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 hyperpolarizability 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 \( \omega_1 \) and \( \omega_2 \), 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

\[
\mathcal{H} = H^{(1)} \{ \lambda_1 (e^{i \omega_1 t} + e^{-i \omega_1 t}) + \lambda_2 (e^{i \omega_2 t} + e^{-i \omega_2 t}) \},
\]

(1)
where the $\lambda$'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, $C^{(\pm)}$, are given as solutions to the SCF matrix equation

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

which must be solved subject to the orthonormality constraints:

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

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 $C$, $C^{(\pm)}$, $n = 1$ 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]

$$F^{(\pm)}_{\lambda\nu} = H^{(0)}_{\lambda\nu} + \sum_{\sigma} \sum_{\lambda} P^{(\pm)}_{\sigma\lambda}(\mu\nu/\sigma\lambda) - 1/2(\mu\lambda/\sigma\nu),$$  \(4\)

$$P^{(\pm)}_{\sigma\lambda} = 2 \sum_{\text{occupied}} \{C^{(0)}_{\alpha\sigma}C^{(\pm)}_{\lambda\mu} + C^{(0)}_{\lambda\mu}C^{(\pm)}_{\alpha\sigma}\}.$$  \(5\)

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

$$A^{(\pm)}_{ij} = -\mathcal{F}_{ij}^{(\pm)}(e^{(0)}_{ij} - e^{(0)}_{jk} \pm w),$$  \(6\)

$$A^{(\pm)}_{ij} = 0,$$  \(7\)

where

$$\mathcal{F}_{ij}^{(\pm)} = \tilde{C}^{(0)}_{ij}F^{(\pm)}C^{(0)}_{ij}.$$  \(8\)

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]

$$P^{(\pm)}_{\lambda\nu} = 2 \sum_{\text{occupied}} \sum_{\kappa\lambda} \{A^{(\pm)}_{\lambda\kappa}C^{(0)}_{\mu\nu} + A^{(\pm)}_{\kappa\lambda}C^{(0)}_{\mu\nu}\}.$$  \(9\)

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

$$P^{(\pm)} = \tilde{P}^{(\mp)}$$  \(10\)

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

3. Second Order

The second and higher-order expansion parameters are $\lambda$, $w_1$ and $w_2$. For a perturbation second order in $\lambda$, there are several distinct combinations of the two frequencies $w_1$ and $w_2$. Accordingly, the notation introduced for the first order...