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# Calculations of First- and Second-Order Nonlinear Molecular Hyperpolarizabilities by Perturbation Methods: I. An Efficient Method for Evaluating Time-Independent Hyperpolarizabilities

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From a suitable reorganisation of the sum-over-states (SOS) equations of the usual time-independent perturbation theory, recurrent expressions for static polarizability ( $\alpha$ ) and second- ( $\beta$ ) and third- ( $\gamma$ ) order hyperpolarizabilities are obtained. These expressions are given in a well-adapted way for computer implementation and lead to an efficient algorithm reducing the computing time by a factor of 50 with respect to a "brute-force" translation of the standard SOS equations.

## I. INTRODUCTION

The development of new optical communication devices requires efficient nonlinear optical properties.<sup>1</sup> Great efforts are presently concerned with the molecular design of organic materials with enhanced nonlinear optical behavior. In the framework of the dipolar approximation, the optical effects are associated with coefficients of the expansion of the induced polarization  $P$  in terms of the applied external electric field  $F$ :

$$P = P_0 + \chi^{(1)} \otimes F + \chi^{(2)} \otimes F \otimes F + \chi^{(3)} \otimes F \otimes F \otimes F + \dots \quad (1)$$

where  $P_0$  is the intrinsic polarization of the material. The coefficients  $\chi^{(i)}$  are the electrical susceptibilities (linear for  $i = 1$ , nonlinear otherwise) and have their equivalent at the molecular level, i.e., the polarizability  $\alpha$  (tensor of order 2) and the hyperpolarizabilities  $\beta$  (tensor of order 3),  $\gamma$  (tensor of order 4), ... which, in turn, are the expansion coefficients of the induced dipole moment with respect to the electric field  $F$ :

$$\mu = \mu_0 + \alpha \otimes F + \beta \otimes F \otimes F + \gamma \otimes F \otimes F \otimes F + \dots \quad (2)$$

where  $\mu_0$  is the permanent dipole moment.

In principle, the (hyper)polarizabilities are obtained variationally by the finite field (FF) procedure of Cohen and Roothaan<sup>2</sup> or

perturbationally by the sum-over-states (SOS) method.

In the FF technique, the dipole moment induced by different electrical fields is calculated and numerically differentiated with respect to the external electric field to give according to the Hellmann-Feynman theorem the various (hyper)polarizabilities. A term,  $-\mu F$ , describing the interaction between the electric field and the molecular dipole moment is included in the molecular Hamiltonian. At the Hartree-Fock (HF) level, this supplementary interaction due to the electric field appears explicitly in the one-electron Fock operator and requires the numerical evaluation of additional one-electron moment integrals whose calculation is, however, fairly standard. This technique is equivalent to the analytic coupled HF scheme at the limit of the zero field. It works well for the calculation of the polarizability,<sup>3</sup> but presents numerical difficulties when computing the hyperpolarizability terms. Indeed, the computation of these properties requires the numerical determination of higher-order derivatives which are not easy to perform<sup>4</sup> and with the consequence that the reliability of the numerical results is not well established at all.

On the other hand, the SOS method uses as a starting point the wave function obtained

in the absence of the external field and is derived from the time-independent perturbation theory where, in the framework of the Hellmann-Feynman theorem, it can be shown that the  $n$ th-order corrections to the energy due to the electric field perturbation correspond to the various coefficients of eq. (2).

In the case of HF theory, the HF wave function is not, by its approximate character, an eigenfunction of the total Hamiltonian, but instead is an eigenfunction of the total HF operator (sum of the one-electron Fock operators) which differs from the total Hamiltonian by the correlation operator. In the standard SOS method, the zeroth-order solution is actually the HF wave function and the unperturbed Hamiltonian is thus the Hartree-Fock total Hamiltonian. In this approximation, the SOS method neglects field-induced coupled reorganizational correlation effects and is not equivalent to the FF theory.<sup>5</sup> Thus, the SOS method is not to be considered as an alternative to the FF technique, but merely as a first step toward a more complete coupled Hartree-Fock technique.

For getting the second-order hyperpolarizability ( $\gamma$ ), one has to expand the perturbation theory till the fourth order, therefore an efficient application needs the elaboration of algorithms to avoid excessive computer time. This is the point that we address in the present article. Furthermore, we pay some attention to the derivation of recurrence formulas in going from one perturbation order to the next.

## II. CALCULATION OF THE HYPERPOLARIZABILITY TENSORS BY THE "SUM-OVER-STATE" (SOS) PROCEDURE

As mentioned, the SOS procedure consists in evaluating the  $n$ th-order energy corrections due to the perturbation by the electric field. For example, the second-order hyperpolarizability ( $\gamma$ ) obtained from the fourth-order energy perturbation has the explicit SOS expression:

$$\gamma_{ijkl} = S_{ijkl} \left[ \sum_{arst} \langle a|\mu_i|r\rangle \langle r|\mu_j|s\rangle \langle s|\mu_k|t\rangle \langle t|\mu_l|a\rangle / [(\epsilon_r - \epsilon_a)(\epsilon_s - \epsilon_a)(\epsilon_t - \epsilon_a)] \right]$$

$$\begin{aligned} & + \sum_{abcr} \langle a|\mu_i|b\rangle \langle b|\mu_j|c\rangle \langle c|\mu_k|r\rangle \langle r|\mu_l|a\rangle / [(\epsilon_r - \epsilon_a)(\epsilon_r - \epsilon_b)(\epsilon_r - \epsilon_c)] \\ & - \sum_{abrs} \langle a|\mu_i|b\rangle \langle b|\mu_j|s\rangle \langle s|\mu_k|r\rangle \langle r|\mu_l|a\rangle / [(\epsilon_r - \epsilon_a)(\epsilon_s - \epsilon_b)(\epsilon_r - \epsilon_b)] \\ & - \sum_{abrs} \langle a|\mu_i|b\rangle \langle b|\mu_j|r\rangle \langle r|\mu_k|s\rangle \langle s|\mu_l|a\rangle / [(\epsilon_r - \epsilon_a)(\epsilon_s - \epsilon_a)(\epsilon_r - \epsilon_b)] \\ & - \sum_{abrs} \langle a|\mu_i|r\rangle \langle r|\mu_j|b\rangle \langle b|\mu_k|s\rangle \langle s|\mu_l|a\rangle / [(\epsilon_r - \epsilon_a)(\epsilon_s - \epsilon_a)(\epsilon_s - \epsilon_b)] \end{aligned} \quad (3)$$

In this expression, the summations over  $a, b, c, r, s$ , and  $t$  are, respectively, over the occupied molecular orbitals ( $a, b, c$ ) and over the unoccupied molecular orbitals ( $r, s, t$ );  $\epsilon_r, \epsilon_s, \epsilon_t, \epsilon_a, \epsilon_b$  and  $\epsilon_c$  are the HF molecular orbitals energies;  $S_{ijkl}$  means summation over all permutations of indices  $ijkl$ . Equation (3) is valid as long as the ground-state molecular energy is nondegenerate. This expression is given in terms of integrals over molecular orbitals and involves quadruple summations over molecular orbitals (occupied or unoccupied in the ground state). Because of these quadruple summations, the numerical evaluation is rather involved and a "brute-force" translation of this expression into computer codes would require an excessive (and thus expensive) computer time. For example, while the HF calculation of the hexatriene in the STO-3G basis set takes about 2 hours on a DEC 20/60 computer, the computation of all components of the second-order hyperpolarizability takes about 16 hours on the same computer. This example demonstrates the need of developing efficient SOS algorithms.

## III. PERTURBATION METHOD REVISITED

Many textbooks produce standard expressions of the Rayleigh-Schrödinger perturbation theory for first-, second-, and third-order corrections to the total energies. In this section, we present general expressions for the  $n$ th-order energies following the general ideas of Szabo & Ostlund,<sup>6</sup> but having in mind to produce recurrent formulae and an efficient algorithm to compute the polarizability and hyperpolarizabilities by the SOS method.

Suppose we wish to solve the eigenvalue problem:

$$H|\psi_i\rangle = (H_0 + V)|\psi_i\rangle = E_i|\psi_i\rangle \quad (4)$$

where  $|\psi_i^{(0)}\rangle$  (or  $|i\rangle$ ) and  $E_i^{(0)}$ , which are respectively the eigenfunctions and eigenvalues of the unperturbed Hamiltonian, are known:

$$H_0|\psi_i^{(0)}\rangle = E_i^{(0)}|\psi_i^{(0)}\rangle \quad (5)$$

If  $V$  is a small perturbation, we can introduce an ordering parameter  $\lambda$  which will later be set equal to unity

$$H = H_0 + \lambda V \quad (6)$$

and expand the exact eigenfunctions and eigenvalues in a Taylor series in  $\lambda$ ,

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \quad (7)$$

$$|\psi_i\rangle = |i\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle + \dots \quad (8)$$

If the so-called intermediate normalization is chosen, i.e.,  $\langle i|\psi_i\rangle = 1$ , and if the eigenvectors are normalized,  $\langle i|i\rangle = 1$ , it can be demonstrated that

$$\langle i|\psi_i^{(n)}\rangle = 0 \quad (9)$$

Substituting eqs. (7) and (8) into eq. (4) leads to:

$$\begin{aligned} (H_0 + \lambda V)(|i\rangle + \sum_q \lambda^q |\psi_i^{(q)}\rangle) \\ = (E_i^{(0)} + \sum_q \lambda^q E_i^{(q)})(|i\rangle + \sum_q \lambda^q |\psi_i^{(q)}\rangle) \end{aligned} \quad (10)$$

and equalizing coefficients of  $\lambda^n$ , we find

$$\begin{aligned} H_0|\psi_i^{(n)}\rangle + V|\psi_i^{(n-1)}\rangle = E_i^{(0)}|\psi_i^{(n)}\rangle \\ + \sum_{q=1, n} E_i^{(q)}|\psi_i^{(n-q)}\rangle \end{aligned} \quad (11)$$

Multiplying each of these equations by  $\langle i|$  and using the orthogonality relations [eq. (9)], the  $n$ th order perturbation energies are given by:

$$E_i^{(n)} = \langle i|V|\psi_i^{(n-1)}\rangle \quad (12)$$

One way of solving such equations is to expand  $\psi_i^{(n)}$  in terms of eigenfunctions of the unperturbed Hamiltonian  $H_0$ , which are taken to be complete:

$$|\psi_i^{(n)}\rangle = \sum_m c_m |m\rangle \quad (13)$$

Since the eigenfunctions of  $H_0$  are orthogonal and still using eq. (9), the  $n$ th-order wave function can be written as:

$$|\psi_i^{(n)}\rangle = \sum'_m |m\rangle \langle m|\psi_i^{(n)}\rangle \quad (14)$$

where the prime on the summation indicates that the term  $m = i$  is excluded. Using the expansion eq. (14) in expression 12, the  $n$ th-order energy is given by:

$$E_i^{(n)} = \sum'_m \langle i|V|m\rangle \langle m|\psi_i^{(n-1)}\rangle \quad (15)$$

where  $\langle m|\psi_i^{(n)}\rangle$  are obtained by multiplying eq. (11) by  $\langle m|$  and using eq. (14):

$$\begin{aligned} \langle m|\psi_i^{(n)}\rangle = \left\{ \sum'_p \langle p|V|m\rangle \langle p|\psi_i^{(n-1)}\rangle \right. \\ \left. - \sum_{q=1, n-1} E_i^{(q)} \langle m|\psi_i^{(n-q)}\rangle \right\} (E_i^{(0)} - E_m^{(0)})^{-1} \end{aligned} \quad (16)$$

An interesting feature of this formulation is the recurrent character of the  $\langle m|\psi_i^{(n)}\rangle$  quantities. Indeed, it is worth noting that the calculation of these matrix elements requires the computation of the lower order matrix elements,  $\langle m|\psi_i^{(n-q)}\rangle$  and the lower order corrections to the energy,  $E_i^{(n-q)}$  (for  $q$  going from 1 to  $n - 1$ ).

In our case, the unperturbed Hamiltonian  $H_0$  and the perturbation  $V$  are, respectively, a sum of one-particle Hartree-Fock Hamiltonians  $h_0(i)$  and a sum of one-particle interactions:

$$H_0 = \sum_i h_0(i)$$

$$V = \sum_i v(i) = \sum_i F r_i$$

where  $r_i$  is the position of the  $i$ th electron. For an  $N$ -electron system, the unperturbed wave function is the Hartree-Fock ground state  $|\psi_o^{(0)}\rangle$  which is a Slater determinant formed from the  $N$  spin-orbitals  $\phi_a$  with lowest energies,

$$|\psi_o^{(0)}\rangle = |\phi_1 \phi_2 \dots \phi_a \dots \phi_N\rangle$$

The convention used throughout this article is that the occupied and virtual spin-orbitals are, respectively, labeled by  $a, b, c \dots$  and  $r, s, u \dots$  subscripts. The  $n$ th-order energy is defined by eq. (15) where the eigenfunctions  $|m\rangle$  are the determinants formed by substituting some occupied spin-orbitals by virtual ones. Because of the one-particle nature of the  $V$  operator, only the matrix elements,

$\langle 0|V|m\rangle$ , between  $\psi_o^{(0)}$  and singly excited states are nonzero:

$$\langle \psi_a^r | V | \psi_o^{(0)} \rangle = \int \phi_a(r) v(r) \phi_r(r) dr = v_{ar}$$

$$\langle \psi_{ab}^{rs} | V | \psi_o^{(0)} \rangle = 0$$

...

and the summations are restricted to these singly excited states:

$$E_o^{(n)} = \sum_a \sum_r v_{ar} \langle \psi_a^r | \psi_o^{(n-1)} \rangle \quad (17)$$

The  $\langle \psi_a^r | \psi_o^{(n)} \rangle$  terms are determined by using eq. (16) in which only the matrix elements involving singly and doubly excited states are different from zero:

$$\langle \psi_a^r | V | \psi_b^s \rangle = -v_{ab} \delta_{rs} + v_{rs} \delta_{ab} + \delta_{ab} \delta_{rs} \sum_c v_{cc}$$

$$\langle \psi_a^r | V | \psi_{bc}^{st} \rangle = v_{bs} \delta_{ac} \delta_{rt} - v_{bt} \delta_{ac} \delta_{sr} + v_{ct} \delta_{rs} \delta_{ab} - v_{cs} \delta_{rt} \delta_{ab}$$

Generally, the calculation of  $\langle i | \psi_o^{(n)} \rangle$ , where  $i$  represents an  $i$ th excited state, requires only the summation over the  $i$ th,  $(i-1)$ th, or  $(i+1)$ th excited states.

Starting from the lower order terms, it is possible to find by recurrence a general formula for the different  $\langle \psi_a^r | \psi_o^{(n)} \rangle$  matrix elements in function of the lower order  $\langle \psi_a^r | \psi_o^{(n-p)} \rangle$  terms:

$$\begin{aligned} \langle \psi_a^r | \psi_o^{(n)} \rangle = & \left\{ \sum_s v_{rs} \langle \psi_a^s | \psi_o^{(n-1)} \rangle \right. \\ & - \sum_b v_{ab} \langle \psi_b^r | \psi_o^{(n-1)} \rangle - \sum_{s,b} v_{sb} \left[ \sum_{p=1, n-1} \langle \psi_a^s | \psi_o^{(p)} \rangle \right. \\ & \left. \left. \langle \psi_b^r | \psi_o^{(n-p)} \rangle \right] \right\} (\epsilon_a - \epsilon_r)^{-1} \quad (18) \end{aligned}$$

#### IV. ALGORITHM FOR THE CALCULATION OF HYPERPOLARIZABILITIES BY THE SOS TECHNIQUE

Expression 18 is easy to implement into computer code. Indeed, if the  $\langle \psi_a^r | \psi_o^{(n)} \rangle$  are collected in a rectangular matrix  $D^{(n)}$  of  $N \times M$  dimension where  $N$  and  $M$  are, respectively, the number of occupied spin-orbitals and the number of virtual spin-orbitals, and if the  $V$  matrix of  $v_{ij}$  elements are partitioned in  $V_o$ ,  $V_v$ , and  $V_{ov}$  submatrices, we get:

$$V = \begin{pmatrix} v_{ab} & v_{ar} \\ v_{ra} & v_{rs} \end{pmatrix} = \begin{pmatrix} V_o & V_{ov} \\ V_v^T & V_v \end{pmatrix}$$

Thus, expression 18 can be written as:

$$D^{(n)} = D^{(n-1)} V_v^T - V_o D^{(n-1)} - \sum_{p=1, n-1} D^{(p)} V_{ov}^T D^{(n-p)} \quad (19)$$

where the elements of the rectangular matrix  $D^{(n)}$  are defined as

$$D_{ar}^{(n)} = (\epsilon_a - \epsilon_r) \langle \psi_a^r | \psi_o^{(n)} \rangle \quad (20)$$

This last expression is well adapted for vector operations.

Proceeding along these lines, we obtain tractable expressions of the polarizability and of the first and second hyperpolarizability tensor components in the SOS method:

$$\alpha_{ij} = -2 S_{ij} \sum_{ar} \langle a | \mu_j | r \rangle D_{ar}^{(1)}(i) \quad (21)$$

$$\beta_{ijk} = S_{ijk} \sum_{ar} \langle a | \mu_k | r \rangle D_{ar}^{(2)}(i, j) \quad (22)$$

$$\gamma_{ijkl} = -(1/3) S_{ijkl} \sum_{ar} \langle a | \mu_l | r \rangle D_{ar}^{(3)}(i, j, k) \quad (23)$$

where,

$$D_{ar}^{(1)}(i) = \langle r | \mu_i | a \rangle / (\epsilon_a - \epsilon_r) \quad (24)$$

$$\begin{aligned} D_{ar}^{(2)}(i, j) = & \left[ \sum_s \langle r | \mu_j | s \rangle D_{as}^{(1)}(i) \right. \\ & \left. - \sum_b \langle a | \mu_j | b \rangle D_{rb}^{(1)}(i) \right] / (\epsilon_a - \epsilon_r) \quad (25) \end{aligned}$$

$$\begin{aligned} D_{ar}^{(3)}(i, j, k) = & \left[ \sum_s \langle r | \mu_k | s \rangle D_{as}^{(2)}(i, j) \right. \\ & - \sum_b \langle a | \mu_k | b \rangle D_{br}^{(2)}(i, j) \\ & \left. - \sum_{bs} \langle b | \mu_k | s \rangle D_{as}^{(1)}(i) D_{br}^{(1)}(j) \right] / (\epsilon_a - \epsilon_r) \quad (26) \end{aligned}$$

The implementation of these equations leads to a very efficient algorithm. Indeed, an analysis of the numerical operations counts shows that the calculation of a single component of the second-order hyperpolarizability,  $\gamma_{ijkl}$ , requires roughly  $25 N^2 M^2$  multiplications,  $5 N^2 M^2$  divisions and  $5 N^2 M^2$  additions. The numerical calculation of this single component using eq. (23) only needs a number of operations proportional to  $N M$  multiplications and additions. It also involves the calculation of the matrix-elements  $D_{ar}^{(3)}$

which only requires  $(N + M + 2N \cdot M)$  multiplications and the core availability of the lower order matrix-elements  $D_{ar}^{(1)}$  and  $D_{ar}^{(2)}$  which appears as necessary elements in the calculation of the polarizabilities ( $\alpha$ ) and the first-order polarizabilities ( $\beta$ ). This procedure results in a computation time of all components of the second order hyperpolarizability,  $\gamma_{ijkl}$ , which takes about 20 minutes for the hexatriene on a DEC 20/60 computer, which means 1/50 of the computer time required by the "brute force" implementation eq. (3). The use of array processors would certainly lead to further improvements in the computing times.

## V. CONCLUSIONS

Our aim was to compute  $\alpha$ ,  $\beta$ , and  $\gamma$  in reasonable computing times. We have shown that, by a suitable analysis of perturbation formulae, it is possible to get *recurrent expressions* for these quantities and thus to *construct a very efficient algorithm* leading to a sensible reduction of computing times. The following step in this way is to deduce such relations and algorithms for the computation

of dynamical (hyper)polarizabilities from the time-dependent perturbation theory. This is the subject of the next paper of this series.

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