

Direct atomic orbital based self-consistent-field calculations of nonlinear molecular properties. Application to the frequency dependent hyperpolarizability of *para*-nitroaniline

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We outline a method for the calculation of nonlinear properties such as dynamic hyperpolarizabilities for self-consistent-field (SCF) wave functions. In this method, two-electron integrals are only addressed in the evaluation of Fock matrices and Fock matrices with one-index transformed integrals. These matrices are determined directly in terms of integrals evaluated in the atomic orbital basis, avoiding expensive integral transformations between atomic and molecular orbital bases as well as storing and retrieving the two-electron integrals. The method is double direct—direct in the sense of constructing Fock matrices from atomic integrals, and direct in the sense of solving the response equations iteratively using direct linear transformations of a generating matrix times trial vectors. Applications can be performed on species of the same size as in direct SCF. The cost of evaluating a single nonlinear molecular property is comparable to that of optimizing the wave function. Additional properties can be obtained at little extra cost by solving all response equations simultaneously. As a demonstration, we calculate the static and dynamic hyperpolarizabilities of *para*-nitroaniline.

I. INTRODUCTION

The characterization of nonlinear properties of extended molecules is an important objective in current research. Experimental progress in determining nonlinear molecular spectra and properties has challenged a similar development in theory and computational techniques. Such a development has taken place recently in the area of analytical response theory. Analytical response functions have been derived for a number of electric and magnetic nonlinear response properties and implemented for accurate multiconfiguration self-consistent-field (MCSCF) reference wave functions.¹⁻³ Such calculations have made it possible to interpret nonlinear properties of small systems and have in some cases even advanced the experimental predictions.

Applications of *ab initio* methods to nonlinear molecular properties have hitherto been confined to small, few-atomic species. Extensions to larger molecules are desirable because it would enable the study of larger model molecules and larger numbers of subunits of extended species and thus prepare for a more systematic modeling of conjugated organic compounds, conducting polymers, and other compounds of technological interest. Similar to the development of direct self-consistent-field (SCF) methods⁴ for total energy calculations of large systems, much effort has been devoted to developing methods where such wave functions are used to evaluate second- and higher-order molecular properties. Second-order properties require the solution of linear equations to determine the first-order

correction to the wave function. When standard techniques such as the LU decomposition are used for these equations, all matrix elements must be calculated explicitly. This is done most conveniently by storing the integrals in the molecular orbital basis, making it difficult to use SCF wave functions when the atomic integrals cannot be stored.

Alternatively, the linear equations can be solved using iterative techniques. In 1982, Backskay⁵ showed that the linear transformations needed for the coupled Hartree-Fock equations can be implemented based on integrals in the atomic orbital basis. In this way, it is possible to solve the coupled Hartree-Fock equations for direct self-consistent field (DSCF) wave functions. This approach has been implemented by several authors and used for calculating, e.g., static polarizabilities. In 1988, Jensen *et al.*⁶ demonstrated how the linear transformations needed for the random phase approximation (RPA) or linear response SCF matrix equations may be set up in the atomic orbital basis and thus how the RPA equations may be solved for DSCF wave functions. Using a slightly modified algorithm, Feyereisen *et al.*⁷ implemented RPA equations and determined the frequency dependent polarizability for some large organic molecules. Recently Koch *et al.*¹¹ have implemented the approach of Ref. 6 for solving the RPA equations and presented calculations of excitation energies, transition moments, and frequency dependent polarizabilities.

The term “direct” is used in two senses in quantum chemistry. In one sense, it means that the Fock matrices or other computational elements are calculated in terms of

atomic orbital (AO) integrals evaluated on the fly, as in Almlöf's direct SCF and in the direct RPA codes referred to above. The other meaning of direct describes a particular way of solving linear equations and eigenvalue equations which avoid the explicit construction of the coefficient matrices. Instead, the equations are solved iteratively in such a way that the linearly transformed trial vectors are generated directly, bypassing the calculation of the transformation matrix. This is the meaning of direct in direct configuration interaction (CI),⁸ direct MCSCF,⁹ direct SCF,^{5,9} and originally also in direct RPA.¹¹ The RPA methods of Koch *et al.*^{6,11} and Feyereisen *et al.*⁷ are thus direct in both senses, and may therefore be coined as double direct (DDRPA).

We demonstrate in this paper how the the frequency dependent hyperpolarizabilities, the two-photon matrix elements, and matrix elements between excited states may be determined from DSCF wave functions for closed shell and one-open shell systems. Our derivation shows how the evaluation of the quadratic response functions can be expressed in terms of integrals over atomic basis functions, without storing or transforming them. The method is direct in both senses referred to above. It thus constructs Fock matrices directly from integrals computed in the AO basis and solves sets of RPA matrix equations using direct linear matrix transformations, here the electronic Hessians times trial vectors. Quadratic response calculations also contain a term where the third energy derivative matrix is multiplied on three trial vectors. We calculate this term as a double linear transformation where the third derivative matrix is multiplied on two trial vectors. This transformation is also carried out in terms of integrals in the atomic orbital basis. A suitable acronym for the proposed method is therefore DDQRPA.

In the following section, we outline our double-direct method for solving the quadratic response SCF matrix equations. In Sec. III, we present results for frequency independent (static) and dependent (dynamic) hyperpolarizabilities for *para*-nitroaniline using a number of different basis sets containing up to 300 basis functions. Finally, in Sec. IV we summarize the paper and discuss some of the prospects of the presented method.

II. METHOD

In this section, we derive the explicit expressions needed to obtain the quadratic response functions based on integrals in the atomic basis. The derivation starts out from the theory of quadratic response functions for MCSCF states presented by Olsen and Jørgensen,¹² and later implemented for quadratic response properties by Hettema *et al.*,² and very recently for quadratic response properties including singlet-triplet excitations and spin-dependent operators by Vahtras *et al.*³ To make a self-contained presentation, we reexpress some of their general formulas for self-consistent field (SCF) closed and one-open shell reference states. In Sec. I A, we describe how the response equations needed for the evaluation of the nonlinear molecular properties are solved iteratively based on a direct technique where the results of the linear transformation are

expressed in terms of inactive and active Fock matrices with one-index transformed integrals. We show how these Fock matrices resolve in terms of contractions of density matrices over two-electron integrals evaluated in the AO basis. These expressions are collected in such a way that the computations are integral driven, thus only one batch of integral calculations is needed to construct all necessary entities in each iteration. The present approach can rather straightforwardly be modified for double-direct MCSCF by means of direct constructions of the so-called Q matrices. However, this case is not implemented and therefore excluded from the derivation given below. In Sec. II B, we give the expressions for the quadratic response functions and in particular demonstrate how the third energy derivative matrix multiplied on two vectors may be described in terms of integral driven double linear transformations.

A. Linear response matrix equations

When evaluating molecular properties from linear response functions for SCF reference wave functions, we need to solve the linear response (RPA) eigenvalue equation

$$(\mathbf{E}^{[2]} - \omega_1 \mathbf{S}^{[2]}) X_f = 0 \quad (1)$$

and the set of linear equations

$$(\mathbf{E}^{[2]} - \omega_1 \mathbf{S}^{[2]}) \mathbf{N}^b(\omega_1) = \mathbf{B}^{[1]}. \quad (2)$$

$\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ are the usual RPA Hessian and metric type matrices given in Eqs. (5.61) and (5.64) of Ref. 12 and $\mathbf{B}^{[1]}$ the property vector is given in Eq. (5.93) of Ref. 12. The solution of Eqs. (1) and (2) can be determined using iterative techniques without inverting or even explicitly constructing $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$. This requires that we are able to carry out the linear transformations $\mathbf{E}^{[2]} N$ and $\mathbf{S}^{[2]} N$, where N is a trial vector of the structure $N = \begin{pmatrix} \kappa_{rs} \\ \kappa_{sr} \end{pmatrix}$. The linear transformation by $\mathbf{S}^{[2]}$ is simple and can be obtained straightforwardly also for direct SCF wave functions. The linear transformation by $\mathbf{E}^{[2]}$ may be written as [see Eq. (5) of Ref. 6]

$$E_{jk}^{[2]} N_k = - \left\{ \begin{array}{l} \langle 0 | [q_j, H_0(\kappa)] | 0 \rangle \\ \langle 0 | [q_j^\dagger, H_0(\kappa)] | 0 \rangle \end{array} \right\}, \quad (3)$$

i.e., in terms of usual electronic gradient elements with a Hamiltonian containing one-index transformed integrals [see Eq. (9) of Ref. 6]

$$H_0(\kappa) = (\kappa_j q_j^\dagger + \kappa'_j q_j, H_0) = \sum_{pq} \bar{h}_{pq} E_{pq} + \sum_{pqrs} (pq\bar{r}s) e_{pqrs}. \quad (4)$$

Here κ'_j is defined in Eq. (21) in Ref. 6 and \bar{h}_{pq} and $(pq\bar{r}s)$ are one-index transformed one- and two-electron integrals with κ , the orbital rotation matrix, as the transforming matrix

$$\bar{h}_{rs} = \kappa_{rp} h_{ps} - \kappa_{ps} h_{rp}, \quad (5)$$

$$(rs\bar{t}u) = \kappa_{rp} (ps|tu) - \kappa_{ps} (rp|tu) + \kappa_{tp} (rs|pu) - \kappa_{pu} (rs|tp). \quad (6)$$

In Eqs. (5) and (6) and in the remainder of this paper, we use the Einstein summation convention. In Ref. 3, expressions have been derived for the gradient with a Hamiltonian H , where the integrals possess no permutational symmetry

$$F_{pq} = \langle 0 | [E_{qp}, H] | 0 \rangle. \quad (7)$$

Denoting inactive orbitals by i, j, k, \dots , active orbitals by x, y, z, \dots , secondary orbitals by a, b, c, \dots , and general orbitals by p, q, r, \dots , we write the elements of Eq. (7) as

$$\begin{aligned} F_{ai} &= 2F_{ai}^I + 2F_{ai}^A & F_{ia} &= -2F_{ia}^I - 2F_{ia}^A \\ F_{wi} &= 2F_{wi}^I - F_{xi}^I D_{xw} + 2F_{wi}^A \\ F_{iw} &= -2F_{iw}^I + F_{ix}^I D_{wx} - 2F_{iw}^A \\ F_{aw} &= F_{ax}^I D_{wx} & F_{wa} &= -F_{xa}^I D_{xw}, \\ F_{wv} &= F_{wx}^I D_{vx} - F_{xv}^I D_{xw}, \end{aligned} \quad (8)$$

where the inactive and active Fock matrices are given as

$$\begin{aligned} 2F_{pq}^I &= 2k_{pq} + 2g_{kkpq} + 2g_{pqkk} - g_{pkkk} - g_{kqpk}, \\ 4F_{pq}^A &= (2g_{xypq} + 2g_{pqxy} - g_{pyxq} - g_{xqpy}) D_{xy}, \end{aligned} \quad (9)$$

and k and g denote the one- and two-electron integrals of H in Eq. (7). Recall that to obtain Eq. (9), we have assumed that the two-electron integrals do not possess any permutational symmetry. Equations (7)–(9) show that the terms in the linear transformation (3) may be expressed in terms of inactive and active Fock matrices with one-index transformed integrals. In our recent paper¹¹ on a direct RPA method, we showed in detail how these inactive and active Fock matrices may be constructed from atomic integrals and thus how the RPA matrix equations may be solved for DSCF wave functions.

$$\begin{aligned} & - \left\{ \frac{\langle 0 | A | j \rangle \langle j | (B - \langle 0 | B | 0 \rangle) | f \rangle}{(\omega_j - \omega_f + \omega_1)} + \frac{\langle 0 | B | j \rangle \langle j | (A - \langle 0 | A | 0 \rangle) | f \rangle}{(\omega_j - \omega_1)} \right\} \\ & = -N_j^a(\omega_f - \omega_1) B_{jl}^{[2]} X_{lf} - N_j^b(-\omega_1) (A_{jl}^{[2]} + A_{lj}^{[2]}) X_{lf} + N_j^a(\omega_f - \omega_1) (E_{jml}^{[3]} + E_{jlm}^{[3]} - \omega_1 S_{jml}^{[3]} - \omega_f S_{jlm}^{[3]}) N_m^b(-\omega_1) X_{lf}. \end{aligned} \quad (12)$$

The double residue gives the transition matrix elements between the excited states $\langle g |$ and $| f \rangle$ and may be expressed in terms of the solutions vector $N^a(\omega_f - \omega_g)$ and the eigenvectors X_f and X_{-g}

$$\begin{aligned} \langle g | A | f \rangle & - \delta_{gf} \langle 0 | A | 0 \rangle \\ & = -(A_{jl}^{[2]} + A_{lj}^{[2]}) X_{j-g} X_{lf} + N_j^a(\omega_f - \omega_g) \\ & \quad \times (E_{jml}^{[3]} + E_{jlm}^{[3]} + \omega_g S_{jml}^{[3]} - \omega_f S_{jlm}^{[3]}) X_{lf} X_{m-g}. \end{aligned} \quad (13)$$

The solution vectors for the RPA matrix equations entering the quadratic response functions and their residues can be determined straightforwardly requiring only two-electron integrals in the atomic basis as described in Sec. II A. The new feature encountered when evaluating the

B. The quadratic response function and its residues

The evaluation of the quadratic response function for a MCSCF wave function can be expressed as

$$\begin{aligned} \langle \langle A; B, C \rangle \rangle_{\omega_1, \omega_2} &= N_j^a(\omega_1 + \omega_2) B_{jl}^{[2]} N_l^c(\omega_2) \\ & \quad + N_j^a(\omega_1 + \omega_2) C_{jl}^{[2]} N_l^b(\omega_1) + N_j^b(\omega_1) \\ & \quad \times (A_{jk}^{[2]} + A_{kj}^{[2]}) N_k^c(\omega_2) - N_j^a(\omega_1 + \omega_2) \\ & \quad \times (E_{jlm}^{[3]} + E_{jml}^{[3]} - \omega_1 S_{jlm}^{[3]} - \omega_2 S_{jml}^{[3]}) \\ & \quad \times N_l^b(\omega_1) N_m^c(\omega_2). \end{aligned} \quad (10)$$

We assume below that A , B , and C refer to one-electron operators. $E^{[3]}$ and $S^{[3]}$ in Eq. (10) are generalizations of the RPA Hessian, while $C^{[2]}$ and $B^{[2]}$ are generalizations of the property matrix $B^{[1]}$ and are given in Eq. (27) of Ref. 3. In order to obtain the solution vectors N^a , N^b , and N^c , one needs to solve the three linear sets of equations

$$\begin{aligned} N^a(\omega_1 + \omega_2) &= [\mathbf{E}^{[2]} - (\omega_1 + \omega_2) \mathbf{S}^{[2]}]^{-1} \mathbf{A}^{[1]T}, \\ N^b(\omega_1) &= (\mathbf{E}^{[2]} - \omega_1 \mathbf{S}^{[2]})^{-1} \mathbf{B}^{[1]}, \\ N^c(\omega_2) &= (\mathbf{E}^{[2]} - \omega_2 \mathbf{S}^{[2]})^{-1} \mathbf{C}^{[1]} \end{aligned} \quad (11)$$

of the same structure as Eq. (2). The single residue of the quadratic response functions gives the second-order transition moment between the reference state $| 0 \rangle$ and the final state $| f \rangle$. It may be expressed in terms of the two solution vectors $N^a(\omega_f - \omega_1)$ and $N^b(\omega_1)$ and the eigenvector X_f [see Eq. (1)]

quadratic response function and residues concerns the linear transformations of trial vectors with the matrices $E^{[3]}$, $S^{[3]}$, $B^{[2]}$, and $A^{[2]}$. Using the simplifications that occur as a result of using an SCF closed shell or one-open shell reference wave function, we obtain the following expressions by applying Eqs. (25)–(28) of Ref. 3: for $E^{[3]}$,

$$\begin{aligned} (E_{jkl}^{[3]} + E_{jik}^{[3]})^{-1} N_k^2 N_l &= \frac{1}{2} \left\{ \frac{\langle 0 | [q_j, H_0(\kappa^1, \kappa^2)] | 0 \rangle}{\langle 0 | [q_j^\dagger, H_0(\kappa^1, \kappa^2)] | 0 \rangle} \right. \\ & \quad \left. + \frac{1}{2} \left\{ \frac{\langle 0 | [q_j, H_0(\kappa^2, \kappa^1)] | 0 \rangle}{\langle 0 | [q_j^\dagger, H_0(\kappa^2, \kappa^1)] | 0 \rangle} \right\} \right\}; \end{aligned} \quad (14)$$

for $S^{[3]}$,

$$S_{jlm}^{[3]1} N_l^2 N_m = \frac{1}{2} \left\{ \langle 0 | [q_j, [(^2\kappa_m q_m^\dagger + ^2\kappa'_m q_m), (^1\kappa_l q_l^\dagger + ^1\kappa'_l q_l)]] | 0 \rangle \right\} \\ = -\frac{1}{2} \left\{ \langle 0 | [q_j^\dagger, [(^2\kappa_m q_m^\dagger + ^2\kappa'_m q_m), (^1\kappa_l q_l^\dagger + ^1\kappa'_l q_l)]] | 0 \rangle \right\}; \quad (15)$$

for $B^{[2]}$ and $C^{[2]}$,

$$V_{jl}^{[2]1} N_l = - \left\{ \langle 0 | [q_j, V^\omega(\kappa)] | 0 \rangle \right\}; \quad (16)$$

for $A^{[2]}$,

$$A_{jk}^{[2]1} N_k = - \left\{ \frac{1}{2} \langle 0 | [q_j^\dagger, A(\kappa)] | 0 \rangle \right\}. \quad (17)$$

Here $H_0(^1\kappa, ^2\kappa)$ is a Hamiltonian with double one-index transformed integrals

$$H_0(^1\kappa, ^2\kappa) = [(^1\kappa_k q_k^\dagger + ^1\kappa'_k q_k), [(^2\kappa_k q_k^\dagger + ^2\kappa'_k q_k), H_0]]. \quad (18)$$

None of the quantities in Eqs. (15)–(17) contain any reference to two-electron integrals and may straightforwardly be constructed from DSCF wave functions. We refer to Ref. 3 for details. Equation (14) is a gradient vector containing a Hamiltonian with double one-index transformed integrals. Just as Eq. (3) could be expressed in terms of Eqs. (7)–(9), we can express Eq. (14) in terms of the general Fock matrix in Eqs. (7)–(9) containing the double one-index transformed Hamiltonian $H_0(\kappa^1, \kappa^2)$. The basic task for evaluating Eq. (14) is therefore to express these inactive and active Fock matrices containing doubly transformed one- and two-electron integrals such that only atomic integrals are required.

We first consider how to evaluate the double one-index transformed inactive Fock matrix

$$\bar{F}_{sr}^1 = \bar{h}_{sr} + \sum_j [2(sr\bar{jj}) - (sj\bar{jr})], \quad (19)$$

where \bar{h}_{ij} and $\bar{g}_{ijkl} = (ij\bar{kl})$ denote double one-index transformed integrals with respect to κ^1 and κ^2 . To obtain Eq. (19) from Eq. (9), we have used the fact that the double one-index transformed integrals have permutational symmetry between particles one and two. Equation (19) may be written in terms of the orbital rotation matrices κ^1 as the (one-index) transforming matrix and the corresponding one-index transformed integrals with κ^2 as transformation matrix, giving

$$\bar{F}_{sr}^1 = \kappa_{sp}^1 \bar{h}_{pr} + \bar{h}_{sp} \kappa_{pr}^1 + \sum_{pj} 2\kappa_{sp}^1 (pr\bar{jj}) - 2(sp\bar{jj}) \kappa_{pr}^1 \\ + 2\kappa_{jp}^1 (sr\bar{pj}) - 2(sr\bar{jp}) \kappa_{pj}^1 - \kappa_{sp}^1 (pj\bar{jr}) \\ + (sp\bar{rj}) \kappa_{pj}^1 - \kappa_{jp}^1 (sj\bar{pr}) + (sj\bar{jp}) \kappa_{pj}^1. \quad (20)$$

This expression is conveniently reassembled according to the first one-index transformation matrices κ_{sp}^1 , κ_{pr}^1 , κ_{jp}^1 and κ_{pj}^1 (j is the index of an inactive orbital) referring to the first one-index transformation

$$\bar{F}_{sr}^1 = \sum_p \kappa_{sp}^1 [\bar{h}_{pr} + 2(pr\bar{jj}) - (pj\bar{jr})] - \sum_p \kappa_{pr}^1 [\bar{h}_{sp} \\ + 2(sp\bar{jj}) - (sj\bar{jp})] + \kappa_{jp}^1 [2(sr\bar{pj}) - (sj\bar{pr})] \\ - \kappa_{pj}^1 [2(sr\bar{jp}) - (sp\bar{jr})]. \quad (21)$$

Resolving these expressions according to the second one-index transformation κ^2 , we obtain the final expression for the double one-index transformed inactive Fock matrix in terms of three intermediate matrices

$$\bar{F}_{sr}^1 = F_{sr}^1 + F_{sr}^2 + F_{sr}^3 \quad (22)$$

where

$$F_{sr}^1 = \sum_{\gamma\delta} (D_{\delta\gamma}^2 - D_{\delta\gamma}^3 - D_{\delta\gamma}^4 - D_{\delta\gamma}^5) \mathcal{L}_{sr\gamma\delta}, \quad (23)$$

$$F_{sr}^2 = \sum_q \kappa_{sq}^2 F_{qr}^{3''}(\kappa^1) - \kappa_{qr}^2 F_{sq}^{3''}(\kappa^1), \quad (24)$$

$$F_{sr}^3 = \sum_q \kappa_{sq}^1 F_{qr}^{3'} - \kappa_{qr}^1 F_{sq}^{3'}. \quad (25)$$

$\mathcal{L}_{sr\gamma\delta}$ is given as $\mathcal{L}_{sr\gamma\delta} = 2(sr|\gamma\delta) - (s\delta|\gamma r)$. The density matrices needed in the construction of F^1 contain both κ^1 or κ^2 ,

$$D_{\delta\gamma}^2 = \sum_{jpq} \kappa_{jp}^1 \kappa_{pq}^2 c_{\delta j} c_{\gamma q}, \quad D_{\delta\gamma}^3 = \sum_{pqj} \kappa_{jp}^1 \kappa_{qj}^2 c_{\gamma p} c_{\delta q},$$

$$D_{\delta\gamma}^4 = \sum_{pqj} \kappa_{pj}^1 \kappa_{jq}^2 c_{\gamma q} c_{\delta p}, \quad D_{\delta\gamma}^5 = \sum_{pqj} \kappa_{pj}^1 \kappa_{qp}^2 c_{\gamma j} c_{\delta q}$$

The $F^{3'}$ matrix is given as

$$F_{sr}^{3'} = F_{sr}^{3''}(\kappa) \sum_q \kappa_{sq}^2 F_{qr}^1 - \kappa_{qr}^2 F_{sq}^1 \quad (26)$$

where

$$F_{sr}^{3''} = \sum_{\delta\gamma} [D^I(\kappa) - D^{II}(\kappa)]_{\delta\gamma} \mathcal{L}_{sr\gamma\delta}. \quad (27)$$

and D^I and D^{II} are the density matrices

$$D_{\delta\gamma}^I(\kappa) = \sum_{pj} \kappa_{jp} c_{\gamma p} c_{\delta j}, \quad (28)$$

$$D_{\delta\gamma}^{II}(\kappa) = \sum_{pj} \kappa_{pj} c_{\delta p} c_{\gamma j}. \quad (29)$$

Here F^I denotes the ordinary inactive Fock matrix [Eq. (9)] and $c_{\gamma j}$ are the linear-combination-of-atomic-orbital (LCAO) coefficients of molecular orbital j and atomic basis function γ . D^I and D^{II} of Eqs. (26) and (27) are also used in the solution of the direct RPA equations (DRPA),¹¹ and are here constructed either over the first or the second one-index transformation κ^1 or κ^2 .

We thus end up with constructions of F^1 , F^2 , and $F^{3''}$ in Eqs. (23), (24), and (25) that have the same structure as the ones in DSCF and DRPA routines. Thus all necessary density matrices are precalculated and used for an integral-driven evaluation of the F^1 , F^2 , and $F^{3''}$ matrices

in one loop over $\mathcal{L}_{s\gamma\delta}$. As for DSCF and DRPA methods, the timing will be determined by the $\sum_{\delta\gamma} D_{\delta\gamma} \mathcal{L}_{s\gamma\delta}$ contraction.

Next we consider the double one-index transformed active Fock matrix

$$\bar{F}_{sr}^A = \sum_{xy} D_{xy} \left[(sr|xy) - \frac{1}{2} (sy|xr) \right]. \quad (30)$$

As for the double one-index transformed inactive Fock matrix, this matrix is written in terms of κ^1 and the one-index transformed integrals with κ^2 as the transformation matrix

$$\begin{aligned} \bar{F}_{sr}^A = & \sum_p \left(\kappa_{sp}^1 \left[\sum_{xy} D_{xy} \left[(pr|xy) - \frac{1}{2} (py|xr) \right] \right] \right. \\ & - \kappa_{pr}^1 \left[\sum_{xy} D_{xy} \left[(sp|xy) - \frac{1}{2} (sy|xp) \right] \right] \\ & + \sum_{xy} \kappa_{xp}^1 D_{xy} \left[\left[(sr|py) - \frac{1}{2} (sy|pr) \right] \right] \\ & \left. \times \sum_{xy} \kappa_{py}^1 D_{xy} \left[\left[(sr|xp) - \frac{1}{2} (sp|xr) \right] \right] \right). \end{aligned}$$

\bar{F}_{sr}^A can be evaluated as

$$\bar{F}_{sr}^A = \sum_p (\kappa_{sp}^1 \bar{F}_{pr}^A - \kappa_{pr}^1 \bar{F}_{sp}^A) + \bar{F}_{sr}^A (D_{py}^1 - D_{xp}^2),$$

where

$$D_{py}^1 = \sum_x \kappa_{xp} D_{xy}, \quad D_{xp}^2 = \sum_y \kappa_{py} D_{xy}$$

and where $\bar{F}^A(D)$ means the active Fock matrix containing one-index transformed integrals with κ^2 as the transformation matrix and where the density matrix of the active Fock matrix is replaced by D . From the previous derivation, it is clear that \bar{F}^A and $\bar{F}^A(D)$ can be evaluated straightforwardly in the atomic orbital basis and that \bar{F}^A therefore can also be calculated in the atomic orbital basis.

The essential steps in the calculation of one nonlinear molecular property are therefore (1) the solution of three sets of response equations (linear or eigenvalue); and (2) the calculation of the linear transformation by the third energy derivative matrix of two vectors. In step 1, it is advantageous to solve the three sets of response equations simultaneously. Improved trial vectors can thus be obtained for all three equations with only one loop through the atomic integrals. Step 2 requires that Fock matrices with double one-index transformed integrals are constructed. This step may also be carried out with only one loop through the atomic integrals by multiplying all appropriate density matrices on a given batch of integrals. If we want to calculate more nonlinear molecular properties at the same time, this can be done with little additional cost. The response equations for all the molecular properties would then have to be solved simultaneously. It is also worth pointing out that when solving the response equations it is an advantage to use the paired structure of the $E^{(2)}$ matrix as described in Ref. 6. For each linear trans-

formation, this allows us to obtain one linear transformation at little extra cost, and at the same time conserve the paired structure in the reduced space. This is especially important when solving the eigenvalue problem in Eq. (1) as it ensures that complex eigenvalues do not arise in the reduced space.

III. APPLICATION

As a first application of the DDQRPA method, we have carried out a basis set investigation of the static and dynamic polarizabilities of *para*-nitroaniline (PNA). Our choice is motivated by the strong donor-acceptor character of PNA, responsible for the large polarizability (α) and in particular the large first- and second-order hyperpolarizabilities (β and γ) of this molecule. PNA has been the subject of a number of experimental studies¹³ as well as theoretical calculations.¹⁴ Recently, Karna *et al.* carried out an *ab initio* study using the coupled Hartree-Fock method.¹⁵ We refer to their work for references to earlier experimental and theoretical studies.

In this work, we explore a number of basis sets containing up to 300 basis functions of compact, polarizing, and diffuse character:

(a) Dunning's double zeta valence (DZV) basis set¹⁶ (9s5p)/[3s2p] on heavy atoms and (4s)/[2s] on H, giving a total of 102 functions;

(b) basis *a* augmented with *d* functions on heavy atoms [$\alpha=0.2$ (see Ref. 15)] and *p* functions on H ($\alpha=0.1$). This gives the scheme (3s2p1d) and (2s1p) with a total of 180 functions;

(c) a stripped-down (5s3p) and (3s) version of the (10s6p4d)/[5s3p2d] and (6s4p)/[3s2p] basis set by Sadlej optimized for atomic polarizabilities,¹⁷ containing a total of 158 functions;

(d) Sadlej's basis¹⁷ leaving out the diffuse *d* functions on C since these give rise to strong linear dependencies. This gave a basis set containing 278 atomic functions—(5s3p1d) on C, (5s3p2d) on N and O, and (3s2p) on H. Due to linear dependencies, further reductions of the MO basis set had to be made based on the eigenvalues of the atomic orbital overlap matrix. Removing all eigenvectors whose eigenvalues were smaller than 10^{-2} , we ended up with a set of 230 molecular orbitals;

(e) a (5s3p1d) (no diffuse *d* functions) and (3s) contraction of Sadlej's basis,¹⁷ giving a total of 218 functions. No reductions were necessary;

(f) basis set *e* with an extra primitive *p* function left uncontracted, giving the scheme (5s4p1d) and (3s) with a total of 248 functions;

(g) basis set *f* with all *s* functions on heavy atoms uncontracted (10s4p1d) and (3s) with a total of 298 functions.

We have used experimental coordinates obtained from crystallographic data¹⁸ and two additional coordinates which completely determine the geometry¹⁹ (see Table I of Ref. 15). In previous calculations, see, e.g., Ref. 20, a planar structure of C_{2v} symmetry has been assumed. In reality, the nitro group is slightly bent and the amino group slightly twisted with a low rotational barrier. As shown by

TABLE I. Calculation of static and frequency dependent ($\omega=0.650$ eV) first hyperpolarizabilities of *para*-nitroaniline for basis sets *a*–*q*.

Hyperpolarizability/ basis set	<i>xxz</i>	<i>zxx</i>	<i>yyz</i>	<i>zyy</i>	<i>zzz</i>	β_{vec}
$\beta(0;0,0)$						
<i>a</i>	−1.05	−1.05	−0.06 ^a	−0.06 ^a	5.75	4.65
<i>b</i>	−0.90	−0.90	−0.11	−0.11	5.10	4.09
<i>c</i>	−1.02	−1.02	−0.18	−0.18	6.33	5.12
<i>d</i>	−0.89	−0.89	−0.16	−0.16	5.03	3.98
<i>e</i>	−0.90	−0.90	−0.19	−0.19	5.37	4.28
<i>f</i>	−0.89	−0.89	−0.19	−0.19	5.37	4.29
<i>g</i>	−0.89	−0.89	−0.18	−0.18	5.37	4.29
$\beta(-2\omega;\omega,\omega)$						
<i>a</i>	−1.08	−1.11	−0.06 ^a	−0.06 ^a	6.24	5.08
<i>b</i>	−0.96	−0.96	−0.12	−0.12	5.58	4.50
<i>c</i>	−1.07	−1.09	−0.19	−0.19	6.88	5.62
<i>d</i>	−0.93	−0.95	−0.17	−0.17	5.49	4.39
<i>e</i>	−0.93	−0.96	−0.19	−0.19	5.84	4.71
<i>f</i>	−0.93	−0.96	−0.19	−0.19	5.85	4.71
<i>g</i>	−0.93	−0.96	−0.19	−0.19	5.84	4.71
$\beta(0;\omega,-\omega)^b$						
<i>a</i>	−1.06	−1.06	−0.06 ^a	−0.06 ^a	5.91	4.79
<i>b</i>	−0.91	−0.91	−0.11	−0.11	5.25	4.23
<i>c</i>	−1.04	−1.03	−0.19	−0.19	6.51	5.28
<i>d</i>	−0.91	−0.90	−0.17	−0.17	5.18	4.11
<i>e</i>	−0.91	−0.91	−0.19	−0.19	5.52	4.42
<i>f</i>	−0.91	−0.90	−0.19	−0.19	5.52	4.43
<i>g</i>	−0.91	−0.90	−0.19	−0.19	5.52	4.42

^a*y* components unstable for basis set *a*.

Karna *et al.*,¹⁵ the choice between the optimized and experimental geometries has little influence on the calculated properties.

Table I presents results for static hyperpolarizabilities as well as the dynamic hyperpolarizabilities $\beta_{ijk}(-2\omega;\omega,\omega)$ and $\beta_{ijk}(0;\omega,-\omega)$. In general, the dynamic hyperpolarizability $\beta_{ijk}(\omega_i;\omega_j,\omega_k)$, where $\omega_i = -\omega_j - \omega_k$, exhibits permutational symmetry with respect to the operators and frequencies (*i*, ω_i), (*j*, ω_j), and (*k*, ω_k), e.g., $\beta_{ijk}(\omega_i;\omega_j,\omega_k) = \beta_{jki}(\omega_j;\omega_k,\omega_i)$. For static hyperpolarizabilities, the so-called Kleinman symmetry holds, giving equivalence between the *xxz* and *zxx* and the *yyz* and *zyy* components. For dynamic hyperpolarizabilities, the Kleinman symmetry does not hold. In general, the larger the frequency, the larger the differences. At $\omega=0.650$ eV, we find the Kleinman symmetry still to be a good approximation for all basis sets.

We present hyperpolarizability components according to standard definitions. The relationships between these and the experimental susceptibilities are given in, e.g., Ref. 19. In Table I, we have also given the average dynamic hyperpolarizabilities $\beta_{vec} = 1/3(\beta_1^2 + \beta_2^2 + \beta_3^2)^{1/2}$, where $\beta_i = \sum_{k=1}^3(\beta_{ikk} + \beta_{kik} + \beta_{kki})$.

Many experiments involving electric-field-induced second-harmonic generation (ESH) measurements for $\beta_{vec}(-2\omega;\omega,\omega)$ have been carried out in solution (see Table III in the paper of Karna *et al.*)¹⁵ The experimental values have been measured at frequencies between 0.650 and 1.494 eV with the first hyperpolarizabilities ranging between 6.4 and 47.67 (in units of 10^{-30} cm⁵ esu). How-

ever, considerable discrepancies are found between different experiments at the same frequency. At $\omega=1.17$ eV, the experimental results vary between 16.9 and 36.^{21,22} Similar differences are observed at other frequencies. Solvent effects are thus substantial, in particular between polar and nonpolar solvents.²³ Also, deviations up to 50% have been reported between different ESH experiments for identical solutions and identical frequencies.

$\beta_{vec}(-2\omega;\omega,\omega)$ has been given in semiempirical [complete neglect of differential overlap (CNDO) and Parr–Pariser–Pople (PPP)] calculations for a variety of frequencies covering those experimentally used. Considerable differences have been obtained in the results, both with respect to experiment and mutually between the different semiempirical calculations. At $\omega=1.17$ eV, the results for $\beta_{vec}(-2\omega;\omega,\omega)$ range from 12.18 to 34.3×10^{-30} (cm⁵ esu),^{24,25} the latter both exploiting the CNDO-CI method.

In view of these conflicting results, it is clear that the systematic approach of the *ab initio* method would be very valuable for exploring size and trends of hyperpolarizabilities of substituted aromatic compounds. The work of Daniel and Dupuis¹⁹ and by Karna *et al.*¹⁵ serves as the first step in this direction.

In this paper, we focus on the recent experimental results by Teng and Garito, who measured ω in the range 0.650–1.494 eV using 1,4-dioxane as solvent.²¹ At these frequencies, they find a dispersion of β ranging from 9.6 to 40 (10^{-30} cm⁵ esu). We chose the lower frequency (0.650 eV) to explore the basis set dependency of the computed dispersion. This frequency is well below a resonance excitation with frequency doubling to the first absorption energy level of PNA, and a comparison between experimental and theoretical results is therefore meaningful.

From Table I, we see that the average polarizabilities do not vary substantially with the basis sets. The calculated $\beta_{ijk}(-2\omega;\omega,\omega)$ values are within 20% of the results for basis *d*, presumably the most accurate. The relative variations are larger for the smaller components, while relatively minor (again about 20%) for the large in-plane β_{zzz} component. The basis set dependencies of the static and dynamic hyperpolarizabilities are similar, but more pronounced for the latter.

Going into some detail in the results presented by Table I, we find that the contraction schemes among an extended manifold of *s* and *p* orbitals work very well (cf. entries *e*, *f*, and *g*). More flexibility among the *s* and *p* orbitals increases the β value by about 5% (cf. *b* and *e*). The polarizing functions, on the other hand, decrease β by about 10% to 15% (cf. *a* with *b* and *c* with *e*). The addition of diffuse functions will lead to a further decrease, here 6%. Using the basis set *d*, we confirm the observation of Karna *et al.*¹⁵ that the order of the dynamic polarizabilities are $\beta_{vec}(-2\omega;\omega,\omega) > \beta_{vec}(0;\omega,-\omega) > \beta_{vec}(-\omega;0,\omega)$, all three being larger than the static polarizability.

Generally, the differences between theoretical and experimental results tend to increase with dispersion. At higher frequencies, the presence of resonances makes the comparison with experiment more difficult. The experi-

mental recordings are carried out at nonzero frequencies, and the static value are arrived at by extrapolation. From a theoretical point of view, it is therefore desirable to compare the frequency dependent hyperpolarizabilities directly. Moreover, the vibrational contributions to the hyperpolarizabilities are small in the dynamic case, while in general significant in the static case. Such contributions are difficult to estimate for a molecule like PNA.

In agreement with previous calculations on PNA and on nitroaniline derivatives using small basis sets,¹⁵ the calculated dynamic hyperpolarizability is too low compared to experiment for PNA in solution. The previous calculations indicate roughly a factor of 2 lower value of the first hyperpolarizability compared to experiment and as much as a factor of 5 for the second hyperpolarizability. We find that our best estimate (the *d* basis), only departs by 0.1×10^{-30} (cm⁵ esu) from the value of Karna *et al.*,¹⁵ indicating that the remaining discrepancies are not due to the basis set. We also find indications that further enlargement of the basis set will not expand the variational space, but instead give linear dependencies (which are tested for and removed). An enlargement of the basis set will therefore be difficult. Still, with experimental uncertainties due to solvent effects in mind, we interpret this as an indication that the remaining discrepancy is due to electron correlation. In fact, differences of the order of 50% between RPA and MCQR hyperpolarizabilities have been observed.²⁶ We are at present exploring the role of correlation on PNA for some of the smaller basis sets using multiconfigurational quadratic response theory.²⁷

IV. SUMMARY

We have presented the double-direct quadratic RPA (DDQRPA) method for calculation of nonlinear properties for direct self-consistent-field (SCF) wave functions. The Fock matrices are constructed directly from atomic integrals and the response equations are solved iteratively using direct linear transformations. In this way, we have obtained the same advantages in a nonlinear property calculation as in direct SCF calculations, namely, we avoid integral transformations between atomic and molecular orbital bases as well as the storing and retrieving of integrals. The method addresses the same range of molecular applications as do wave function calculations with traditional direct SCF and at the same cost.

Applications are presented for dynamic hyperpolarizabilities. The method can straightforwardly be applied to other nonlinear effects such as two-photon absorption. We have chosen *para*-nitroaniline as a demonstration because it has been used as a prime case for theoretical (mostly semiempirical) and experimental investigations (performed in solutions). However, the best applicability of the presently devised DDQRPA method will be for larger systems containing spatially well separated subunits. In fact, direct techniques of the kind presented here are more efficient for larger molecules with moderate basis sets than for small molecules with large basis sets due to the performance of integral screening in the former case. The effort in direct nonlinear property calculations will show the

same drastic decrease with size as traditional DSCF; for a linear chain, this will go as N^2 , N being the number of subunits, just as in ordinary DSCF calculations. Furthermore, the basis set dependency of the hyperpolarizabilities, notably on the diffuse functions, seems to decrease for larger molecules, as indicated by a recent investigation on polyenes²⁸ using conventional techniques. We find these indications gratifying for applications of DDQRPA on nonlinear properties of large systems, as will be further demonstrated in the near future.

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