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Application of Second-Order SCF Perturbation Theory to the Calculation of Mixed-Frequency Hyperpolarizabilities from Time-Dependent Hartree–Fock Theory

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Second-order SCF perturbation theory is used to solve the TDHF equations of Dalgarno and Victor through the introduction of frequency dependent density matrices. Exploratory calculations are reported for the frequency dependent polarizability and hyper-polarizability of LiH.

Key words: Frequency dependent polarizabilities

1. Introduction

Time-dependent Hartree–Fock (TDHF) theory [1] has found wide application in the calculation of atomic and molecular optical properties. The TDHF equations have been derived at both the uncoupled [2] and coupled levels of approximation [3] and solved by a variety of techniques [4–9]. In two recent papers [6, 8], the methods of time independent self-consistent field (SCF) perturbation theory [10] were applied to the solution of the perturbative TDHF equations. In the present paper this approach is extended to the solution of the second order TDHF equations with two distinct frequencies for the applied perturbation.

2. Theory

The solution of the TDHF equation is considered here for a molecule or atom interacting with a long established oscillating electric field. The field in question is assumed to have two components of frequency w_1 and w_2, respectively, and consequently lead to a variety of electrical polarizations in the system. The Hamiltonian for the interaction, to be treated here as a perturbation, is given by

$$\mathscr{H} = H^{(1)}\{\lambda_1(e^{iw_1t} + e^{-iw_1t}) + \lambda_2(e^{iw_2t} + e^{-iw_2t})\}, \tag{1}$$

where the λ's are perturbation parameters and $H^{(1)}$ the dipole moment operator. Under the LCAO method $H^{(1)}$ is represented by a matrix over atomic orbital basis functions.

Following Dalgarno *et al.* [3, 5], the molecular orbitals for the perturbed molecule are expanded in a perturbation series. The first order changes in the coefficient matrix, $C^{(\pm w)}$, are given as solutions to the SCF matrix equation

$$F^{(0)}C^{(\pm)} \pm wS^{(0)}C^{(\pm)} + F^{(\pm)}C^{(0)} = S^{(0)}C^{(\pm)}E^{(0)} + S^{(0)}C^{(0}E^{(\pm)} \tag{2}$$

which must be solved subject to the orthonormality constraints:

$$\tilde{C}^{(0)}S^{(0)}C^{(\pm)} + \tilde{C}^{(\mp)}S^{(0)}C^{(0)} = 0, \tag{3}$$

where $F^{(0)}$, $C^{(0)}$, $S^{(0)}$ and $E^{(0)}$ in the above equations are, respectively, the zero-order Fock, coefficient, overlap and orbital energy matrices [11]. The above equations may be used to calculate all first-order changes in C, $C^{(\pm w_n)}$ $n = 1$ or 2, by the substitution of the appropriate w into Eq. (2). The first-order frequency-dependent Fock and density matrices are given by [7]

$$F_{\mu\nu}^{(\pm)} = H_{\mu\nu}^{(1)} + \sum_{\sigma}\sum_{\lambda} P_{\sigma\lambda}^{(\pm)}\{(\mu\nu/\sigma\lambda) - 1/2(\mu\lambda/\sigma\nu)\}, \tag{4}$$

$$P_{\sigma\lambda}^{(\pm)} = 2\sum_{i}^{\text{occupied}} \{C_{\sigma i}^{(0)}C_{\lambda i}^{(\pm)} + C_{\sigma i}^{(\mp)}C_{\lambda i}^{(0)}\}. \tag{5}$$

The $C^{(\pm)}$ are calculated by expanding them in terms of the zero order, unperturbed, molecular orbitals [7]. The coefficients, $A_{ij}^{(\pm)}$ in this expansion are given by [7]

$$A_{ij}^{(\pm)} = -\mathscr{F}_{ij}^{(\pm)}/(\varepsilon_i^{(0)} - \varepsilon_j^{(0)} \pm w), \tag{6}$$

$$A_{ii}^{(\pm)} = 0, \tag{7}$$

where

$$\mathscr{F}_{ij}^{(\pm)} = \tilde{C}_i^{(0)}F^{(\pm)}C_j^{(0)}. \tag{8}$$

Since $F^{(\pm)}$ depends on $A^{(\pm)}$ through $P^{(\pm)}$, Eq. (6) must be solved by iteration. The first order change in the density matrix is given by [7]

$$P_{\mu\nu}^{(\pm)} = 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}} \{A_{ki}^{(\mp)}C_{\mu k}^{(0)}C_{\nu i}^{(0)} + A_{ki}^{(\pm)}C_{\mu i}^{(0)}C_{\nu k}^{(0)}\}. \tag{9}$$

Although neither $P^{(\pm)}$ nor $F^{(\pm)}$ are symmetric, it can easily be shown from Eqs. (6) and (9) that

$$P^{(+)} = \tilde{P}^{(-)} \tag{10}$$

and that this relation holds for all non-Hermitian matrices treated here.

3. Second Order

The second and higher-order expansion parameters are λ, w_1 and w_2. For a perturbation second order in λ, there are several distinct combinations of the two frequencies w_1 and w_2. Accordingly, the notation introduced for the first order theory has to be elaborated slightly. If M is one of the matrices treated in the theory, then its first-order changes will be represented as:

$$M^{(\pm w_1,0)} = M^{(\pm,0)}, \tag{11}$$

$$M^{(0,\pm w_2)} = M^{(0,\pm)}. \tag{12}$$

Similarly, the various second-order changes are written as, for example

$$M^{(+w_1,+w_2)} = M^{(+,+)}, \tag{13}$$

$$M^{(0,+2w_2)} = M^{(0,+2)}. \tag{14}$$

Of all the possible second-order frequency combinations, the density matrix for only the $(-w_1 + w_2)$ combination will be treated in detail. Expressions for all of the remaining density matrices may be obtained from that for $P^{(-,+)}$ by appropriate changes to the two frequencies, w_1 and w_2.

The second-order equations may be obtained through the extension of the Dalgano–Victor approach to the second-order. The frequency difference SCF equations are given by

$$\begin{aligned} &F^{(0)}C^{(-,+)} + (w_2 - w_1)S^{(0)}C^{(-,+)} + F^{(-,0)}C^{(0,+)} + F^{(0,+)}C^{(-,0)} + F^{(-,+)}C^{(0)} \\ &\quad = S^{(0)}C^{(-,+)}E^{(0)} + S^{(0)}C^{(-,0)}E^{(0,+)} + S^{(0)}C^{(0,+)}E^{(-,0)} + S^{(0)}C^{(0)}E^{(-,+)}, \end{aligned} \tag{15}$$

with the second-order orthonormalization constraint

$$\tilde{C}^{(+,-)}S^{(0)}C^{(0)} + \tilde{C}^{(+,0)}S^{(0)}C^{(0,+)} + \tilde{C}^{(0,-)}S^{(0)}C^{(-,0)} + \tilde{C}^{(0)}S^{(0)}C^{(-,+)} = 0. \tag{16}$$

The first-order Fock matrices are those of Eq. (4) while the second-order Fock matrices are given by

$$F_{\mu\nu}^{(-,+)} = \sum\sum P_{\sigma\lambda}^{(-,+)}\{(\mu\nu/\sigma\lambda) - 1/2(\mu\lambda/\sigma\nu)\}, \tag{17}$$

where

$$P_{\sigma\lambda}^{(-,+)} = 2\sum_{i}^{\text{occ}}\{C_{\sigma i}^{(+,-)}C_{\lambda i}^{(0)} + C_{\sigma i}^{(+,0)}C_{\lambda i}^{(0,+)} + C_{\sigma i}^{(0,-)}C_{\lambda i}^{(-,0)} + C_{\sigma i}^{(0)}C_{\lambda i}^{(-,+)}\}. \tag{18}$$

The method of solution is similar to that presented above for the first-order expressions. The neglect of Eq. (16) would lead to the appearance of further terms in Eq. (15). The second-order coefficient matrices, $C^{(-,+)}$ and $C^{(+,-)}$ are expanded in terms of the known zeroth-order molecular orbitals according to

$$C^{(\mp,\pm)} = C^{(0)}B^{(\mp,\pm)}. \tag{19}$$

Substitutions for the first- and second-order C matrices in Eqs. (15) and (16), followed by multiplication of (15) with $\tilde{C}^{(0)}$ on the left, yields

$$\begin{aligned} &E^{(0)}B^{(-,+)} + (w_2 - w_1)B^{(-,+)} + \mathscr{F}^{(-,0)}A^{(0,+)} + \mathscr{F}^{(0,+)}A^{(-,0)} + \mathscr{F}^{(-,+)} \\ &\quad = B^{(-,+)}E^{(0)} + A^{(-,0)}E^{(0,+)} + A^{(0,+)}E^{(-,0)} + E^{(-,+)} \end{aligned} \tag{20}$$

and

$$\tilde{B}^{(+,-)} + \tilde{A}^{(+,0)}A^{(0,+)} + \tilde{A}^{(0,-)}A^{(-,0)} + B^{(-,+)} = 0. \tag{21}$$

Since $E_{ki}^{(2)} = 0$ for $k \neq i$, the equations for $B_{ki}^{(-,+)}$ and $B_{ki}^{(+,-)}$ may be obtained from (20) as $(k \neq i)$.

$$B_{ki}^{(-,+)} = \frac{\begin{aligned} -\mathscr{F}_{ki}^{(-,+)} - \sum_{l}^{\text{all}} \{\mathscr{F}_{kl}^{(-,0)} A_{li}^{(0,+)} + \mathscr{F}_{kl}^{(0,+)} A_{li}^{(-,0)}\} \\ + A_{ki}^{(-,0)} \varepsilon_{i}^{(0,+)} + A_{ki}^{(0,+)} \varepsilon_{i}^{(-,0)}\} \end{aligned}}{(\varepsilon_k - \varepsilon_i - w_1 + w_2)}. \tag{22}$$

The expression for $B^{(+,-)}$ may be obtained from (22) by a careful interchange of the signs of the two frequencies. The equivalent expression for the $k = i$ terms is obtained from Eq. (21) as

$$\tilde{B}_{ii}^{(+,-)} + B_{ii}^{(-,+)} = -\sum_{l}^{\text{all}} \{\tilde{A}_{li}^{(+,0)} A_{li}^{(0,+)} + \tilde{A}_{li}^{(0,-)} A_{li}^{(-,0)}\}. \tag{23}$$

After appropriate substitution for the higher-order coefficient matrices in (18), the second-order density matrix may be written as,

$$\begin{aligned} P_{\mu\nu}^{(-,+)} = 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{all}} \{ & B_{ki}^{(+,-)} C_{\mu k}^{(0)} C_{\nu i}^{(0)} + \sum_{l}^{\text{all}} (A_{ki}^{(+,0)} A_{li}^{(0,+)} C_{\mu k}^{(0)} C_{\nu l}^{(0)} \\ & + A_{ki}^{(0,-)} A_{li}^{(-,0)} C_{\mu k}^{(0)} C_{\nu l}^{(0)}) + B_{ki}^{(-,+)} C_{\mu i}^{(0)} C_{\nu k}^{(0)}\}. \end{aligned} \tag{24}$$

This equation may be simplified by taking advantage of the relationships expressed in Eqs. (20)–(23). Apart from leading to computationally more efficient equations, these simplifications are important since they eliminate apparent singularities which would occur if some of the zeroth-order orbitals were degenerate [12].

The reduction algebra for Eq. (24) follows logically from that given for the derivation of the corresponding second-order frequency independent density matrix given as an appendix to Ref. [12]. The final expression for $P^{(-+)}$ may be conveniently written as:

$$\begin{aligned} P_{\mu\nu}^{(-,+)} = {} & 2 \sum_{i}^{\text{all}} \sum_{k}^{\text{all}} \{\mathfrak{B}_{ki}^{(-,+)} C_{\mu i}^{(0)} C_{\nu k}^{(0)} + \mathfrak{B}_{ki}^{(+,-)} C_{\mu k}^{(0)} C_{\nu i}^{(0)}\} \\ & + 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \{b_{ki}^{(-,+)} C_{\mu i}^{(0)} C_{\nu k}^{(0)} + b_{ki}^{(+,-)} C_{\mu k}^{(0)} C_{\nu i}^{(0)}\} \end{aligned} \tag{25}$$

where, when both i and k label occupied orbitals,

$$\mathfrak{B}_{ki}^{(-,+)} = \tfrac{1}{2} \sum_{l}^{\text{vac}} \{A_{kl}^{(-,0)} A_{li}^{(0,+)} + A_{kl}^{(0,+)} A_{li}^{(-,0)}\}, \tag{26}$$

when both i and k label vacant orbitals

$$\mathfrak{B}_{ki}^{(-,+)} = -\tfrac{1}{2} \sum_{l}^{\text{occ}} \{A_{kl}^{(-,0)} A_{li}^{(0,+)} + A_{kl}^{(0,+)} A_{li}^{(-,0)}\}, \tag{27}$$

when i labels a vacant and k an occupied orbital

$$\mathfrak{B}_{ki}^{(-,+)} = 0, \tag{28}$$

and when i labels an occupied and k a vacant orbital

$$\mathfrak{B}_{ki}^{(-,+)} = \frac{\left\{\sum_{l}^{\text{occ}} (A_{kl}^{(0,+)}\mathscr{F}_{li}^{(-,0)} + A_{kl}^{(-,0)}\mathscr{F}_{li}^{(0,+)}) - \sum_{l}^{\text{vac}} (\mathscr{F}_{kl}^{(0,+)}A_{li}^{(-,0)} + \mathscr{F}_{kl}^{(-,0)}A_{li}^{(0,+)})\right\}}{(\varepsilon_k^{(0)} - \varepsilon_i^{(0)} + w_2 - w_1)}. \tag{29}$$

The $\mathfrak{B}$ contributions are distinguished from the b contributions by the fact that the former may be calculated non-iteratively from data generated from the first order calculations, whereas the latter must be calculated iteratively and are the second order analogue of Eqs. (6) and (9). The b, of Eq. (25), is given by

$$b_{ki}^{(-,+)} = -\mathscr{F}_{ki}^{(-,+)}/(\varepsilon_k^{(0)} - \varepsilon_i^{(0)} + w_2 - w_1). \tag{30}$$

The $(-, +)$ terms corresponding to Eqs. (25–30) may be obtained by reversing the signs of w_1 and w_2 in these equations.

Expressions for the frequency-dependent polarizability and hyperpolarizability may be derived by the method given in Ref. [13]. Accordingly, the xy component of the polarizability tensor, $\alpha(w)$, is given by:

$$\alpha_{xy}^{(w)} = -\sum_{\mu}\sum_{\nu} P_{\mu\nu}^{(x)} H_{\mu\nu}^{(y)} \tag{31}$$

where $P_{\mu\nu}^{(x)}$ is the first order density matrix, $P^{(+)}$ or $P^{(-)}$, for the applied field in the x direction and $H^{(y)}$ is the dipole matrix for the field in the y direction. Although expression (31) is not symmetric in the tensorial indices, it reduces to that of Dalgarno and Victor [3] when the Cartesian subscripts are the same or to the static polarizability when the frequency equals zero.

Similarly, the hyperpolarizability is assumed by analogy with the equations of Ref. [13] to be given by

$$\beta_{x,y,z}^{(w_1,w_2)} = -\sum_{\mu}\sum_{\nu} P_{\mu\nu}^{(x,y)} H_{\mu\nu}^{(z)}. \tag{32}$$

Here, $P^{(x,y)}$ is the second order change in the density matrix corresponding to applied fields along the x and y direction of frequencies w_1 and w_2, respectively. This equation reduces to the tensorially symmetric expression for the static hyperpolarizability when the frequency equals zero.

4. Calculation for $\alpha(w)$ and $\beta(w_1, w_2)$ for LiH

Calculations were undertaken for LiH hydride using a bond length of 3.015 a.u. and a basis set as close as possible to that of Stewart *et al.* [5] to permit a comparison with their calculations. The details of the basis set, and results for various zero frequency calculations are as follows. The slightly modified Stewart basis was expanded as GTO's [14] according to the scheme: for Li, $1s(5)$, $1s'(4)$, $2s(5)$, $2s'(4)$, $4s(3)$, $2p(4)$, $2p'(3)$, $3p(2)$, and $3d(1)$; and for H, $1s(5)$, $2s(4)$, $2s'(3)$, $2p(4)$, and $2p'(3)$. The modification involved omitting the $3s$ orbital to compensate for the $3d_{(x^2+y^2+z^2)}$ orbital calculated using the POLYATOM [15] integral package. Both $3s$ and $3d$ orbitals have the same orbital exponent $\zeta = 0.333$. The total energy, static polarizability, and static hyperpolarizability calculated for this basis are -7.97595 a.u., 20.77 a.u., and -326.1 a.u., respectively.

The component of the frequency dependent polarizability, α_{zz}, parallel to the molecular axis was calculated for LiH by the method presented here. The results from these calculations, shown in Fig. 1, agree well with those reported by Stewart *et al.* Convergence was found to be particularly slow, especially near the resonance frequency, but some improvement may be possible through the incorporation of a predictor-corrector method.

All previous calculations by the present method used relatively simple basis sets of the Slater or double zeta variety and uniformly diverged at a resonance frequency equal to the virtual excitation energy [9]. The present LiH calculation utilizes a rather more extensive basis set and, significantly, diverges at a frequency well removed from the lowest virtual excitation energy of the appropriate symmetry. This result suggests that the use of a suitable basis set is especially important for frequency dependent polarizability calculations. Fortunately, a recipe [16] exists for choosing good basis sets for static-polarizability calculations which might well prove applicable to the dynamic case.

Calculations were also undertaken for the frequency dependent hyperpolarizability of LiH. Of all the large number of components and frequencies, only $\beta_{zzz}^{(2w)}$ and $\beta_{zzz}^{(\mathrm{null})}$ were calculated, simply as a test of the proposed computational method. The results from these calculations are shown in Fig. 2. The previous calculations of β

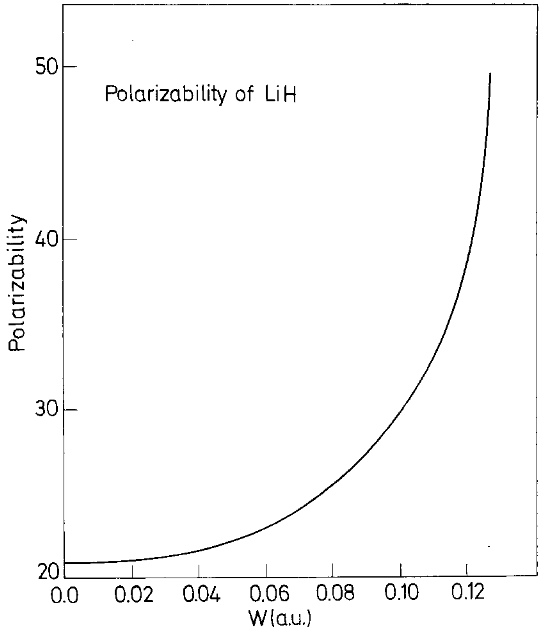

Fig. 1. Parallel component of the frequency dependent polarizability of LiH. All quantities are in atomic units

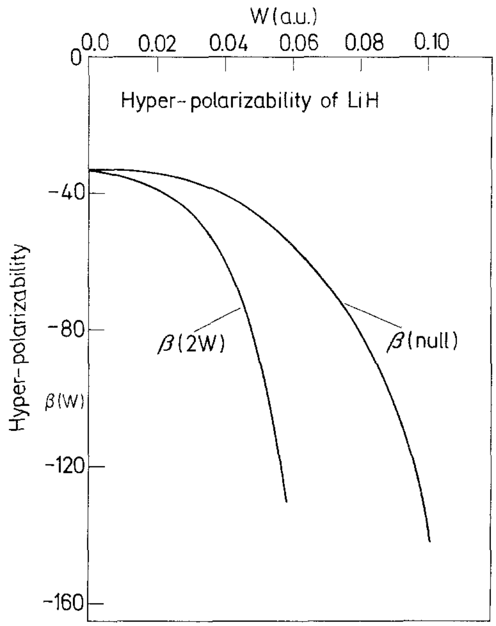

Fig. 2. Parallel component of the double and null frequency hyperpolarizability of LiH. All quantities are in atomic units

used relatively simple Slater or double zeta basis sets and, in the case of $\beta(2w)$, were found to diverge at a resonant frequency of one half the appropriate virtual excitation energy. Thus, as in the case of $\alpha(w)$, the use of a poor basis set can be expected to yield particularly poor excitation energies.

5. Conclusions

A SCF perturbative method for the solution of first and second order TDHF equations has been presented; higher order solutions can likely be obtained by the same approach. The results from the first-order calculations are found to agree well with those already in the literature.

Sufficient calculations have not as yet been undertaken to provide an estimate of the relative computational efficiency of the proposed method. However, the introduction of the frequency-dependent density matrix has clear pedagogical advantages and provides a straightforward approach to the solution of higher order equations. The limited set of calculations available to date, strongly suggest that the choice of basis-set is particularly important for the calculation of both the frequency dependent polarizability and hyperpolarizability.

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