Use of Symmetry in Coupled Hartree-Fock Calculations of Non-linear Response Tensors in Molecules *

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A new computational scheme for electric dipole hyperpolarizabilities has been devised within the coupled Hartree-Fock method. Only the projection of second-order perturbed orbitals onto the subspace spanned by unperturbed virtual orbitals is computed. The entire molecular symmetry is exploited to reduce computational effort: a reduced two-electron integral file containing only symmetry-distinct matrix elements over the atomic basis functions is processed at each iteration. In addition, only symmetry-independent first- and second-order perturbed density matrices need to be calculated. An efficient computer program implementing the present approach has been developed.

Key words: Second hyperpolarizability; *Ab initio* calculation; Molecular symmetry.

Introduction

In the presence of a static uniform electric field E_α, the electronic cloud of atomic and molecular systems gets polarized. The energy, W, can be written as a Taylor series [1]

$$W = W_0 - \sum_\alpha \mu_\alpha E_\alpha - \frac{1}{2}\sum_{\alpha\beta} \alpha_{\alpha\beta} E_\alpha E_\beta - \frac{1}{6}\sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{24}\sum_{\alpha\beta\gamma\delta} \gamma_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta + \ldots,$$

where W_0 is the unperturbed energy, μ_α is the permanent electric dipole moment and the coefficients $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, etc. are known as (static) electric polarizabilities. Non-linear response of the system is rationalized via hyperpolarizabilities $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$.

A computer program for the theoretical determination of electric polarizabilities and hyperpolarizabilities has been implemented at the *ab initio* level of accuracy using a computational scheme based on coupled Hartree-Fock (CHF) perturbation theory. Zero-order self-consistent-field (SCF) and first- and second-order CHF equations are solved to obtain the corresponding perturbed wavefunctions and density matrices. Then $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ tensors are evaluated.

Solution of Second-Order CHF Equation

We outline a method to compute the second-order wavefunction and density matrix exploiting the entire molecular symmetry: the second-order CHF equation is

$$(\varepsilon_i^{(0)} - \hat{F}^{(0)})\,\phi_i^{(2)} = \hat{F}^{(1)}\,\phi_i^{(1)} - \sum_k^{\text{occ}} \varepsilon_{ki}^{(1)}\,\phi_k^{(1)} + \hat{F}^{(2)}\,\phi_i^{(0)} - \sum_k^{\text{occ}} \varepsilon_{ki}^{(2)}\,\phi_k^{(0)}, \qquad (1)$$

where $\hat{F}^{(0)}$, $\hat{F}^{(1)}$ and $\hat{F}^{(2)}$ are the zero-, first-, and second-order Fock operators, $\boldsymbol{\varepsilon}^{(0)}$, $\boldsymbol{\varepsilon}^{(1)}$ and $\boldsymbol{\varepsilon}^{(2)}$ are Lagrange multipliers, the label i refers to occupied orbitals, and molecular orbitals are expanded over the atomic basis set $\boldsymbol{\chi}$:

$$\phi_i^{(2)} = \sum_{p=1}^{m} \chi_p\, c_{pi}^{(2)}, \quad \phi_i^{(1)} = \sum_{p=1}^{m} \chi_p\, c_{pi}^{(1)}, \quad \phi_i^{(0)} = \sum_{p=1}^{m} \chi_p\, c_{pi}^{(0)}. \qquad (2)$$

Using matrix notation and for an orthonormal basis set, (1) becomes

$$[\boldsymbol{\varepsilon}_i^{(0)} - \mathbf{F}^{(0)}]\,\mathbf{c}_i^{(2)} = \mathbf{F}^{(1)}\,\mathbf{c}_i^{(1)} - \sum_k^{\text{occ}} \mathbf{c}_k^{(1)}\,\varepsilon_{ki}^{(1)} + \mathbf{F}^{(2)}\,\mathbf{c}_i^{(0)} - \sum_k^{\text{occ}} \mathbf{c}_k^{(0)}\,\varepsilon_{ki}^{(2)}. \qquad (3)$$

By means of the projection operators $\hat{R}_1$ and $\hat{R}_2$, with representations

$$\mathbf{R}_1 \equiv \mathbf{R}^{(0)} = \sum_k^{\text{occ}} \mathbf{c}_k^{(0)}\,\mathbf{c}_k^{(0)\dagger} \qquad (4)$$

and

$$\mathbf{R}_2 \equiv (\mathbf{1} - \mathbf{R}^{(0)}) = \sum_l^{\text{vir}} \mathbf{c}_l^{(0)}\,\mathbf{c}_l^{(0)\dagger}, \qquad (5)$$

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the second-order coefficients $\mathbf{c}_i^{(2)}$ can be separated into projections on the subspaces of occupied and virtual molecular orbitals:

$$\mathbf{c}_i^{(2)} = \mathbf{o}_i^{(2)} + \mathbf{v}_i^{(2)}, \tag{6}$$

$$\mathbf{o}_i^{(2)} = \mathbf{R}_1\, \mathbf{c}_i^{(2)}, \tag{7}$$

$$\mathbf{v}_i^{(2)} = \mathbf{R}_2\, \mathbf{c}_i^{(2)}. \tag{8}$$

In addition, the second-order density matrix

$$\mathbf{R}^{(2)} = \sum_k^{\text{occ}} (\mathbf{c}_k^{(2)}\mathbf{c}_k^{(0)\dagger} + \mathbf{c}_k^{(1)}\mathbf{c}_k^{(1)\dagger} + \mathbf{c}_k^{(0)}\mathbf{c}_k^{(2)\dagger}) \tag{9}$$

can be resolved into projection components [2–3],

$$\mathbf{R}^{(2)} = \mathbf{R}_{11}^{(2)} + \mathbf{R}_{12}^{(2)} + \mathbf{R}_{21}^{(2)} + \mathbf{R}_{22}^{(2)}, \tag{10}$$

where

$$\mathbf{R}_{mn}^{(2)} = \mathbf{R}_m\, \mathbf{R}^{(2)}\, \mathbf{R}_n, \quad m, n = 1, 2. \tag{11}$$

By substitution of (4), (5) and (9) in (10) it can be shown that [4]

$$\mathbf{R}^{(2)} = -\mathbf{X}\mathbf{X}^\dagger + \mathbf{Y} + \mathbf{Y}^\dagger + \mathbf{X}^\dagger\mathbf{X}, \tag{12}$$

where

$$\mathbf{X} = \sum_k^{\text{occ}} \mathbf{c}_k^{(0)}\mathbf{c}_k^{(1)\dagger} \tag{13}$$

and

$$\mathbf{Y} = \sum_k^{\text{occ}} \mathbf{c}_k^{(0)}\mathbf{v}_k^{(2)\dagger}, \tag{14}$$

i.e. only the projection of second-order coefficient over the virtual-orbitals subspace is needed to compute the second-order density matrix.

Multiplying (3) on the left by $\mathbf{c}_j^{(0)\dagger}$, j virtual, observing that

$$\mathbf{c}_j^{(0)\dagger}\,\mathbf{F}^{(0)} = \varepsilon_j^{(0)}\,\mathbf{c}_j^{(0)\dagger}, \tag{15}$$

and choosing

$$\varepsilon_{ki}^{(1)} = \mathbf{c}_k^{(0)\dagger}\,\mathbf{F}^{(1)}\,\mathbf{c}_i^{(0)}, \tag{16}$$

we obtain

$$(\varepsilon_i^{(0)} - \varepsilon_j^{(0)})\,\mathbf{c}_j^{(0)\dagger}\mathbf{c}_i^{(2)} = \mathbf{c}_j^{(0)\dagger}\mathbf{F}^{(1)}\mathbf{c}_i^{(1)} + \mathbf{c}_j^{(0)\dagger}\mathbf{F}^{(2)}\mathbf{c}_i^{(0)} - \mathbf{c}_j^{(0)\dagger}\mathbf{X}^\dagger\mathbf{F}^{(1)}\mathbf{c}_i^{(0)}. \tag{17}$$

Multiplying on the left by $\mathbf{c}_j^{(0)}$ and summing over the virtual orbitals we get

$$\sum_j^{\text{vir}} \mathbf{c}_j^{(0)}\mathbf{c}_j^{(0)\dagger}\mathbf{c}_i^{(2)} = \sum_j^{\text{vir}} (\varepsilon_i^{(0)} - \varepsilon_j^{(0)})^{-1}\,\mathbf{c}_j^{(0)}\mathbf{c}_j^{(0)\dagger} \cdot \{\mathbf{F}^{(2)}\mathbf{c}_i^{(0)} + \mathbf{F}^{(1)}\mathbf{c}_i^{(1)} - \mathbf{X}^\dagger\mathbf{F}^{(1)}\mathbf{c}_i^{(0)}\}, \tag{18}$$

where it can be observed that the left-hand side of (18) is the projection of the second-order coefficients defined by (8).

Introducing the quantities

$$\mathbf{M}^{(i)} = \sum_j^{\text{vir}} (\varepsilon_i^{(0)} - \varepsilon_j^{(0)})^{-1}\,\mathbf{c}_j^{(0)}\mathbf{c}_j^{(0)\dagger} \tag{19}$$

and

$$\boldsymbol{k}_i^{(2)} = \mathbf{M}^{(i)}(\mathbf{F}^{(1)}\mathbf{c}_i^{(1)} - \mathbf{X}^\dagger\mathbf{F}^{(1)}\mathbf{c}_i^{(0)}), \tag{20}$$

the iterative scheme for the second-order CHF calculation becomes

$$\mathbf{v}_i^{(2)} = \mathbf{M}^{(i)}\,\mathbf{F}^{(2)}\,\mathbf{c}_i^{(0)} + \mathbf{k}_i^{(2)}, \tag{21}$$

$$\mathbf{Y} = \sum_k^{\text{occ}} \mathbf{c}_k^{(0)}\mathbf{v}_k^{(2)\dagger}, \tag{22}$$

$$\mathbf{R}^{(2)} = -\mathbf{X}\mathbf{X}^\dagger + \mathbf{Y} + \mathbf{Y}^\dagger + \mathbf{X}^\dagger\mathbf{X}, \tag{23}$$

$$\mathbf{F}^{(2)} \equiv \mathbf{G}^{(2)} = \mathbf{G}(\mathbf{R}^{(2)}). \tag{24}$$

$\mathbf{M}^{(i)}$ and $\mathbf{X}$ matrices have been computed only once to solve the first-order CHF problem, i.e. to determine the polarizability $\boldsymbol{\alpha}$. Together with $\boldsymbol{k}_i^{(2)}$ they are saved onto a file to be processed also at each step of the iterative calculation (21)–(24): it seems to be worth noticing that the present CHF algorithm, based on the Hartree-Fock propagator (19), is quite general, compact and suitable for efficient determination of both first- and second-order perturbed orbitals. In addition, it can easily be extended to perturbations of higher order.

Transformation of Second-Order Density

The electron density is a scalar field with perturbation expansion

$$P(\mathbf{r}) = P^{(0)}(\mathbf{r}) + \sum_\alpha P^\alpha(\mathbf{r})\,E_\alpha + \frac{1}{2}\sum_{\alpha\beta} P^{\alpha\beta}(\mathbf{r})\,E_\alpha E_\beta + \ldots. \tag{25}$$

Introducing a basis set $\boldsymbol{\chi}$ of atomic functions, for the second-order term one defines the expansion

$$P^{\alpha\beta}(\mathbf{r}) = 2\sum_{pq=1}^{m} R_{pq}^{\alpha\beta}\,\chi_p(\mathbf{r})\,\chi_q^*(\mathbf{r}). \tag{26}$$

For any symmetry operator t (rewritten τ when operating on the domain of basis functions $\boldsymbol{\chi}$), with representation $\mathbf{T}$ over a basis set of Cartesian unit vectors, and belonging to a group G, one has

$$\tau \chi_p(\mathbf{r}) = \chi_p(T^{-1}\mathbf{r}) = \sum_{q=1}^{m} \chi_q(\mathbf{r}) S_{qp}. \qquad (27)$$

In the transformed coordinate system one has

$$P^{\alpha'\beta'}(\mathbf{r}) = \sum_{\gamma\delta} T^{-1}_{\alpha\gamma} P^{\gamma\delta}(\mathbf{r}) T^{-1}_{\beta\delta}, \qquad (28)$$

$$P^{\alpha'\beta'}_{\text{trans}}(T\mathbf{r}) = \sum_{\gamma\delta} T^{-1}_{\alpha\gamma} P^{\gamma\delta}_{\text{trans}}(T\mathbf{r}) T^{-1}_{\beta\delta} = P^{\alpha\beta}(\mathbf{r}), \qquad (29)$$

$$\begin{aligned}\sum_{\alpha\beta} P^{\alpha\beta}(\mathbf{r}) T_{\lambda\alpha} T_{\mu\beta} &= \sum_{\alpha\beta\gamma\delta} T_{\lambda\alpha} T^{-1}_{\alpha\gamma} T_{\mu\beta} T^{-1}_{\beta\delta} P^{\gamma\delta}_{\text{trans}}(T\mathbf{r}) \\ &= \sum_{\gamma\delta} \delta_{\lambda\gamma} \delta_{\mu\delta} P^{\gamma\delta}_{\text{trans}}(T\mathbf{r}) = P^{\lambda\mu}_{\text{trans}}(T\mathbf{r}). \qquad (30)\end{aligned}$$

Hence the transformation law for second-order density is

$$P^{\lambda\mu}_{\text{trans}}(\mathbf{r}) = \sum_{\alpha\beta} T_{\lambda\alpha} T_{\mu\beta} P^{\alpha\beta}(T^{-1}\mathbf{r}), \qquad (31)$$

$$\begin{aligned}P^{\alpha\beta}(T^{-1}\mathbf{r}) &= 2 \sum_{pq=1}^{m} R^{\alpha\beta}_{pq} \chi_p(T^{-1}\mathbf{r}) \chi^*_q(T^{-1}\mathbf{r}) \\ &= 2 \sum_{pqrs=1}^{m} R^{\alpha\beta}_{pq} \chi_r S_{rp} \chi^*_s S^*_{sq}. \qquad (32)\end{aligned}$$

Since the transformation belongs to the group G, one has

$$P^{\lambda\mu}_{\text{trans}}(\mathbf{r}) = P^{\lambda\mu}(\mathbf{r}), \qquad (33)$$

and the second-order density matrices transform according to

$$\mathbf{R}^{\lambda\mu} = \sum_{\alpha\beta} T_{\lambda\alpha} T_{\mu\beta} \mathbf{S} \mathbf{R}^{\alpha\beta} \mathbf{S}^{\dagger}. \qquad (34)$$

Introducing the symmetrized Kronecker square of $\mathbf{T}$, with matrix elements [5]

$$(\mathbf{T}^{[2]}_s)_{\alpha\beta,\gamma\gamma} = T_{\alpha\gamma} T_{\beta\gamma}, \qquad (35)$$

$$(\mathbf{T}^{[2]}_s)_{\alpha\beta,\gamma\delta} = (T_{\alpha\gamma} T_{\beta\delta} + T_{\alpha\delta} T_{\beta\gamma}), \quad \gamma \neq \delta, \qquad (36)$$

one finds the final transformation law for the second-order density matrices ($\lambda \leqq \mu$),

$$\mathbf{R}^{\lambda\mu} = \sum_{\alpha \leqq \beta} (\mathbf{T}^{[2]}_s)_{\lambda\mu,\alpha\beta} \mathbf{S} \mathbf{R}^{\alpha\beta} \mathbf{S}^{\dagger}. \qquad (37)$$

Hence, according to the present method, only the symmetry-distinct density matrices need to be computed.

Within our approach the entire molecular symmetry is exploited to increase the efficiency of the code in every step of the calculation. For a molecule belonging to point group G of order $|G|$, only $\approx n^4/(8\,|G|)$ symmetry-distinct two-electron integrals over a basis set of n Gaussian atomic functions are calculated and processed at each iteration within SCF, first- and second-order CHF procedures. A skeleton Coulomb repulsion matrix $\hat{\mathbf{G}}^{\alpha\beta}$ is obtained by processing the non-redundant list of unique two-electron integrals, then the actual repulsion matrices $\mathbf{G}^{\alpha\beta}$, $\alpha \leqq \beta$, are obtained via the equation

$$\mathbf{G}^{\alpha\beta} = \sum_{t \in G} \Bigl(\sum_{\gamma \leqq \delta} (\mathbf{T}^{[2]}_s)_{\alpha\beta,\gamma\delta} (\mathbf{S}^{-1})^{\dagger} \hat{\mathbf{G}}^{\gamma\delta} \mathbf{S}^{-1} \Bigr). \qquad (38)$$

This method turns out to be a major computer saver, as (i) the iterative steps become much faster, owing to the reduced number of integrals, and (ii) the occupancy of the mass storage gets smaller. Accordingly, one can afford large problems that would be otherwise intractable.

Results

Using the polarized basis sets from [6] we obtained the results reported in Tables 1–3 for some small molecules.

A substantial amount of computer effort can be saved by the present method. For the molecules examined here the use of symmetry can reduce computer

Table 1. Electric polarizability α for water, ammonia and methane in a.u.

Comp.	H_2O†	NH_3‡	CH_4§
xx	7.850	12.753	16.038
yy	9.191	12.753	16.038
zz	8.517	13.274	16.038
av.	8.519	12.927	16.038

† Coordinates in bohr: $O_1 = (0, 0, 0.12414)$,
$H_1 = (0, 1.43153, -0.98527)$.
‡ Coordinates in bohr: $N_1 = (0, 0, 0.12780)$,
$H_1 = (1.77100, 0, -0.59196)$.
§ Coordinates in bohr: $C_1 = (0, 0, 0)$,
$H_1 = (1.19034, 1.19034, 1.19034)$.

Table 2. First hyperpolarizability β for water, ammonia and methane in a.u.

Comp.	H_2O	NH_3	CH_4
xxx	0.000	−9.546	0.000
xxz	0.577	6.751	0.000
xyy	0.000	9.546	0.000
xyz	0.000	0.000	−12.160
yyz	9.787	6.751	0.000
zzz	4.657	6.415	0.000

Table 3. Second hyperpolarizability γ for water, ammonia and methane in a.u.

Comp.	H_2O	NH_3	CH_4
$xxxx$	1216.6	1078.1	1861.7
$xxxz$	0.0	−139.4	0.0
$xxyy$	293.3	359.4	746.7
$xxzz$	327.9	1068.1	746.7
$xyyz$	0.0	139.4	0.0
$yyyy$	475.4	1078.1	1861.7
$yyzz$	282.5	1068.1	746.7
$zzzz$	772.4	4246.1	1861.7

times necessary to calculate second hyperpolarizabilities at least by an order of magnitude. From these findings we conclude that the present computational scheme, owing to its use of complete molecular symmetry, and to the efficiency of the iterative procedure (21)–(24) for the projection of the second-order orbitals onto the virtual orbital subspace, represents a step forward with respect to other methods presently available [7].

Comparison with previous CHF theoretical values reported for the water molecule by Maroulis [8] shows very good agreement for α: his predictions are virtually identical to those reported here (see Table II of [8]). Our theoretical estimates for γ are roughly 10% smaller than those of [8], which may depend on the features of the Sadlej basis sets [6], less extended than those adopted in [8].

The theoretical β tensor components obtained in this study are slightly different from those of Maroulis [8] and from those evaluated in a systematic investigation [9]. This behaviour is expected, in the light of the discussion reported in [9], owing to the strong dependence of the first-hyperpolarizability tensor upon the characteristics of the basis set.

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