On the Calculation of Local Field Factors for Microscopic Static Hyperpolarizabilities of Molecules in Solution with the Aid of Quantum-Mechanical Methods

Roberto Cammi,[†] Benedetta Mennucci,[‡] and Jacopo Tomasi*,[‡]

Dipartimento di Chimica Generale ed Inorganica, Università di Parma, viale delle Scienze, 43100 Parma, Italy, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy

Received: August 18, 1997; In Final Form: November 3, 1997

We present a simple computational method to connect the computed *ab initio* values of static dipole polarizabilities and hyperpolarizabilities of molecules in solution with their experimental counterparts. The connection is done in terms of local field factors. We show that formulas used by experimentalists are not adequate, and that they can be replaced by a reformulation of the quantum-mechanical codes for the calculation of (hyper)polarizabilities in solution by using a realistic description of the solvent reaction field (i.e., a cavity with the proper molecular shape). This reformulation leads to an additional set of hyperpolarizability values which take into account local modifications to the external static field. This second set of values has a direct relation with the macroscopic susceptibility tensors and, when compared to that derived from standard calculations, allows one to evaluate realistic local field factors.

1. Introduction

The large amount of literature on the ab initio calculation of static dipole polarizability and hyperpolarizabilities of molecules is mainly based on procedures applied to the evaluation of the response functions of the single molecule when subjected to an external static electric field in the limit of a weak polarization. In the latter approximation, the dipolar interaction with the radiation field can be described as an expansion on the external electric field components. There are two equivalent definitions, based either on the Stark energy or on the dipole moment, which is the negative derivative of the energy with respect to the field. In the following we shall adopt the latter one.

Still within this assumption, in the literature one can find different conventions used to define hyperpolarizabilities, making it difficult to compare calculated and experimental values or experimental values obtained using different techniques; a very clear analysis of these practical aspects can be found in a paper by Willetts et al.[1]. Generally, the two most used conventions are those based on a perturbation series expansion of the induced dipole moment or on the parallel Taylor series expansion:

$$\vec{\mu} = \vec{\mu}^0 + \gamma^{(1)}\vec{E} + \gamma^{(2)}: \quad \vec{E}\vec{E} + ... \tag{1}$$

$$\mu_a = \mu_a^0 + \sum_b \gamma_{ab}^{(1)} E_b + \frac{1}{2!}\sum_{bc}\gamma_{abc}^{(2)} E_b E_c + \frac{1}{3!}\sum_{bcd}\gamma_{abcd}^{(3)} E_b E_c E_d + ... \tag{2}$$

where $\vec{\mu}^0$ is the molecular permanent dipole and $\gamma^{(n)}$ are the microscopic (hyper)polarizability tensors at the various orders; in eq 2 we have preferred to make explicit the contracted matrix formalism of eq 1 in terms of the Cartesian components *a*, *b*, *c*, ... The relation between the two sets of coefficients is immediate: the hyperpolarizabilities defined in the two conventions are simply related by factors of (*n*!).

The coefficient $\gamma^{(1)}$ (more often indicated as α) is the dipole polarizability tensor of the molecule and is related to the second derivative of the energy and first derivative of the dipole moment with respect to the field $\vec{E}$. The polarizability term describes the linear interaction with the field and accounts for linear absorption and refraction behavior of the molecule. The coefficients $\gamma^{(2)}$ and $\gamma^{(3)}$ (more often indicated as $\boldsymbol{\beta}$ and γ), being third- and fourth-rank tensors, respectively, are called first and second hyperpolarizabilities and constitute the molecular origin of the nonlinear interactions.

What was reported until now regards microscopic molecular properties in vacuo; anyway, in the last few years there has been a remarkable progress in ab initio calculations of the same properties in solution.[2−9] The latter can be still defined in terms of an expansion of the dipolar moment (or of the free energy of the molecule in solution) with respect to a uniform field exactly in the same way as in vacuo (see eqs 1 and 2). The elaboration of methods able to compute microscopic (hyper)polarizabilities in solution has led to a more reliable comparison with respect to the experimental measurements usually performed on macroscopic samples (i.e., condensed phases). Actually, these data give information on the corresponding susceptibility tensors $\chi^{(n)}$ defined as the expansion coefficient of the polarization $\vec{P}$ in terms of the macroscopic uniform external field $\vec{E}$:

$$\vec{P} = \chi^{(1)}\vec{E} + \chi^{(2)}: \quad \vec{E}\vec{E} + ... \tag{3}$$

Usually, the macroscopic polarization $\vec{P}$ is found by summing over the dipole moments per unit volume, where the latter are calculated with the aid of the expansions 1 or 2; this clearly leads to an erroneous valuation as, while $\vec{P}$ is defined in terms of the external macroscopic field, each molecular dipole moment

---

* Corresponding author. Email: tomasi@dcci.unipi.it.

[†] Dipartimento di Chimica Generale ed Inorganica.

[‡] Dipartimento di Chimica e Chimica Industriale.

S1089-5639(97)02680-7 CCC: $15.00

depends on the components of the local field acting on the single molecule. Clearly, in rarefied media such as gases, the differences between the two fields are so small to be safely neglected. On the contrary, the corrections to be taken into account in the case of molecules in condensed matter are by far larger, and they may have a significant effect on the comparison of experimentally determined coefficients with those obtained from microscopic theories. In order to extract the expressions for the macroscopic susceptibilities from those of the microscopic hyperpolarizabilities, or vice versa, the relation between local and macroscopic fields must be defined. In determining the local field one must, in general, take into account the depolarizing field acting on any particular molecule due to the influence of the surrounding molecules.

The local field problem, even for a dielectric with an idealized linear response, is quite difficult. It has received the attention of the theoreticians over many decades, although this has yielded practical results in only a few simple cases.[13] Before summarizing them shortly, we recall that in the already introduced dipole approximation (i.e., the molecules are assumed to interact through the dipolar field of the induced dipole) the field acting locally at the site of the single molecule can be written as

$$\vec{E}_{\mathrm{loc}} = \mathbf{f}\vec{E} \tag{4}$$

where $\mathbf{f}$ is a 3 × 3 tensor whose components are known as "local-field factors".

The classical approach to the problem was established over 80 years ago by Lorentz.[10] He showed that for atoms or nonpolar molecules with well-localized bound electrons the local field tensor may be replaced by a scalar quantity f_{L} (i.e.,

$$\vec{E}_{\mathrm{loc}} = f_{\mathrm{L}}\vec{E} = \frac{2+\epsilon}{3}\vec{E} \tag{5}$$

where ϵ is the dielectric constant of the medium).

The validity of this approach rests on the hypothesis that the polarization within the dense medium is uniform; it is found that the value obtained depends, not on the size of the cavity embedding the molecule in the dielectric, but on its shape; the case considered by Lorentz is limited to the spherical symmetry.

So far in this discussion of local fields we have considered only induced dipoles; however, external fields, especially static fields, can also orient molecules with permanent electric-dipole moments. A refinement to the Lorentz model, taking into account the orientational reactive forces among molecules, is due to Onsager.[11] These forces can be represented as reaction fields. The reaction field acting on a molecule depends on the dipole of the molecule itself and therefore cannot contribute to its own orientation. Onsager showed that the local-field tensor which appears in eq 4 can be approximated, for a polar liquid, by the scalar

$$f_{\mathrm{O}} = \frac{(\epsilon^{\infty}+2)\epsilon}{\epsilon^{\infty}+2\epsilon} \tag{6}$$

where ϵ^{∞} denotes a value of the dielectric constant obtained by extrapolating the results of electrical measurements to high frequencies.

Both eqs 5 and 6 are the usual corrections exploited to relate gas-phase computations and solution-phase measurements; in particular for static (or dc) electric field the local field factor is often given by the Onsager expression.

In order to derive more refined considerations, which will be important in the following analysis, further details are here required.

The Onsager equation (eq 6) is derived in the case of a polar liquid with molecules of spherical shape; in this framework the global effect of the external field can be seen as a sum of two contributions: the first due to the electronic polarization and the second due to the orientation of the permanent dipole. Thus if one wants to derive the proper correction factor to be applied to quantities calculated through solvation models which already take into account the electronic polarization effects of the solvent molecules (and this is the case of the method exploited in the present paper), the model described above has to be partially changed. In this framework, the local field correction has to be evaluated by considering the field inside the empty spherical cavity when subject to a homogeneous external field (often this contribution is called the "cavity field" and it can also be defined as the reaction field induced by a nonpolarizable dipole at the center of the sphere). In this case, eq 6 reduces to

$$f_{\mathrm{O}}^{\mathrm{sp}} = \frac{3\epsilon}{2\epsilon+1} \tag{7}$$

The same model can be easily generalized to a molecule with an ellipsoidal shape.[12] By choosing a Cartesian coordinate system with its axes in the direction of the principal axes 2a, 2b, and 2c of the ellipsoid and defining a diagonal tensor $\mathbf{A}$ with components:

$$A_{\alpha} = \frac{abc}{2}\int_0^{\infty}\frac{ds}{(s+\alpha^2)R} \qquad (\alpha = a, b, c) \tag{8}$$

and $R = (s+a^2)(s+b^2)(s+c^2)$, we can express the local field factor express by a diagonal tensor as follows:

$$\mathbf{f}_{\mathrm{O}}^{\mathrm{el}} = \left[1 - \frac{(\epsilon-1)}{\epsilon}\mathbf{A}\right]^{-1} \tag{9}$$

When the ellipsoid degenerates into a sphere, we have $a = b = c$ and therefore all components A_{α} have the value $^1/_3$ and the tensor of eq 9 reduces to the scalar $f_{\mathrm{O}}^{\mathrm{sp}}$ of eq 7.

Having thus described the two main theoretical approaches used to solve the local-yield problem, we may go back to the connection between microscopic and macroscopic formulas. As a preliminary step, it is compulsory to define the assumed convention. In the present work we have exploited the perturbation series expansion (eq 3) to define the polarization in the experimental measurements, while the theoretical calculations, described in detail in the following sections, are based on a Taylor series expansion of the induced dipole moment (eq 2); by adopting this convention the comparison between measurements and calculation is defined by the following recipe:

$$\chi^{(n)} = \frac{N}{n!}\prod_k \mathbf{f}_k\cdot\gamma^{(n)} \tag{10}$$

where N is the number of target molecules per unit volume and $\gamma^{(n)}$ is the related microscopic hyperpolarizability tensors at the various orders. In the case of a static external field, the product reduces to n static local field tensors.

As already stressed, the definition of the proper local field correction is a difficult one, and at least for a general shaped molecule it has not been analytically resolved; however, in most of the papers focussed on the study of electric response functions of molecules in solution use is made of approximate analogs of the relations 10, in which the tensors $\mathbf{f}_k$ are reduced to scalar quantities and replaced by the Lorentz or Onsager model-derived factors despite the lack of spherical symmetry in the shape of the target molecule. As the related correction factors are of not negligible entity (suffice it to say that for water as solvent the Onsager factor f_O^{sp} of eq 7 is about 1.5), in some cases this procedure can lead to completely wrong comparisons with experimental data.

In the next section we present a numerical procedure which allows the direct calculation of the static local field tensors for any kind of molecule with the aid of QM calculations performed with the polarizable continuum model (PCM)[14−16] in which a cavity modelled on the real shape of the molecule is exploited.

2. Method

In the PCM method, the electrostatic problem of the evaluation of the interaction energy between solute and solvent, including also mutual polarization effects, is solved by introducing an apparent charge distribution σ spread on the cavity surface (ASC approximation).[15] In the computational practice this continuous distribution is discretized by point charges $\{q_i\}$, each associated with a small portion (tessera) of the cavity surface, and defined through a set of linear equations. In the following we report a general matrix formulation which applies to all the different versions of the PCM method now in use (namely, the standard one presented in ref 16 but also a very recent one, called IEF, whose first presentation can be found in ref 17. Here it is worth stressing that a complete generalization with respect to the still limited version presented in this source paper has already been obtained, see ref 18 for details). In this general framework the expression to be used is

$$\mathbf{q} = \Sigma\boldsymbol{\sigma} = -\Sigma\mathbf{O}^{-1}\mathbf{p}^{M} \qquad (11)$$

Here Σ is a diagonal square matrix with elements given by the areas of the surface tesserae and $\mathbf{p}^M$ a column vector depending on the solute charge distribution ρ_M. $\mathbf{O}$ is a nonsymmetric square matrix with dimension equal to the number of tesserae, whose elements depend on geometrical cavity parameters and on the dielectric constant; in a quite rough way we can say that it takes into account the effects that the response (both in terms of the reaction electrostatic field and the reaction potential) of the solvent induces on itself.

The procedure for the calculation of solute energy and wavefunction with the PCM method has been reported in several papers, and we skip here all the details. Suffice it to say that, in order to get solvation quantities, one has to resort to a direct minimization of the functional of the free energy G of the whole solute−solvent system. For a closed-shell solute, described by an SCF wave function with orbitals expanded over a finite basis set, the variational condition $\delta G = 0$ leads to the following equation:

$$\tilde{\mathbf{F}}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon} \qquad (12)$$

where

$$\tilde{\mathbf{F}} = \mathbf{h} + {}^1/_2(\mathbf{j} + \mathbf{y}) + \mathbf{G}(\mathbf{P}) + \mathbf{X}(\mathbf{P}) = \tilde{\mathbf{h}} + \tilde{\mathbf{G}}(\mathbf{P}) \qquad (13)$$

here the tilde stresses that the related matrices contain terms accounting for the presence of the solvent field.

The matrices $\mathbf{h}$ and $\mathbf{G}(\mathbf{P})$ collect the usual one- and two-electron integrals over the basis set used for the *vacuum* SCF calculation, while $\mathbf{P}$ is the one-electron density matrix; the matrices $\mathbf{j}$, $\mathbf{y}$, and $\mathbf{X}(\mathbf{P})$ collect the one- and two-electron integrals to be added when the interactions with the polarized dielectric medium are explicitly taken into account within the PCM framework. More details on these matrices can be found elsewhere.[16]

Recently a PCM implementation allowing the computation of (hyper)polarizabilities both in the static[8] and frequency dependent[9] cases has been done; in this framework, use is made of the coupled perturbed Hartree−Fock (CPHF) and time-dependent coupled Hartree−Fock (TDCHF) formulations, respectively.[19,20] The formal aspects of the implementation can be found in the already quoted source papers.[8,9] Here it is sufficient to recall that, when an external static field $\vec{E}$ is applied, a further monoelectronic term has to be introduced in the Fock operator of eq 13:

$$\tilde{\mathbf{h}} = \mathbf{h} + \sum_a \mathbf{m}_a E^a + {}^1/_2(\mathbf{j} + \mathbf{y}) \qquad (14)$$

where $\mathbf{m}_a$ collects the integrals of the ath Cartesian component of the dipole moment operator.

By expanding $\mathbf{F}$, $\mathbf{C}$, ϵ, and $\mathbf{P}$ in terms of the external electric field components one gets expansions as a function of the magnitude and direction of the field; then substituting the latter in eq 12 and equating coefficients of same exponential terms on both sides leads to various CPHF equations in different orders; for example, for the first order one obtains:

$$\tilde{\mathbf{F}}^a\mathbf{C}^0 + \tilde{\mathbf{F}}^0\mathbf{C}^a = \mathbf{S}\mathbf{C}^a\epsilon^0 + \mathbf{S}\mathbf{C}^0\epsilon^a \qquad (15)$$

with:

$$\tilde{\mathbf{F}}^a = \mathbf{m}_a + \tilde{\mathbf{G}}(\mathbf{P}^a) \qquad (16)$$

It is immediate to see that from eq 15 and from the higher order analogs, one can derive the density matrix derivatives and hence the various (hyper)polarizabilities tensor components by

$$\gamma^{(n)}_{a_1 a_2, ..., a_{n+1}} = -\mathrm{Tr}[\mathbf{m}_{a_1}\mathbf{P}^{a_2, ..., a_{n+1}}] \qquad (17)$$

where $n + 1$ is the rank of the tensor and a_x the Cartesian coordinates specifying its components.

The procedure briefly described above does not take into account the differences between the macroscopic external field and the local one really acting on the molecule; anyway the way to be followed to go beyond this first approximation is quite easy and physically well understandable.

Let us consider an empty cavity with shape adapted to the hypothetical molecular solute to be studied immersed in a continuum dielectric with permittivity ϵ, and switch on an external uniform field $\vec{E}^{ex}$. As already said, the immediate effects of this field are to induce a polarization of the solvent molecules so that to produce a reaction field inside the cavity. In the ASC framework exploited by PCM, this field is easily described in terms of an apparent surface charge σ^{ex} (or equivalently of a set of point charges $\{q_i^{ex}\}$ placed on the previously defined surface tesserae), and simple electrostatic considerations of the same type of those leading to eq 11 yield to the following equation:

$$\mathbf{q}^{ex} = -\boldsymbol{\Sigma}\mathbf{D}^{-1}\mathbf{E}_n^{\ ex} \qquad (18)$$

where $\mathbf{E}_n^{ex}$ is the matrix collecting the components of the external field perpendicular to the cavity surface, computed at each tessera i. The matrix $\mathbf{D}$, tightly related to the general $\mathbf{O}$

matrix of eq 11, collects the effects of the reaction field the induced charges produce on themselves.

When the molecular solute is put inside the cavity the total solvent effects to be considered in order to derive its response functions can be thus represented by a set of effective point charges $\{q_i^{\mathrm{eff}}\}$ given by the sum of two contributions, namely the "solute field" and the "external field" induced charges, $\{q_i\}$ (see eq 11) and $\{q_i^{\mathrm{ex}}\}$ (see eq 18), respectively. This is reflected in the definition of the monoelectronic matrix $\tilde{\mathbf{h}}$ of eq 14 in which a further term, $\mathbf{h}^{\mathrm{ex}}$, has to be added:

$$\mathbf{h}^{\mathrm{ex}} = \sum_a \tilde{\mathbf{m}}_a E_a^{\mathrm{ex}} \tag{19}$$

where the field $\vec{E}^{\mathrm{ex}}$ is now the external macroscopic one. The matrix $\tilde{\mathbf{m}}_a$ is derived from the interaction energy between the "external field" induced charges and the solute electronic charge:

$$\tilde{\mathbf{m}}_a = -\sum_i \mathbf{V}^i \frac{\partial q_i^{\mathrm{ex}}}{\partial E_a^{\mathrm{ex}}} \tag{20}$$

where the matrix $\mathbf{V}$ collects the potential integrals over the basis set computed at each tessera i.

As we already said, in the CPHF formalism, the various Hartree–Fock equations to be solved to get the density matrix derivatives (and then the hyperpolarizability tensor via eq 22) are obtained by considering the derivatives of eq 12 with respect to the field. It is easy to see that the new term $\mathbf{h}^{\mathrm{ex}}$, being linear in the field, explicitly acts at the first order only, as a constant contribution to be inserted in eq 21; namely,

$$\tilde{\mathbf{F}}^a = \mathbf{m}_a + \tilde{\mathbf{m}}_a + \tilde{\mathbf{G}}[\mathbf{P}^a(\mathbf{h}^{\mathrm{ex}})] \tag{21}$$

At zero order it disappears, being the related equation obtained in the limit of zero external field. By applying the same procedures indicated above one derives the new set of density matrix derivatives $\mathbf{P}^{a_1a_2\cdots}(\mathbf{h}^{\mathrm{ex}})$ from which new (hyper)polarizabilities are easily computed:

$$\gamma^{(n)}_{a_1a_2,...,a_{n+1}}(\mathbf{h}^{\mathrm{ex}}) = -\mathrm{Tr}[\mathbf{m}_{a_1}\mathbf{P}^{a_2,...,a_{n+1}}(\mathbf{h}^{\mathrm{ex}})] \tag{22}$$

Within this framework it is immediate to derive the local effects acting on the macroscopic external field and the related local field tensor $\mathbf{f}$; namely, it is sufficient to consider the ratio between the various component of the polarizability tensors obtained by solving the first CPHF equations in which the further constant term $\mathbf{h}^{\mathrm{ex}}$ is, or is not, explicitly introduced in the Fock matrix, respectively,

$$\mathbf{f}_{ab} = \frac{\alpha_{ab}(\mathbf{h}^{\mathrm{ex}})}{\alpha_{ab}} \tag{23}$$

The relation 23 can be easily extended to higher order hyperpolarizability tensors, at least for the diagonal terms; namely, we have

$$(\mathbf{f}_{aa...a})^n = \frac{\gamma^{(n)}_{aa...a}(\mathbf{h}^{\mathrm{ex}})}{\gamma^{(n)}_{aa...a}} \tag{24}$$

3. Numerical Results and Discussion

The results here reported and analyzed regard static (hyper)-polarizabilities α, β, and γ of various molecules (H_2CO, CH_3COH, CH_3CH_2COH, $C(CH_3)_3COH$, CH_2C_2O, and CH_2C_3O) in water (ϵ=78.5) at 298 K.

TABLE 1: Diagonal Values of Static Polarizability and Hyperpolarizability Tensors Corresponding to the Cartesian Component a^a with the Largest Value of Polarizability

	α_{aa}		β_{aaa}		γ_{aaaa}	
cavity	sphere	mol cav[b]	sphere	mol cav	sphere	mol cav
H_2CO	23.04	21.62	97.86	76.96	201.13	200.32
CH_3COH	34.73	33.35	140.90	133.62	621.50	717.84
CH_3CH_2COH	49.10	45.47	75.40	89.92	1839.65	1334.94
$C(CH_3)_3COH$	60.49	60.73	146.30	145.29	3980.89	4154.57

[a] Tensors in au. [b] Mol cav = molecular-shaped cavity.

All the calculations have been performed using the already quoted IEF version of the PCM method[17,18] and a 6-31G basis set. Clearly, this quite limited basis set gives a very poor description of the various response functions, as they are quantities which require extended basis sets including polarization and diffuse functions. However, as the scope of the present paper is not the evaluation of the best (hyper)polarizability values but the analysis of relative quantities obtained as ratios of values computed at the same level of approximation, the absolute quality of the calculation is at least a second-order effect, not important in the analysis below.

Within the PCM framework, the cavity in the dielectric medium which contains the molecular solute is defined in terms of interlocking spheres centered on the solute nuclei, with radii R_k equal to 1.2 times the corresponding van der Waals[21] values R_k^{vdw}; namely, for our solutes we have $R_H = 1.44$ Å, $R_C = 2.04$ Å, and $R_O = 1.80$ Å. Moreover, in order to test the reliability of the method through a direct comparison with analytical formulas of the local field factors, we have repeated the calculations with simplified cavities: for the first group of solutes (H_2CO, CH_3COH, CH_3CH_2COH, and $C(CH_3)_3COH$) we have exploited a single sphere centered on the mass center of the molecule and with radius such that to give the same volume of the molecular cavity, while for CH_2C_2O a three-sphere cavity with the spheres of radius 2.4 Å centered on the carbon and the oxygen atoms, and for CH_2C_3O, the analog four-sphere cavity. The latter two cavities are quite good representations of an elliptical cavity for which the expression 9 can be applied.

In Table 1 we report, for the first group of molecules, the diagonal values of each static (hyper)polarizability tensor (in au) corresponding to the Cartesian component with the largest value of the polarizability tensor as obtained by exploiting a spherical and a molecular shaped cavity, respectively.

The results of Table 1 are here reported not as reliable absolute values, but as a clear demonstration of the importance of the choice of the proper cavity shape. Numerical data in fact show that the exploitation of a cavity well modelled on the shape of the molecule leads to important differences with respect to the use of a simplified cavity; namely, the largest variations are of the order of 10% in α, of 27% in β, and of 37% in γ. In Table 2 we report the local field factors of the same molecules and the same conditions used in Table 1 as obtained from eqs 23 and 24. For a comparison with analytical values we recall that the Onsager formula of eq 7 gives $f_O^{\mathrm{sp}} = 1.490$ for $\epsilon = 78.5$.

From the data in Table 2 several interesting features can be derived. First, it is evident that also in the case of spherical cavities the computed values deviate from the theoretical one (i.e., $f = 1.490$). This behavior can be easily explained if one considers that the spherical cavity reproducing the molecular volume can induce important border effects on those atoms

TABLE 2: Local Field Factors of the Various Solutes in Water Obtained From Equations 23 and 24 of the Text by Exploiting a Spherical- and a Molecular-Shaped Cavity

	from α_{aa}		from β_{aaa}		from γ_{aaaa}	
cavity	sphere	mol cav[a]	sphere	mol cav	sphere	mol cav
H_2CO	1.470	1.342	1.474	1.334	1.530	1.339
CH_3COH	1.458	1.405	1.387	1.394	1.115	1.375
CH_3CH_2COH	1.441	1.361	1.375	1.366	1.446	1.392
$C(CH_3)_3COH$	1.486	1.550	1.487	1.618	1.477	1.548

[a] mol cav = molecular cavity.

which are very close to the surface where the local field is strongly nonuniform; the bigger these effects the larger is the difference with respect to the theoretical value obtained supposing a completely uniform field inside the whole cavity. These discrepancies are easily reduced by enlarging the sphere; for the specific molecules listed in Table 2 it is sufficient to double the radius derived from the molecular volume to obtain values exactly equivalent to the theoretical one. The same border effects are also reflected in the differences among values obtained from the ratio of different order hyperpolarizabilities (see eq 24); better showing this point is worth a brief digression.

As the theoretical framework described in the previous section shows, the local field effects explicitly act at the first CPHF order only (through the presence of h^{ex} in the first derivative of the Fock matrix) but indirectly they change the results at all the higher orders. Thus, being the solutions of the CPHF equations generally not exact, the magnitude of the inherent error is related to the order, the effects due to an eventual nonuniform shape of the local field will be differently reflected on the resulting α, β, or γ values, and indirectly on the local field factors derived by them. Also, small differences in the values of the factors computed from different hyperpolarizability ratios indicate small border effects. An evident proof of this statement is given by $C(CH_3)_3COH$; here both the deviations of the computed factor with respect to the theoretical value and the differences among the three local field factors are almost negligible, and as a matter of fact a sufficiently uniform behavior of the external field inside the cavity has been numerically found.

Now that we have stressed this technical but not minor aspect, we consider the effects of a molecular cavity with general shape.

First it is worth noting that, while in the case of the sphere the deviations of the computed values from the theory are always in the direction of a smaller local field with respect to the Onsager value, here the effects can go in both the directions. This more complex behavior is obviously related to the tensorial nature of the local field factors to be always taken into account when no spherical symmetry can be exploited. Just by limiting our attention to the simple case of the elliptical cavity, from eq 9 one derives components of the local field tensor both smaller and larger than the spherical limit. Thus, as the data of Table 2 report a single diagonal component of the **f** tensor and all the considered molecules are embedded in complex cavities, what we can only derive is that the specific shape of each solute acts in different ways on the different components of the (hyper)-polarizability tensors and that it is impossible to find a common trend for all the analyzed cases.

These general observations, even if quite simple, have important consequences; namely, they clearly show that the use of a theoretical model which a priori defines a value of the local field factor to be applied to all the molecules, irrespective of their real nature, is at least suspicious and, in some cases, leads to conclusions that can invalidate the whole comparison between computed and experimental data.

TABLE 3: Local Field Values Obtained by Solving Equation 8 of the Text for the Two Molecules Placed in Elliptical Cavities with the Major Axis along z

	$f_{xx} = f_{yy}$	f_{zz}
H_2C_2O	1.612	1.295
H_2C_3O	1.658	1.240

TABLE 4: Diagonal Components of the Static Polarizability Tensor (in au) of the Two Solutes in Water[a]

	α_{xx}		α_{yy}		α_{zz}	
cavity	∼ellip.	mol cav	∼ellip.	mol cav	∼ellip.	mol cav
H_2C_2O	15.02	15.42	8.55	8.88	43.84	48.12
H_2C_3O	17.65	18.17	11.26	11.64	89.87	100.5

[a] Computed by exploiting the simplified cavity, below-indicated as "∼ellip.", and the molecular cavity (mol cav).

TABLE 5: Local Field Factors of the Two Solutes in Water

	f_{xx}		f_{yy}		f_{zz}	
cavity	∼ellip.	mol cav	∼ellip.	mol cav	∼ellip.	mol cav
H_2C_2O	1.593	1.527	1.620	1.644	1.277	1.261
H_2C_3O	1.633	1.579	1.660	1.684	1.216	1.198

[a] Computed through the eq 23 of the text in the case of a simplified cavity, below indicated as "∼ellip.", and of the molecular cavity (mol cav).

The same considerations derived from results of Tables 1 and 2 can be applied to the second group of solutes (H_2C_2O and H_2C_3O) for which the analytical reference is given by the extension of the Onsager model to the elliptical cavity.

In Table 3 we report the theoretical values obtained by solving eq 8 for the two molecules placed with their major axis along z ($a = b = 2.4$ Å for both and $c = 3.637$ Å for H_2C_2O and 4.279 Å for H_2C_3O) and applying eq 9 for the diagonal components of the **f** tensor.

In Table 4 for each solute we report the diagonal components of the polarizability tensor (in au) computed both by exploiting the simplified cavity (in terms of the number of the spheres), indicated below as "∼ellip.", and the actual molecular cavity.

Here, even if the difference between the simplified and the real cavities is smaller than the difference between those found in the first group of solutes, where a single sphere has to replace many interlocking spheres cavity (from 4 spheres in H_2CO to 16 in $C(CH_3)_3CO$), the differences between corresponding values in the first and the second column of Table 4 are of the same order of those found in Table 1 (i.e., ∼10% for the largest $\boldsymbol{\alpha}$ component). This result, once again, shows the fundamental importance of the use of a cavity well modeled on the molecular shape in the evaluation of this kind of properties. In Table 5 we report the local field factors of the same molecules and the same conditions used in Table 4 as obtained from eq 23; for a comparison with analytical values we recall that the Onsager values are reported in Table 3.

Data in Table 5 give us information about the validity to shift to the ellipsoid the considerations previously done for the comparison spherical molecular cavities. The only evident difference to be stressed is that the nonexact equality between theoretical and computed values of the local field factors are here also due to the imperfect elliptical shape of the simplified cavity, in addition to the border effects, which are still present. Anyway, these differences are so small that the comparison with the hypothetical ellipse has to be considered reliable.

The results of Table 5, which show a general better agreement between simplified-cavity- and molecular-cavity-derived values with respect to those of Table 2, lead to a quite obvious conclusion; namely, that for these two solutes, the errors one makes in using theoretical (i.e., Onsager-model-derived) values to fill the gap between computed and experimental data are smaller than for the previous group of solutes, for which the theoretical factors can differ from the computed ones even of 9% (see for example the first two column for H_2CO). This conclusion has been defined quite obvious as it can be easily derived by geometrical considerations on the shape of the molecules; for H_2C_xO compounds in fact, the molecular cavity is clearly better approximated by an ellipse than that of the RCOH compounds of the previous group by a single sphere. Here, only the largest component (i.e., $C(CH_3)_3COH$) seems to be well represented by the sphere, as it is easily predictable by geometrical considerations on the relative values of the internuclear distances and the sphere radii.

4. Conclusions

We have reported an analysis of the relationship between microscopical $\gamma^{(n)}$ hyperpolarizability tensors and macroscopical $\chi^{(n)}$ susceptibility tensors which follows that done in many books of nonlinear optics (see, e.g., Butcher and Cotter[13]) but also opens the way of giving an operational definition of the proper local field factors with the aid of ab initio QM calculations.

It is worth remarking that the present paper clearly shows that the local field factors can be computed with a modest computational effort and, being derived as ratios of two quantities (namely the polarizability tensor components computed in two different versions of the method, see eq 23) obtained with the same approximations (e.g., the same basis set), they are almost free from basis set-dependent errors (for example, for H_2CO the polarizability derived field factor goes from 1.337, to 1.341, and to 1.342 passing from STO-3G, 3-21G, and 6-31G basis set). Hence, the procedure here presented can be also used by experimentalists not wishing to perform complex calculations.

A necessary further step in this kind of analysis will be presented in a future communication, in which the more interesting case, from the practical point of view, of frequency dependent hyperpolarizabilities will also be treated. In the latter case the problem is complicated by the presence of a further term associated with the resulting frequency ω_σ which has to be included in eq 10, giving the general local field tensor; its theoretical derivation is not as evident as that presented here for the static terms.

Even if incomplete, as limited to the static problem only, the present paper should suffice to show how proper QM methods for the study of molecules in solution can be exploited to recognize, and overcome a "trap", as Bishop says in an authoritative review,[22] very common issue in this kind of analyses where the comparisons between experimental and computed data are so delicate and still in question.

For completeness' sake we quote a very interesting still unpublished paper by R. Wortmann and D.M. Bishop[23] we had the chance to read during the last revision of the present paper. There an extension of Onsager's reaction field to nonlinear-optical experiments in condensed media is presented and is used to derive effective polarizabilities and local field corrections for the spherical and the ellipsoidal cases. We think that Wortmann and Bishop article and the present one, if correctly taken together, could give an almost complete elucidation on the connection between experimentally derived molecular (hyper)polarizabilities and the results of quantum-chemical calculations.

Acknowledgment. The authors thank Professor D.M. Bishop for helpful discussions. The financial support by the Consiglio Nazionale delle Ricerche is also acknowledged.

References and Notes

(1) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(2) Mikkelsen, K. V.; Jørgensen, P.; Jensen, M. J. A. *J. Chem. Phys.* **1994**, *100*, 6597.

(3) Mikkelsen, K. V.; Lou, Y.; Ågren, M.; Jørgensen, P. *J. Chem. Phys.* **1994**, *100*, 8240.

(4) Mikkelsen, K. V.; Sylvester-Hvid, K. O. *J. Phys. Chem.* **1996**, *100*, 9116.

(5) Stähelin, M.; Moylan, C. R.; Burland, D. M.; Willets, A.; Rice, J.; Shelton, D. P.; Donley, E. A. *J. Chem. Phys.* **1993**, *98*, 5595.

(6) Willetts, A.; Rice, J. E. *J. Chem. Phys.* **1993**, *99*, 426.

(7) Wong, M. W.; Wiberg, K. B.; Frish, M. *J. Chem. Phys.* **1991**, *95*, 8991.

(8) Cammi, R.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1996**, *104*, 4611.

(9) Cammi, R.; M. Cossi, M.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1996**, *105*, 10556.

(10) Lorentz, H. A. *The Theory of Electrons*; Teubner: Leipzig, 1916; reprinted Dover: New York, 1951.

(11) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1456.

(12) Böttcher, C. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973.

(13) Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, 1990.

(14) Miertuš, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* **1981**, *55*, 117.

(15) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(16) Cammi, R.; Tomasi, J. *J. Comp. Chem.* **1995**, *16*, 1449.

(17) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032.

(18) Mennucci, B.; Cancès, E.; Tomasi, J. *J. Phys. Chem.*, in press.

(19) Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *85*, 976.

(20) Karna, S. P.; Dupuis, M. *J. Comput. Chem.* **1991**, *12*, 487.

(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(22) Bishop, D. M. *Int. Rev. Phys. Chem.* **1994**, *13*, 21.

(23) Wortmann, R.; Bishop, D. M. *J. Chem. Phys.*, submitted for publication.