nu}^{ee} + \tau_{\mu\nu}^{Ne} = -\frac{2\pi\epsilon}{\epsilon - 1}\sum_i q_{\mu\nu}(i) q^e(i) \left(\frac{U_\Gamma^x(i)}{a_i} \right) \tag{56}$$

Here $V^{N,x}(i)$ and $V_{\mu\nu}^x(i)$ are the derivatives of the electrostatic potentials (computed on the ith tessera) due to the nuclear charge distribution γ_{N} and to the elementary charge distribution $\chi_\mu^* \chi_\nu$. In eqs 51−56 explicit reference is made to the apparent charges introduced in the PCM approach to describe solvent reaction field; in particular, $q^N(i)$, $q_{\mu\nu}(i)$, and $q^e(i)$ represent the apparent charges induced on the surface cavity (one for each tessera i of area a_i) by γ_{N}, $\chi_\mu^* \chi_\nu$, and the total electronic charge distribution of the solute, respectively.

The term appearing between parentheses in eqs 53 and 56 takes into account the movement of the cavity with respect to the motion of the nucleus; it only depends on the cavity geometry and it assumes a very simple expression when such cavity is built in terms of interlocking spheres centered on the nuclei.[6]



(**1**) (**2**)

Figure 1. Cis and trans conformations of the enol form of malonaldehyde.

TABLE 1: MP2 and HF Energies (au) for the Two Isomers in Vacuo and in Solution, and Solvation Free Energies ΔG_{sol} (kcal/mol) for the Solvated Systems

	cis		trans	
	vacuo	water	vacuo	water
		MP2		
energy	−266.41728	−266.42493	−266.39670	−266.41446
MP2 corr	−0.76972	−0.76662	−0.76721	−0.76256
ΔG_{sol}		−4.8		−11.1
		HF		
energy	−265.65295	−265.66314	−265.63421	−265.65567
ΔG_{sol}		−6.4		−13.5

5. Numerical Applications

Malonaldehyde is an extensively studied molecular system, from both the experimental[25] and the computational[26,27] point of view. This large interest is mainly due to the intramolecular hydrogen bond acting in the cyclic conformation of the *cis*-enol form (system **1** in Figure 1) which also shows an interesting six-membered ring arrangement. The geometry of **1** has been well studied experimentally and thus it offers an useful example to compare with in order to test ab initio calculations.

Here we present a study of this and the related conformer (*trans*-enol **2**) of malonaldehyde at both HF and MP2 level. The calculations of one-electron properties and optimized geometries were done using a 6-31++G** basis set both in vacuo and in solution. In the latter case we have used the HF and MP2 implementations of PCM introduced in the Gaussian99 code.[28] As additional information about the PCM solvation model (applying for both HF and MP2 theories), we recall that the cavity in which the solute is placed is defined in terms of interlocking spheres centered on the solute nuclei. In the present case the radii R_k are equal to 1.2 times the corresponding van der Waals values R_k^{vdw}; that is, we have $R_{\mathrm{H}} = 1.44$ Å, $R_{\mathrm{C}} = 2.04$ Å, and $R_{\mathrm{O}} = 1.80$ Å. The solvation calculations are performed for a medium having dielectric constant $\epsilon = 78.5$ corresponding to the static dielectric constant of liquid water at 298 K.

Previous calculations on the same systems have shown the limits of the HF method to describe both the geometrical structure and the molecular properties of the two isomers.[27] This finding assumes an even more interesting aspect in the present context where the attention is mainly focused on the solvent effects. Indeed, the solvent can largely modify both the geometry and the response properties of the solute, combining its action with that due to correlation. In this way, the solvation introduces a larger complexity with respect to calculations on isolated systems in the analysis of the changes induced by the correlated MP2 calculations on the energies, the one-electron properties, and more in general the charge density distribution of the solute.

In Table 1 we report the HF and MP2 energies (with indication of the MP2 corrections) of the two systems both in

TABLE 2: MP2 and HF Dipoles (D) and Mulliken Net Charges (au) for the Two Isomers Both in Vacuo and in Solution[a]

	MP2				HF			
	cis		trans		cis		trans	
	vacuo	water	vacuo	water	vacuo	water	vacuo	water
μ	2.820	3.798	4.640	6.249	2.964	3.901	4.991	6.657
C_c	0.1714	0.1952	0.1804	0.2073	0.3602	0.3857	0.3420	0.3787
O_c	−0.4780	−0.5502	−0.3807	−0.5002	−0.5884	−0.6676	−0.4831	−0.6141
C	−0.1419	−0.1707	−0.2087	−0.2856	−0.3070	−0.3469	−0.3514	−0.4478
C_h	0.1071	0.1167	0.1694	0.2250	0.2544	0.2644	0.3091	0.3722
O_h	−0.4646	−0.5074	−0.4427	−0.5059	−0.5557	−0.5889	−0.5157	−0.5772
H_a	0.4225	0.4347	0.3805	0.4316	0.4540	0.4642	0.3994	0.4495

[a] The subscript c on C and O indicates the carbonyl group, while h refers to C−OH group. The hydrogen (H_a) refers to the hydroxyl.

vacuo and in water. In the latter case also the solvation free energies ($\Delta G_{sol} = G_{vac} - G_{aq}$) are presented.

Two are the main aspects to be observed. First, we note that the stabilizing effect of the intramolecular H-bond acting in the cis isomer is amplified by correlation; the isomerization energy from the cis to the trans form of the isolated system goes from −11.8 kcal/mol at HF level to −12.9 kcal/mol at MP2 level. This effect, already known from previous calculations,[27] is due to both the decrease of charge density within the bonding regions between nuclei and on the nuclei themselves, and the parallel increase in the diffuse regions around atoms. In particular, the concentration of charge found at the MP2 level in the intermediate region between the two oxygens is more pronounced for **1** as the hydroxyl hydrogen resides within such region.

The second and new aspect introduced by data of Table 1 is the solvent effect. The main result is the change in the relative stability of the two isomers: even if solvent does not invert the picture found in vacuo, the isomerization energy is reduced to −4.7 kcal/mol at HF level and −6.6 kcal/mol at MP2 level. Such preferential stabilization of the solvent for the trans form (see also the values of solvation energies ΔG_{sol}) is contrasted by the opposite action due to correlation, which more efficiently stabilizes the cis form. The resulting effect is the smaller solvent-induced stabilization of the trans form going from HF to MP2 calculations ($\Delta G_{sol}(trans) - \Delta G_{sol}(cis)$ is −7.1 and −6.3 kcal/mol, respectively).

Passing now to one-electron properties, in Table 2 we report HF and MP2 dipoles and Mulliken net charges for the two isomers both in vacuo and in water.

The limits of the HF theory in predicting reliable dipole moments are largely known, it suffices to recall the CO example in which not only the magnitude but also the direction of the dipole cannot be reproduced in the HF limit. For the two isomers of malonaldehyde the situation is not so unlucky but some effects are still evident passing from HF to MP2 calculations. In particular, all the dipole values are significantly reduced by correlation (of 5.1% for the cis form and of 7.6% for the trans of the molecule in vacuo). In the presence of the solvent the analysis is more articulate as solvation induces an opposite effect leading to increase dipole values; the decrease of the MP2 dipole values is thus reduced to 2.7% and 6.5 %, in the cis and in the trans isomer, respectively. Also, the net atomic charges show a similar trend; the inclusion of correlation leads to a global reduction of their absolute values both for the isolated and the solvated system, but in the latter case such reduction is smaller because of the opposite action due to solvation.

A different, but still related, analysis can be done on two electrostatic properties: the molecular electrostatic potential (MEP) and the electric field gradient (EFG).

The MEP is a very common and effective tool to visualize the effects of charge density and of its modifications due to different levels of calculation. The 3D shape of the MEP function is generally rather intricate, and its analysis is often done with the help of graphical display of maps on selected planes. We shall limit ourselves to present the map of the molecular electrostatic energy (obtained by multiplying the MEP by a unit charge) for the molecular plane of the two isomers obtained at MP2 level with inclusion of the solvent (see Figures 2 and 3). They are not qualitatively different from those of the isolated systems on the one hand, and from those obtained with HF calculations on the other hand.

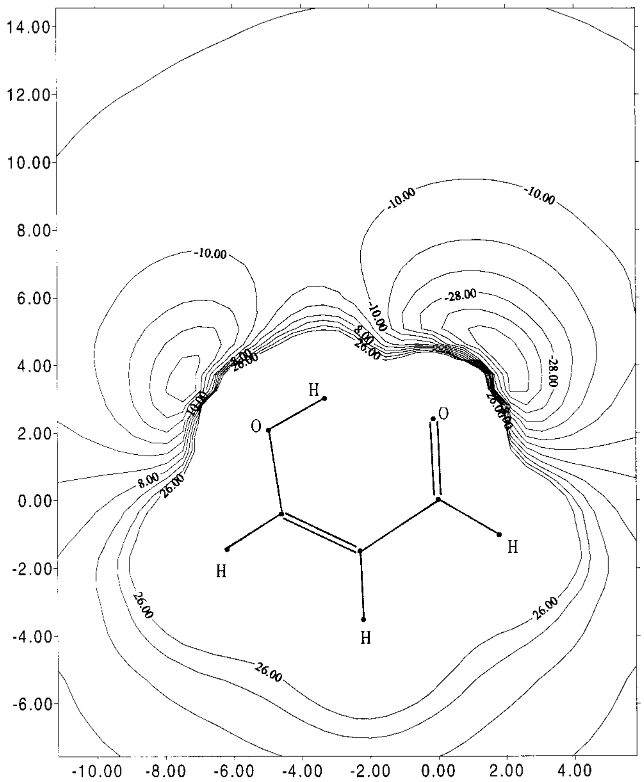


Figure 2. MP2 molecular electrostatic potential (kcal/mol) computed for the *cis*-enol in water. The plot is for the molecular plane (au are used for both axes) and the contour lines increase by 6 kcal/mol.

TABLE 3: Minimum Values of the MEP (kcal/mol) at MP2 and HF Levels for the Cis and Trans Isomers Both in Vacuo and In Solution

	MP2		HF	
	cis	trans	cis	trans
vacuum	−43.9	−62.0	−53.9	−70.3
water	−54.0	−79.0	−65.6	−89.9

The main aspect which distinguishes HF and MP2 calculations, as well as solvated and isolated systems, is the relative magnitude of the property while the general shape of the map remains almost unchanged introducing correlation and/or solvent effects. The numerical data are shown in Table 3 where we

TABLE 4: ^{17}O (MHz) and ^{2}H (KHz) ν and η Values at HF and MP2 Levels Both in Vacuo and in Solution[a]

	MP2				HF			
	cis		trans		cis		trans	
	vacuo	water	vacuo	water	vacuo	water	vacuo	water
$\nu(O_c)$	−9.68	−9.44	−11.26	−10.81	−11.20	−10.81	−12.59	−11.81
$\eta(O_c)$	0.17	0.10	0.38	0.26	0.24	0.12	0.45	0.25
$\nu(O_h)$	7.20	7.16	8.72	8.28	9.35	9.23	10.45	9.90
$\eta(O_h)$	0.34	0.38	0.66	0.58	0.47	0.49	0.61	0.55
$\nu(H_a)$	−212.98	−212.72	−313.89	−297.06	−292.34	−292.66	−359.21	−337.63
$\eta(H_a)$	0.18	0.19	0.13	0.20	0.14	0.14	0.13	0.13

[a] The subscript c on O indicates the carbonyl group, while h refers to the hydroxyl oxygen.

TABLE 5: Selected MP2- and HF-Optimized Geometry Parameters for the Two Isomers Both in Vacuo and in Solution[a]

	MP2				HF			
	cis		trans		cis		trans	
	vacuo	water	vacuo	water	vacuo	water	vacuo	water
r(C−C)	1.440	1.438	1.465	1.453	1.453	1.448	1.472	1.458
r(C═C)	1.366	1.365	1.352	1.356	1.345	1.346	1.332	1.340
r(C═O)	1.253	1.257	1.234	1.242	1.208	1.216	1.193	1.207
r(C−O)	1.332	1.338	1.354	1.350	1.312	1.316	1.327	1.323
$r(O-H_a)$	0.995	0.995	0.966	0.970	0.956	0.956	0.942	0.947
$r(C-H_b)$	1.083	1.082	1.085	1.084	1.075	1.074	1.078	1.076
$r(C-H_c)$	1.079	1.074	1.081	1.081	1.073	1.073	1.075	1.074
$r(C-H_d)$	1.098	1.095	1.104	1.100	1.091	1.088	1.096	1.092
r(O···O)	2.600	2.599	2.846	2.871	2.690	2.700	2.890	2.904
∠C═C−C	119.9	120.4	125.9	126.5	121.2	121.8	126.4	126.8
∠C−C═O	123.3	123.1	125.7	124.0	124.0	123.9	126.4	126.7
∠C═C−O	124.3	123.9	123.4	123.6	126.2	125.9	124.9	124.8
$\angle C-O-H_a$	106.0	106.1	109.3	109.0	110.1	110.3	111.7	111.2

[a] Bond lengths are in Å. The indices defining the nuclei are reported in Figure 1.

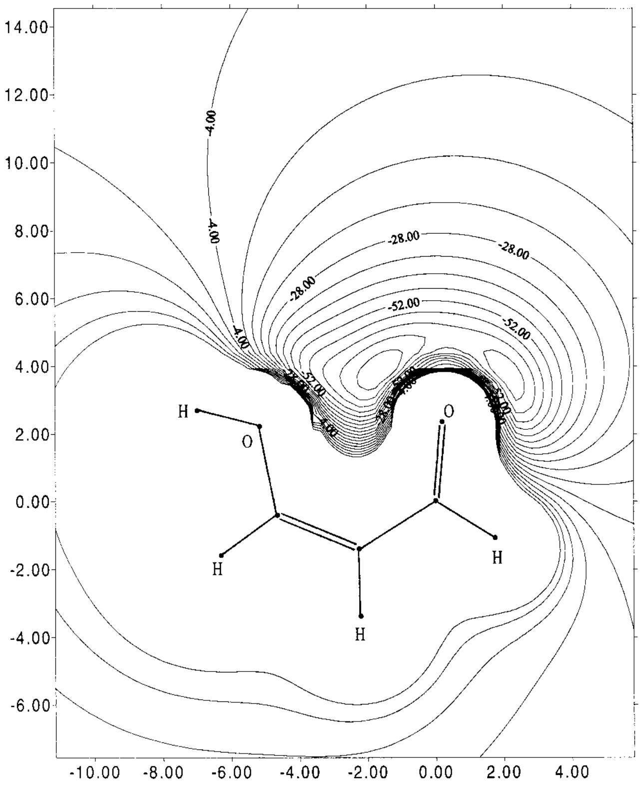


Figure 3. MP2 molecular electrostatic potential (kcal/mol) computed for the *trans*-enol in water. The plot is for the molecular plane (au are used for both axes) and the contour lines increase by 6 kcal/mol.

report the minimum values for the two molecular systems both in vacuo and in water at MP2 and HF level of calculation. It is worth noting that the position of the minima are almost equivalent for both HF and MP2 calculations. Also, solvation effects are not significant; the minima are only slightly displaced but they always remain well inside the molecular cavity containing the solute.

As regards electric field gradients (EFG's), the interest is mainly due to their proportionality to the nuclear quadrupole coupling constants (NQCC's) used to estimate the relative widths of nuclei NMR signals.

The principal axis (PA) components (in atomic units) q_{zz}, q_{yy}, and q_{xx} of the traceless EFG tensor correlate with the experimental quantities, the NQCC, ν, (measured in Hz) and the asymmetry parameter, η, through the relationships

$$\nu = (eq)(eQ/h) = e^2qQ/h$$

$$\eta = (q_{xx} - q_{yy})/q_{zz}$$

where eq is the largest EFG component, i.e., eq_{zz}, as by definition the PA components are assigned such that $|q_{zz}| > |q_{yy}| > |q_{xx}|$. To calculate e^2qQ/h from the computed q_{zz} value, a literature value for Q, the nuclear quadrupole, is required: in the present work, where we shall limit the analysis to the two oxygens and the hydroxyl hydrogen, values of $Q_H = 2.860 \times 10^{-3}$ barn[29] and $Q_O = -0.0265$ barn[30] have been assumed, although other values have been also used. The resultant conversion factors from q_{zz} to e^2qQ/h values are as follows: for hydrogen (here considered in its ^{2}H isotopic form), 672.0 kHz/au and for oxygen (as ^{17}O isotope), −6.227 MHz/au.

In Table 4 we report ν and η values for the two isomers at MP2 and HF level both in vacuo and in solution.

Data of Table 4 are to be interpreted here as a further index of the combined correlation−solvent effects more than as a specific molecular property. More detailed comments should in fact require analyses of different type, namely based on the influence of the H-bond and of the relative position of the hydrogen with respect to oxygens, which go beyond the scope of the paper. What we want to stress is on the one hand the significant decrease of both cis and trans absolute NQCC and η of all the nuclei passing from HF to MP2 calculations, and on the other hand the solvent effects. While the correlation effect could be expected on the bases of the previous comments on the changes it induces on the charge distribution, the solvent effect on NQCC is quite unexpected. Here, in fact, solvation seems to go in the same direction of correlation inducing a decrease of both ν and η in all the calculations; once again the effect on the trans form is more evident than on the cis analog.

Let us now pass to consider the geometrical analysis. As said at the beginning of the section, previous calculations have shown that geometry parameters of both cis and trans isomers are sensitive to correlation;[27] in particular the HF approximation gives geometries in poor agreement with experiments as the O−O distance is found to be too large. On the contrary, the same distance computed at the MP2 level compares well with experimental geometry. The same considerations can be derived from data of Table 5 where both HF and MP2 geometry optimization results both in vacuo and in solution are reported.

The available experimental data refer to cis isomer in vacuo where the O−O distance is 2.553 Å.[31] The MP2 result, 2.60 Å, shows a better behavior of correlated methods in the description of charge density distributions; here in fact the smaller O−O distance reflects a shift of charge from the bonding regions toward the periphery around and between atoms, in particular the two oxygens, which can then approach each other more closely. The solvent does not significantly change the results found for the isolated systems both in the absolute values and in the MP2-HF modifications; the main differences are found in the MP2 trans form where in particular the O−O distance passes from the in vacuo value of 2.846−2.871 Å. This seems to further confirm the larger solvent effect on the trans form already found in the analysis of energies and one-electron response properties.

6. Conclusions

We have presented a methodology to evaluate MP2 energy and first derivatives for solvated systems described within the polarizable continuum model (PCM). The analysis has been mainly focused on the redefinition of the relaxed MP2 density taking into account solvent effects in the related *Z*-vector expression. Applications of the method to the evaluation of one-electron properties and nuclear gradients to be used in geometry optimizations have been considered and discussed.

The method presents many advantages with respect to previous formulations; as concerns the energy, it does not add any further complexity to the standard HF calculations for solvated systems, while the new formulation of the *Z*-vector required to get MP2 density is complete, without the necessity of introducing approximations or neglection of terms. In addition, computational costs of this procedure when including solvent effects are of the same magnitude of a standard PCM-CPHF calculation while the accuracy in the analytical gradients is completely comparable with those of the parallel calculations in vacuo (as shown by the checks on the agreement with finite displacement values). Finally, this approach presents many possible developments; the application to higher-order MP2 derivatives (for example to get vibrational frequencies and electric polarizabilities) has been already considered, and numerical applications will be presented soon. Other less direct applications such as the extension of the *Z*-vector technique to the evaluation of derivatives within the Tamm−Dancoff and random phase approximations and, more in general, the generalization of the whole methodology to coupled cluster techniques are now in progress.

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