

# Large scale random phase calculations for direct self-consistent field wavefunctions

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We present an implementation of the double-direct random phase approximation (DDRPA) method for closed-shell and one-open-shell systems. The method is termed double-direct since (1) it is driven directly by the atomic orbital integrals, and since (2) it uses iterative techniques based on direct linear transformations for solving the RPA eigenvalue equations and sets of linear equations. The method can be used for calculating linear response properties such as polarizabilities and excitation spectra of large species. We demonstrate its potential by calculating excitation energies and transition moments as well as static and dynamic polarizabilities of para-nitroaniline.

## 1. Introduction

Direct techniques for calculating *ab initio* self-consistent field (SCF) wavefunctions have been used for almost a decade. Since the early work of Almlöf and co-workers [1], direct SCF (DSCF) techniques have significantly broadened the scope of applicability for the SCF method and are now routinely used for systems like fullerene and large metallic clusters. With the recent developments in methods for analytical calculations of molecular properties, efforts have also been devoted to large scale calculations of molecular properties from DSCF wavefunctions. The bottleneck of such calculations is the same as for DSCF wavefunctions: the evaluation, storage, and retrieval of the two-electron integrals. To alleviate these problems, one must resort to a direct handling of the

atomic orbital (AO) integrals, computing them on the fly when they are needed.

A recent example of DSCF property calculations is provided by the direct random phase approximation (RPA) calculations of static and dynamic polarizabilities by Feyereisen et al. [2]. In 1988 Jensen et al. [3] described how the RPA equations may be solved iteratively in terms of linear transformations driven by the AO integrals. This approach has certain advantages over that of Feyereisen et al. and it is the purpose of this work to present an implementation of this method.

We coin the present RPA implementation double-direct (DDRPA) since it is direct both in the handling of the integrals and in the solution of the matrix equations. DDRPA is formulated in terms of general Fock matrices constructed from one-index trans-

formed integrals as in current multiconfigurational SCF (MCSCF) property calculations. This approach is more general than that of Feyereisen et al. [2] since canonical Hartree–Fock orbitals are not assumed. The sets of linear equations and the eigenvalue equations are solved by the same AO based direct techniques. It exploits the paired structure of the RPA equations, avoiding spurious complex solutions. With this approach we can calculate static and dynamic polarizabilities as well as excitation spectra and transition moments for closed-shell and one-open-shell wavefunctions. In a separate paper we present the corresponding expressions for non-linear quadratic response properties and calculate molecular dynamic hyperpolarizabilities [4].

In section 2 we present the DDRPA method and give computationally tractable expressions for the RPA linear transformation in terms of density matrices and atomic two-electron integrals. Special attention is devoted to the contraction of density matrices with two-electron AO integrals, since this is the time consuming step of the calculations. In section 3 we demonstrate the method by calculating the linear polarizabilities and excitation spectra of para-nitroaniline using a number of different basis sets.

## 2. Theory

We describe in this section a double-direct implementation of the linear response function for single configuration (LRSC) closed shells and doublet one-open-shell reference states.

### 2.1. RPA equations

The poles of the linear response functions represent electronic excitation energies and the residues give the transition matrix elements. The linear response function itself determines second-order molecular properties such as frequency dependent polarizabilities. We use the notation of ref. [5] for the LRSC eigenvalue equation

$$(\mathbf{E}^{(2)} - \lambda_j \mathbf{S}^{(2)}) \mathbf{X}_j = 0, \quad (1)$$

where the eigenvalue  $\lambda_j$  determines the energy of the excitation described by the eigenvector  $\mathbf{X}_j$ . The matrices  $\mathbf{E}^{(2)}$  and  $\mathbf{S}^{(2)}$  are defined as

$$\begin{aligned} \mathbf{E}^{(2)} &= \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \\ &= \begin{pmatrix} \langle 0 | [q_i, [H_0, q_j^+]] | 0 \rangle & \langle 0 | [q_i, [H_0, q_j]] | 0 \rangle \\ \langle 0 | [q_i^+, [H_0, q_j^+]] | 0 \rangle & \langle 0 | [q_i^+, [H_0, q_j]] | 0 \rangle \end{pmatrix} \end{aligned} \quad (2)$$

and

$$\begin{aligned} \mathbf{S}^{(2)} &= \begin{pmatrix} \Sigma & \Delta \\ -\Delta^* & -\Sigma^* \end{pmatrix} \\ &= \begin{pmatrix} \langle 0 | [q_i, q_j^+] | 0 \rangle & \langle 0 | [q_i, q_j] | 0 \rangle \\ -\langle 0 | [q_j^+, q_i^+] | 0 \rangle & -\langle 0 | [q_j, q_i] | 0 \rangle \end{pmatrix}, \end{aligned} \quad (3)$$

where  $\{q_j, q_j^+\}$  are singlet one-electron excitation operators.

The transition matrix element between the reference state  $|0\rangle$  and the state  $|j\rangle$  is determined as

$$\langle 0 | V | j \rangle = \bar{\mathbf{X}}_j \mathbf{V}_\mu^{(1)}, \quad (4)$$

where

$$\mathbf{V}_\mu^{(1)} = \begin{pmatrix} \langle 0 | [q, V_\mu] | 0 \rangle \\ \langle 0 | [q^+, V_\mu] | 0 \rangle \end{pmatrix}, \quad (5)$$

and  $V_\mu$  refers to a component of the dipole operator. Second-order molecular properties at frequency  $\omega$  are obtained by first solving the LRSC equations

$$(\mathbf{E}^{(2)} - \omega \mathbf{S}^{(2)}) \mathbf{X}_\mu = \mathbf{V}_\mu^{(1)} \quad (6)$$

and then calculating the properties according to the expression

$$\bar{\mathbf{V}}_\nu^{(1)} (\mathbf{E}^{(2)} - \omega \mathbf{S}^{(2)})^{-1} \mathbf{V}_\mu^{(1)} = \bar{\mathbf{V}}_\nu^{(1)} \mathbf{X}_\mu. \quad (7)$$

When  $V_\nu$  and  $V_\mu$  are the components of the dipole operator eq. (7) determines the  $\nu\mu$ th component of the polarizability  $\alpha_{\nu\mu}(\omega)$ .

### 2.2. Linear transformations

Eqs. (1) and (6) may be solved iteratively if we are able to carry out the linear transformations

$$\mathbf{u} = \mathbf{E}^{(2)} \mathbf{b}, \quad (8)$$

$$\mathbf{m} = \mathbf{S}^{(2)} \mathbf{b}. \quad (9)$$

The transformation in eq. (9) is trivial since it requires density matrix elements only. On the other

hand, the transformation in eq. (8) is difficult, involving two-electron integrals. We here describe how this transformation may be carried out from two-electron integrals in the atomic basis.

For a closed-shell or doublet one-open-shell SCF reference state  $|0\rangle$  the linear transformation with  $\mathbf{E}^{(2)}$  as transformation matrix becomes

$$\begin{pmatrix} {}^1u \\ {}^2u \end{pmatrix} = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} {}^1b \\ {}^2b \end{pmatrix} = - \begin{pmatrix} \langle 0 | [q_j, H_0(\kappa)] | 0 \rangle \\ \langle 0 | [q_j^+, H_0(\kappa)] | 0 \rangle \end{pmatrix}. \quad (10)$$

The one-index transformed Hamiltonian is defined as

$$\begin{aligned} H_0(\kappa) &= \sum_j [\kappa_j q_j + \kappa'_j q_j^+, H_0] \\ &= \sum_{rs} \tilde{h}_{rs} E_{rs} + \sum_{rstu} (\widetilde{rs|tu}) (E_{rs} E_{tu} - \delta_{st} E_{ru}), \quad (11) \end{aligned}$$

where the one-index transformed integrals are given as

$$\tilde{h}_{rs} = \sum_p (\kappa_{rp} h_{ps} - \kappa_{ps} h_{rp}), \quad (12)$$

$$\begin{aligned} (\widetilde{rs|tu}) &= \sum_p (\kappa_{rp} g_{pstu} - \kappa_{ps} g_{rptu} + \kappa_{tp} g_{rspu} - \kappa_{pu} g_{rstp}) \quad (13) \end{aligned}$$

and the electronic Hamiltonian is expressed as

$$H_0 = \sum_{rs} h_{rs} E_{rs} + \frac{1}{2} \sum_{pqrs} g_{pqrs} (E_{pq} E_{rs} - \delta_{qr} E_{ps}). \quad (14)$$

We have here arranged the components of the trial vector

$$\begin{pmatrix} {}^1b \\ {}^2b \end{pmatrix} = \begin{pmatrix} \kappa_{rs} & \text{for } r > s \\ \kappa'_{rs} & \text{for } r < s \end{pmatrix} \quad (15)$$

as a matrix

$$\begin{aligned} \kappa_{rs} &= \kappa_{rs}, & \text{for } r > s, \\ &= 0, & \text{for } r = s, \\ &= \kappa'_{rs}, & \text{for } r < s. \end{aligned} \quad (16)$$

An explicit expression for the one-index transformed Hamiltonian is given in ref. [3]. The indices  $rs$  in eq. (16) refer to the non-redundant set of orbital excitations.

The linearly transformed vectors may be expressed in terms of the inactive and active Fock matrices in-

roduced by Siegbahn et al. [6]. When the operator manifold is of singlet symmetry

$$\begin{pmatrix} q_j \\ q_j^+ \end{pmatrix} = \begin{pmatrix} E_{rs} \\ E_{sr} \end{pmatrix}, \quad (17)$$

where

$$E_{rs} = E_{rs}^\alpha + E_{rs}^\beta, \quad (18)$$

we may write the linearly transformed vector in eq. (8) as

$$\begin{pmatrix} {}^1u_j \\ {}^2u_j \end{pmatrix} = - \begin{pmatrix} \langle 0 | [q_j, H_0(\kappa)] | 0 \rangle \\ \langle 0 | [q_j^+, H_0(\kappa)] | 0 \rangle \end{pmatrix} = \begin{pmatrix} \tilde{F}_{sr} \\ \tilde{F}_{rs} \end{pmatrix}, \quad (19)$$

where the Fock matrices constructed from one-index transformed integrals  $\tilde{F}_{rs}$  are given by the following expressions (implied summations):

$$\begin{aligned} F_{ai} &= 2F_{ai}^1 + 2F_{ai}^A, & F_{ia} &= -2F_{ia}^1 - 2F_{ia}^A, \\ F_{wi} &= 2F_{wi}^1 - F_{xi}^1 D_{xw} + 2F_{wi}^A, \\ F_{iw} &= -2F_{iw}^1 + F_{ix}^1 D_{wx} - 2F_{iw}^A, \\ F_{aw} &= F_{ax}^1 D_{wx}, & F_{wa} &= -F_{xa}^1 D_{xw}, \\ F_{vw} &= F_{vx}^1 D_{vx} - F_{xv}^1 D_{xw}, \end{aligned} \quad (20)$$

where the Fock matrices are given by

$$\begin{aligned} F_{pq}^1 &= h_{pq} + \sum_k (2g_{pqkk} - g_{pkkq}), \\ 2F_{pq}^A &= \sum_{xy} (2g_{pqxy} - g_{pyxq}) D_{xy}. \end{aligned} \quad (21)$$

Here the inactive orbitals are denoted by  $i, j, k, \dots$ , active orbitals by  $x, y, z, \dots$ , secondary orbitals by  $a, b, c, \dots$ , and general orbitals by  $p, q, r, \dots$ . The expressions for the Fock matrices above are obtained from a Hamiltonian whose only symmetry is permutation of the electrons.

We now show how the inactive Fock and the active Fock matrices can be expressed in terms of AO integrals, as we then can determine the linear transformed vectors from the AO integrals. We consider first the inactive Fock matrix:

$$\tilde{F}_{sr}^1 = \tilde{h}_{sr} + \sum_j [2(\widetilde{sr|jj}) - (\widetilde{sj|jr})], \quad (22)$$

where  $\tilde{h}_{ij}$  and  $\tilde{g}_{ijkl} = (\widetilde{ij|kl})$  denote one-index transformed one- and two-electron integrals with respect to the orbital rotation matrix  $\kappa$  of eq. (16):

$$\tilde{h}_{rs} = \sum_p (\kappa_{rp} h_{ps} - \kappa_{ps} h_{rp}), \quad (23)$$

$$\begin{aligned} (\widetilde{rs|tu}) = \sum_p [\kappa_{rp}(ps|tu) \\ - \kappa_{ps}(rp|tu) + \kappa_{ip}(rs|pu) - \kappa_{pu}(rs|tp)] . \end{aligned} \quad (24)$$

Expanding the inactive Fock matrix  $\tilde{\mathbf{F}}^1$  in terms of the one-index transformed integrals and collecting terms according to  $\kappa$  one obtains

$$\tilde{F}_{sr}^1 = \sum_p (\kappa_{sp} F_{pr}^1 - \kappa_{pr} F_{sp}^1) + \sum_{\gamma\delta} (\tilde{D}_{\delta\gamma}^{11} - \tilde{D}_{\delta\gamma}^{12}) \mathcal{L}_{sr\gamma\delta}, \quad (25)$$

where

$$\mathcal{L}_{sr\gamma\delta} = 2(sr|\gamma\delta) - (s\delta|\gamma r)$$

are the two-electron integrals evaluated over the AO basis set. The  $\tilde{\mathbf{D}}^{11}$  and  $\tilde{\mathbf{D}}^{12}$  matrices denote modified inactive density matrices in the AO basis

$$\tilde{D}_{\delta\gamma}^{11} = \sum_{pj} \kappa_{jp} c_{\gamma p} c_{\delta j}, \quad (26)$$

$$\tilde{D}_{\delta\gamma}^{12} = \sum_{pj} \kappa_{pj} c_{\delta p} c_{\gamma j}, \quad (27)$$

where  $c_{\gamma j}$  denotes the LCAO coefficient pertaining to molecular orbital  $j$  and atomic basis function  $\gamma$ .

In a similar fashion one can resolve the active Fock matrix with one-index transformed integrals

$$\tilde{F}_{sr}^A = \sum_{xy} D_{xy} [(sr|xy) - \frac{1}{2}(sy|xr)] \quad (28)$$

into a one-index transformed active Fock matrix plus a contraction of AO integrals over an active density matrix:

$$\tilde{F}_{sr}^A = \sum_p (\kappa_{sp} F_{pr}^A - \kappa_{pr} F_{sp}^A) + \sum_{\delta\gamma} (D_{\delta\gamma}^{A1} - D_{\delta\gamma}^{A2}) \mathcal{L}_{sr\gamma\delta}, \quad (29)$$

where

$$D_{\delta\gamma}^{A1} = \frac{1}{2} \sum_{pxy} D_{xy} \kappa_{xp} c_{\gamma p} c_{\delta y}, \quad (30)$$

$$D_{\delta\gamma}^{A2} = \frac{1}{2} \sum_{pxy} D_{xy} \kappa_{px} c_{\delta p} c_{\gamma y}. \quad (31)$$

### 2.3. Tools to speed up DDRPA calculations

The most expensive step of a DDRPA calculation is the linear transformation eq. (8), which requires a

recalculation of all two-electron integrals. The following points are important in order to reduce the number of integral reevaluations:

(1) Use algorithms that converge the matrix equations in as few linear transformations as possible.

(2) Converge only to the accuracy necessary, keeping in mind that the numerical errors in the calculated properties are quadratic in the errors of the solution vectors.

(3) Solve all matrix equations simultaneously, since the solutions for all equations can then be obtained at the cost of solving a single equation.

The following measures have been undertaken to attain these goals:

Ad (1). We described in ref. [7] algorithms for solving the eigenvalue equation (eq. (1)) and the linear equations (eq. (6)). Significantly, these algorithms exploit the paired structure of the RPA matrices, giving one extra linear transformation at no extra cost in each iteration. For example, when the linear transformation

$$\begin{pmatrix} {}^1u \\ {}^2u \end{pmatrix} = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} {}^1X \\ {}^2X \end{pmatrix}, \quad (32)$$

$$\begin{pmatrix} {}^1m \\ {}^2m \end{pmatrix} = \begin{pmatrix} \Sigma & \Delta \\ -\Delta & -\Sigma \end{pmatrix} \begin{pmatrix} {}^1X \\ {}^2X \end{pmatrix}, \quad (33)$$

is carried out, then the transformation is also known for the paired vector

$$\begin{pmatrix} {}^2u \\ {}^1u \end{pmatrix} = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} {}^2X \\ {}^1X \end{pmatrix}, \quad (34)$$

$$-\begin{pmatrix} {}^2m \\ {}^1m \end{pmatrix} = \begin{pmatrix} \Sigma & \Delta \\ -\Delta & -\Sigma \end{pmatrix} \begin{pmatrix} {}^2X \\ {}^1X \end{pmatrix}. \quad (35)$$

Therefore, each time we include a trial vector

$$\begin{pmatrix} {}^1X \\ {}^2X \end{pmatrix}$$

in the reduced basis, we also include

$$\begin{pmatrix} {}^2X \\ {}^1X \end{pmatrix}.$$

In addition to faster convergence, this scheme preserves the paired structure of the solution. This is important when solving the eigenvalue equation eq. (1) since it means that we never encounter complex roots. Furthermore, we have monotonic convergence to ex-

citation energies of the full space just as in CI algorithms.

Ad (2). When solving eqs. (1) and (6), it is important to identify the convergence threshold for the matrix equations needed for the desired accuracy in the calculated property. Convergence to higher accuracy is clearly a wasted effort. The excitation energies have errors quadratic in the residual vector

$$\mathbf{R} = (\mathbf{E}^{(2)} - \lambda_j^A \mathbf{S}^{(2)}) \mathbf{X}_j^A. \quad (36)$$

Here  $\lambda_j^A$  denotes the approximate excitation energy and  $\mathbf{X}_j^A$  the corresponding eigenvector. The errors in the transition moments are linear in the residual vector. In contrast, second-order properties can be calculated in such a way that their errors are quadratic in the errors of the solution vectors [8–10]:

$$\begin{aligned} & \mathbf{V}_\nu^{(1)} (\mathbf{E}^{(2)} - \omega \mathbf{S}^{(2)})^{-1} \mathbf{V}_\mu^{(1)} \\ & \simeq \mathbf{V}_\nu^{(1)} \mathbf{X}_\mu^A + \mathbf{X}_\nu^A \mathbf{V}_\mu^{(1)} - \mathbf{X}_\nu^A (\mathbf{E}^{(2)} - \omega \mathbf{S}^{(2)}) \mathbf{X}_\mu^A \\ & = \mathbf{V}_\nu^{(1)} \mathbf{X}_\mu^A + \mathbf{X}_\nu^A \mathbf{R}_\mu. \end{aligned} \quad (37)$$

Here  $\mathbf{X}_\mu^A$  is the approximate solution and  $\mathbf{R}_\mu$  the residual,

$$\mathbf{R}_\mu = (\mathbf{E}^{(2)} - \omega \mathbf{S}^{(2)}) \mathbf{X}_\mu^A - \mathbf{V}_\mu^{(1)}. \quad (38)$$

It is easy to check that eq. (37) gives an error that is quadratic in the error of the solution. To do this we insert

$$\mathbf{X}_\mu^A = \mathbf{X}_\mu^E + \delta_\mu \quad (39)$$

( $\mathbf{X}_\mu^E$  denotes the exact solution and  $\delta_\mu$  the error in  $\mathbf{X}_\mu^A$ ) into the right-hand side of eq. (37) and obtain straightforwardly the desired result.

Ad (3). If the matrix equations for all excitation energies and second-order properties are solved simultaneously, one iteration for each equation is obtained with each reevaluation of the AO integrals. This can be accomplished if in each iteration the integrals are contracted with the densities of all the improved trial vectors. Since this contraction step is inexpensive compared to the integral evaluation, the solutions to all matrix equations are obtained essentially at the price for one equation.

### 3. Applications

As a demonstration of the DDRPA method, we

have calculated the static and dynamic dipole polarizabilities, excitation energies, and dipole oscillator strengths for para-nitroaniline (PNA). This molecule is of interest since among disubstituted benzenes it possesses a particularly strong donor–acceptor character due to a strong localization of the HOMO and LUMO orbitals and a small HOMO–LUMO gap. In the ultraviolet spectra of such compounds, bands appear which cannot be interpreted as local excitations within donor/acceptor groups or the connecting rings. Instead, these bands are interpreted in terms of charge transfer configurations [11,12]. Such excitations also give special features and anomalies at other energies, for example in X-ray core photoelectron spectra [13].

As for other aromatic donor–acceptor compounds, the PNA HOMO orbital is localized on the donor and the LUMO on the acceptor, thus the HOMO  $\pi 4b_1$  orbital is essentially a nitro orbital and the LUMO  $\pi 5b_1$  an amino orbital. The HOMO–LUMO excitation is therefore associated with a considerable nitro-to-amino charge transfer. In addition to the low-lying UV transitions, this leads to large polarizabilities ( $\alpha$ ) and hyperpolarizabilities ( $\beta$  and  $\gamma$ ).

We use PNA for a basis set investigation of polarizabilities, excitation energies, and oscillator strengths. The static and dynamic polarizabilities of this molecule have recently been calculated by Karna et al. [14] using the coupled Hartree–Fock method and by Feyereisen et al. [2] using a DDRPA method different from ours. A similar basis set investigation of the PNA dynamic hyperpolarizabilities is presented elsewhere [4]. We refer to the work of Karna et al. [14] for references to experimental and theoretical studies of PNA.

The basis sets used in the present work are:

(a) Dunning and Hay's double zeta valence (DZV) basis [15]: (9s5p)/[3s2p] on heavy atoms and (4s)/[2s] on hydrogens, giving 102 functions.

(b) Basis (a) augmented with d functions on heavy atoms (exponent=0.2, see ref. [14]) and p functions on hydrogens (exponent=0.2), giving 180 functions.

(c) Basis set (d) below without d functions on heavy atoms and p functions on hydrogen, giving a total of 158 functions.

(d) Sadlej's (10s6p4d)/[5s3p2d] and (6s4p)/[3s2p] basis optimized for atomic polarizabilities

[16]. It includes both polarizing and diffuse d (p) functions on heavy atoms (hydrogens). However, the diffuse d functions on carbon atoms had to be removed due to linear dependencies, giving 278 functions.

(e) Equal to basis set (d) but including only polarizing (thus no diffuse) d functions on heavy atoms and no p functions on hydrogens, giving 218 functions.

(f) Equal to basis set (e) but (6p)–[4p] functions on heavy atoms (an extra uncontracted p function), giving 248 functions.

(g) Equal to basis set (f) but with all s functions on heavy atoms uncontracted, giving 298 functions.

We have used atomic coordinates obtained from crystallographic data [17], supplemented with two additional coordinates from Daniel and Dupuis [18] that completely determine the geometry. These coordinates agree well with those optimized by Daniel and Dupuis [18]. Calculated results using the optimized and experimental geometries differed negligibly, see also Karna et al. [14]. A planar PNA molecule is assumed with a  $C_{2v}$  molecular point group, and the molecule is placed in the  $xz$  plane with the long axis (the  $C_2$  axis) along the  $z$  axis and the short axis in the  $x$  direction.

Table 1 lists the  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$  components of the linear polarizability as well as the average polarizability  $\alpha_{av}$ . The average polarizabilities are quite stable. Except for the smallest basis set (a), the average polarizability varies within 10%: between 13.14 and 14.26 ( $10^{-24}$  cm<sup>3</sup>) in the static case and between 13.21 and 14.33 ( $10^{-24}$  cm<sup>3</sup>) in the dynamic case. The chosen frequency  $\omega=0.650$  eV ( $\lambda=1.907$   $\mu$ m) is the lowest in the series of measurements by Teng and Garito [19] for PNA solvated in 1,4-dioxane. It was also included in the series of calculations of Karna et al. [14].

The components of the polarizabilities vary in the same way as the average value. The basis set dependency of the static and dynamic polarizabilities are quite similar, probably because the chosen frequency is well below the first resonance excitation. The effect of contraction among an extended manifold of s and p orbitals is negligible, compare entries (e), (f) and (g) in table 1. Greater flexibility among the s and p orbitals reduces the value for the polarizability somewhat, see (b) and (e). On the other hand, polariza-

Table 1

Calculation of frequency independent and frequency dependent ( $\omega=0.650$  eV) polarizabilities of para-nitroaniline for basis sets (a)–(g) ( $10^{-24}$  cm<sup>3</sup>)

Basis set	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{av}$	$E_{HF}$
$\omega=0$					
2P <sup>a)</sup>	14.63	7.94	20.94	14.51	–488.281
(a)	13.15	4.85	17.83	11.94	–489.0505
(b) <sup>b)</sup>	14.32	7.22	20.15	13.90	–489.1116
(c)	13.71	6.70	19.00	13.14	–489.0798
(d)	14.39	7.83	20.55	14.26	–489.3136
(e)	13.93	7.37	19.71	13.67	–489.2946
(f)	13.96	7.38	19.75	13.70	–489.3032
(g)	13.97	7.40	19.76	13.71	–489.3089
$\omega=0.650$ eV					
(a)	13.20	4.87	17.96	12.01	
(b) <sup>b)</sup>	14.37	7.23	20.29	13.96	
(c)	13.76	6.72	19.14	13.21	
(d)	14.44	7.84	20.71	14.33	
(e)	13.98	7.39	19.85	13.74	
(f)	14.01	7.40	19.89	13.77	
(g)	14.02	7.42	19.91	13.78	

<sup>a)</sup> Results from “2P” [5,4,1/4,1] basis set of Feyereisen et al. [2].

<sup>b)</sup> Same basis set as used by Karna et al. [14]. Karna et al. used the optimized geometry of ref. [18].

tion functions lead to a marked increase in  $\alpha$ , compare (a) with (b) and (c) with (e). Diffuse functions further increase the polarizability as indicated by a comparison of (e) with (d).

The calculated excitation energies and oscillator strengths are listed in table 2. Excluding basis set (a), we find insignificant variations in calculated numbers, in particular among those obtained using polarized basis sets. Another measure of the basis set quality is provided by the degree of gauge invariance obtained between oscillator strengths in dipole length and velocity forms. For RPA, invariance is obtained in the limit of a complete one-electron basis set, but for a given basis set agreement clearly depends on the type of transition considered. Table 3 collects oscillator strengths in the two gauges for the representative two cases of the intensive charge transfer transition  $1^1A_1 \rightarrow 2^1A_1$  and the weak  $1^1A_1 \rightarrow 1^1B_2$  transition. Considering the CT transition, a gauge invariance within 1% is obtained for basis sets (d) to (g). The invariance is notably poorer for (a) to (c), which lack polarizing functions. Apparently, this “short-axis polarized”  $1^1A_1 \rightarrow 1^1B_2$  transition does

Table 2  
RPA excitation energies (eV) and oscillator strengths (length gauge) for para-nitroaniline using basis sets (a)–(g)

Basis set	State	A <sub>1</sub> exc	A <sub>1</sub> osc	B <sub>2</sub> exc	B <sub>2</sub> osc	B <sub>1</sub> exc	B <sub>1</sub> osc	A <sub>2</sub> exc
(a)	1	5.20	0.456	5.76	1.29×10 <sup>-2</sup>	4.88	5.16×10 <sup>-4</sup>	4.46
(a)	2	7.26	0.323	6.30	6.61×10 <sup>-2</sup>	7.46	2.92×10 <sup>-4</sup>	8.37
(b)	1	5.04	0.429	5.53	1.05×10 <sup>-2</sup>	6.91	1.63×10 <sup>-3</sup>	4.62
(b)	2	7.03	0.305	6.28	4.17×10 <sup>-2</sup>	5.01	5.05×10 <sup>-4</sup>	7.42
(c)	1	5.06	0.456	5.69	1.00×10 <sup>-2</sup>	4.86	5.79×10 <sup>-4</sup>	4.47
(c)	2	7.00	0.149	6.15	6.82×10 <sup>-2</sup>	5.90	2.23×10 <sup>-4</sup>	6.61
(d)	1	5.01	0.415	5.41	1.36×10 <sup>-2</sup>	5.33	5.78×10 <sup>-4</sup>	4.87
(d)	2	6.88	0.274	6.40	1.31×10 <sup>-2</sup>	5.75	1.80×10 <sup>-4</sup>	6.47
(e)	1	5.01	0.417	5.45	1.30×10 <sup>-2</sup>	5.31	5.56×10 <sup>-4</sup>	4.85
(e)	2	6.89	0.269	6.40	1.69×10 <sup>-2</sup>	5.74	7.85×10 <sup>-5</sup>	6.45
(f)	1	5.01	0.416	5.45	1.33×10 <sup>-2</sup>	5.32	5.54×10 <sup>-4</sup>	4.85
(f)	2	6.89	0.265	6.40	1.74×10 <sup>-2</sup>	5.74	6.02×10 <sup>-5</sup>	6.44
(g)	1	5.01	0.416	5.45	1.34×10 <sup>-2</sup>	5.23	5.47×10 <sup>-4</sup>	4.86
(g)	2	6.89	0.265	6.40	1.74×10 <sup>-2</sup>	5.73	6.40×10 <sup>-5</sup>	6.44

Table 3  
RPA oscillator strengths in dipole length and dipole velocity gauges for 1<sup>1</sup>A<sub>1</sub>→2<sup>1</sup>A<sub>1</sub> and 1<sup>1</sup>A<sub>1</sub>→1<sup>1</sup>B<sub>2</sub> transitions of para-nitroaniline using basis sets (a)–(g)

Set	1 <sup>1</sup> A <sub>1</sub> →2 <sup>1</sup> A <sub>1</sub>		1 <sup>1</sup> A <sub>1</sub> →1 <sup>1</sup> B <sub>2</sub>	
	<i>f</i> <sub>len</sub>	<i>f</i> <sub>vel</sub>	<i>f</i> <sub>len</sub>	<i>f</i> <sub>vel</sub>
(a)	0.4561	0.2778	1.291×10 <sup>-2</sup>	1.236×10 <sup>-2</sup>
(b)	0.4287	0.3399	1.054×10 <sup>-2</sup>	8.791×10 <sup>-3</sup>
(c)	0.4560	0.2778	1.001×10 <sup>-2</sup>	9.019×10 <sup>-3</sup>
(d)	0.4148	0.4188	1.360×10 <sup>-2</sup>	1.397×10 <sup>-2</sup>
(e)	0.4167	0.4200	1.296×10 <sup>-2</sup>	1.681×10 <sup>-2</sup>
(f)	0.4160	0.4191	1.333×10 <sup>-2</sup>	1.715×10 <sup>-2</sup>
(g)	0.4157	0.4186	1.337×10 <sup>-2</sup>	1.720×10 <sup>-2</sup>

not depend so strongly on the presence of polarizing d functions as the “long-axis polarized” CT transition, see rows 3 and 4 in table 2. Best agreement is obtained for basis set (d), containing diffuse functions.

Although the intensive charge transfer excitation is known to be the main contributor to the low-lying absorption spectrum of PNA, there is still some controversy over the number and character of other excitations. Several semi-empirical calculations have been conducted to explore the spectrum. We refer to the CNDO/CI work of Khalik et al. [20], Lalama and Garito [21] and Freund and Bigelow [22] for further discussion on assignments and for references to earlier theoretical and experimental studies. Two ex-

perimental indicators characterizing the PNA spectrum are the polarization of the absorption and the solvatochromatic (red or blue) solvent shifts. The ordering of the low-intensity transitions is still unsettled. Khalik et al. [20] argue that the low-lying intensive band is built up by the 1<sup>1</sup>B<sub>2</sub>→1<sup>1</sup>A<sub>1</sub> transition in addition to the well-established (π→π\*) 1<sup>1</sup>A<sub>1</sub>→2<sup>1</sup>A<sub>1</sub> charge transfer transition, with the (π→π\*) 1<sup>1</sup>A<sub>1</sub>→2<sup>1</sup>B<sub>2</sub> transition emerging as a weak structure at the high energy side. The CNDO/CI calculations predict these three transitions at 4.425 eV (→1<sup>1</sup>B<sub>2</sub>; *f*=0.003), at 4.791 eV (→2<sup>1</sup>A<sub>1</sub>; *f*=0.247), and at 5.569 eV (→2<sup>1</sup>B<sub>2</sub>; *f*=0.005), thus with only the 2<sup>1</sup>A<sub>1</sub> transition receiving a large *f* number [20]. The overall red-shift of this band supports these assignments.

Our RPA results (we here report values from basis (d), which we consider almost complete) support the assertion that only 1<sup>1</sup>A<sub>1</sub> and 1<sup>1</sup>B<sub>2</sub> states are needed for the assignment of the low-energy feature: The n→π\* 1<sup>1</sup>B<sub>1</sub> states have too low oscillator strengths and the 1<sup>1</sup>A<sub>2</sub> states are dipole forbidden. RPA predicts the intensive 1<sup>1</sup>A<sub>1</sub>→2<sup>1</sup>A<sub>1</sub> CT transition to occur at 5.01 eV (*f*=0.415), while the first 1<sup>1</sup>B<sub>2</sub> state occurs at higher energy, 5.41 eV (*f*=0.014). The second 2<sup>1</sup>B<sub>2</sub> transition is given an RPA value of 6.40 eV (*f*=0.013). The next intensive CNDO/CI transition (3<sup>1</sup>A<sub>1</sub>) occurs at 6.632 eV (*f*=0.425) [20], the RPA result is 6.88 eV (*f*=0.274). Comparison with experiment is complicated by the presence of a solvent,

implying a general lowering of  $\pi \rightarrow \pi^*$  transitions, in particular for the CT transition. As expected, this transition is associated with a pronounced reaction field effect. For PNA in hydrocarbon solution, the low energy intensive band is observed at 3.25 eV [20] to be compared with the vapour phase value of 4.35 eV [17]. The CNDO/CI and RPA values for the strong CT transition are 4.79 and 5.01 eV, respectively.

We obtain the dipole forbidden  $^1A_2$  transition as high up as 4.87 eV, and the first out-of-plane polarized  $n \rightarrow \pi^*$  transition at 5.33 eV. It has been suggested that the latter contributes to the high flank of the intensive low-energy band [23], but this has later been disputed as artifacts of the semiempirical MO treatments [20]. Our low RPA oscillator strengths confirm the latter view, which is also supported by polarization measurements and the absence of blue shifts.

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