



# Calculations of two-photon absorption cross sections by means of density-functional theory

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Received 4 February 2003; in final form 25 March 2003

## Abstract

We present density-functional theory and calculations for two-photon absorption spectra of molecules. The two-photon absorption cross sections are defined in terms of the single residues of the quadratic response function, which was recently derived for density-functional theory using the time-dependent variation principle and the quasi-energy ansatz. The cross-section dependence on different functionals, including the general gradient approximation and hybrid theory, is examined for a set of small molecules. The results of hybrid density-functional theory compare favorably with those from singles-and-doubles coupled-cluster response calculations.

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## 1. Introduction

Among the optical properties that can be treated by contemporary quantum-chemistry methods, the two-photon absorption (TPA) cross section has recently attracted much interest – primarily since a number of technical applications can be derived from the fact that the TPA cross section depends quadratically on the intensity of the exciting light and that fundamental excitations can be reached by applying half the wavelength, thereby considerably increasing the penetrability

of materials and tissue. From these facts, many applications in the area of optical materials – optical limiting, upconverted lasing and confocal spectroscopy – and in medicine – singlet-oxygen therapy and fluorescence marking – can be derived. In spite of this recent interest in TPA, it seems that perhaps the most popular of quantum-chemical theories – namely, density-functional theory (DFT) – has not yet been applied to the calculation of TPA cross sections, except for a few cases in which so-called few-state approximations have been used [1,2]. This is unfortunate in that DFT offers considerable advantages over traditional *ab initio* methods for many types of species. However, with the recent advances in the theory and application of DFT to time-dependent properties and dynamical response

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functions, such applications have become a practical proposition.

Since the generalization of the Kohn–Sham equations by Runge and Gross [3] the interest in time-dependent DFT has steadily increased as is reflected by a great number of publications in the area, see listings given, for example, in [4,5]. A recent formulation of time-dependent DFT by the present authors forms a basis for effective calculations of static and frequency-dependent nonlinear properties [5]. It was the first complete implementation of DFT frequency-dependent nonlinear properties beyond the local-density approximation (LDA), in the sense that the response of the density always is obtained using the same density functional as the one for the unperturbed density. In particular, it makes it possible to compute the third-order frequency-dependent response function from the second hyperpolarizability, the imaginary part of which is related to the TPA cross section. Alternatively, the TPA cross section may be obtained as implemented for ab initio calculations – that is, by taking the residue of the second-order response function or the first hyperpolarizability. The latter, more effective, way of computing the TPA cross section is described for DFT in the present work. To illustrate this technique, we have chosen a set of small molecules to examine the potential of DFT for TPA calculations – in particular, by comparing with Hartree–Fock and coupled-cluster calculations.

In Section 2, we briefly describe the theory behind the calculations of DFT two-photon cross sections. Some aspects of the implementation are given in Section 3, and details for the present computations in Section 4. Next, in Section 5, we present results for the H<sub>2</sub>O, HF, C<sub>2</sub>H<sub>4</sub> molecules with respect to computational parameters (basis sets and functionals), comparing with wave-function calculations.

## 2. Theory

Response functions are defined by considering a property as a function of an external perturbation, which is expanded in orders of the perturbation strength

$$\begin{aligned}
 A &= A_0 + \int d\omega \langle \langle \hat{A}; \hat{V} \rangle \rangle_{\omega} e^{-i\omega t} \\
 &+ \frac{1}{2} \int \int d\omega_1 d\omega_2 \langle \langle \hat{A}; \hat{V}; \hat{V} \rangle \rangle_{\omega_1, \omega_2} e^{-i(\omega_1 + \omega_2)t} \\
 &\dots
 \end{aligned}
 \tag{1}$$

The first term in this expansion is the expectation value with respect to the unperturbed wave function, whereas the second and third terms define the linear and quadratic response functions, respectively. It is well known that the residue of a quadratic response function at an excitation frequency yields a product of first- and second-order transition amplitudes [6]

$$\lim_{\omega_2 \rightarrow \omega_f} (\omega_2 - \omega_f) \langle \langle \hat{A}; \hat{B}; \hat{C} \rangle \rangle_{-\omega_1, \omega_2} = -T_f^{AB} T_f^C. \tag{2}$$

Here  $T_f^{AB}$  is the induced transition amplitude of an operator  $\hat{A}$  between the ground state (0) and an excited state (f) due to a perturbation  $\hat{B}$

$$\begin{aligned}
 T_f^{AB} &= \sum_{k>0} \left( \frac{\langle 0 | \hat{A} | k \rangle \langle k | \hat{B} - B_0 | f \rangle}{\omega_k - \omega_f + \omega_1} \right. \\
 &\quad \left. + \frac{\langle 0 | \hat{B} | k \rangle \langle k | \hat{A} - A_0 | f \rangle}{\omega_k - \omega_1} \right).
 \end{aligned}
 \tag{3}$$

With the specific choice of dipole operators, this can be interpreted as a two-photon absorption amplitude. The second factor in Eq. (2) is the matrix element

$$T_f^C = \langle f | \hat{C} | 0 \rangle, \tag{4}$$

which in turn can be obtained from the residue of the linear response function

$$\lim_{\omega \rightarrow \omega_f} (\omega - \omega_f) \langle \langle \hat{C}; \hat{C} \rangle \rangle_{\omega} = |T_f^C|^2. \tag{5}$$

The fact that operator  $\hat{C}$  can be chosen arbitrarily allows us to identify the transition amplitude with the corresponding expressions derived for approximate wave functions – except for an arbitrary phase, which is of no consequence for transition probabilities.

In our Kohn–Sham formulation of [5], first-order transition amplitudes are obtained from the linear response function

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle = -\mathbf{A}^\dagger (\mathbf{E} - \omega \mathbf{S})^{-1} \mathbf{B}, \quad (6)$$

where the property vectors  $\mathbf{A}$  and  $\mathbf{B}$  are defined as

$$\mathbf{A} = \langle 0 | [\hat{\mathbf{q}}, \hat{A}] | 0 \rangle. \quad (7)$$

Here  $\hat{\mathbf{q}}$  is a column vector of nonredundant orbital-rotation operators and the expectation value is with respect to the reference Kohn–Sham determinant. Given an energy functional of the density  $E[\rho]$ , the matrices  $\mathbf{E}$  and  $\mathbf{S}$  are defined in this basis as

$$\begin{aligned} \mathbf{E} = & \int d\tau \frac{\delta E}{\delta \rho(\mathbf{r})} \langle 0 | [\hat{\mathbf{q}}, [\hat{\rho}(\mathbf{r}), \hat{\mathbf{q}}^\dagger]] | 0 \rangle \\ & + \int \int d\tau d\tau' \langle 0 | [\hat{\mathbf{q}}, \hat{\rho}(\mathbf{r})] | 0 \rangle \frac{\delta^2 E}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \\ & \times \langle 0 | [\hat{\rho}(\mathbf{r}'), \hat{\mathbf{q}}^\dagger] | 0 \rangle, \end{aligned} \quad (8)$$

and

$$\mathbf{S} = \langle 0 | [\hat{\mathbf{q}}, \hat{\mathbf{q}}^\dagger] | 0 \rangle, \quad (9)$$

respectively, and they have a common set of eigenvectors  $\mathbf{X}_k$ :

$$\mathbf{X}_k^\dagger \mathbf{E} \mathbf{X}_k = \omega_k, \quad (10)$$

$$\mathbf{X}_k^\dagger \mathbf{S} \mathbf{X}_k = \pm 1. \quad (11)$$

Since the resolvent in Eq. (6) has the same eigenvectors, with poles at the excitation energies, we find that the residues are given by

$$\lim_{\omega \rightarrow \omega_f} \langle\langle \hat{A}; \hat{B} \rangle\rangle = \mathbf{A}^\dagger \mathbf{X}_f \mathbf{X}_f^\dagger \mathbf{B}, \quad (12)$$

and we may define the matrix elements as

$$\langle 0 | \hat{A} | f \rangle = \mathbf{A}^\dagger \mathbf{X}_f, \quad (13)$$

$$\langle f | \hat{B} | 0 \rangle = \mathbf{X}_f^\dagger \mathbf{B}. \quad (14)$$

The quadratic response function is constructed from a set of three linear response vectors

$$\kappa^A = \mathbf{A}^\dagger [\mathbf{E} - (\omega_b + \omega_c) \mathbf{S}]^{-1}, \quad (15)$$

$$\kappa^B = (\mathbf{E} - \omega_b \mathbf{S})^{-1} \mathbf{B}, \quad (16)$$

$$\kappa^C = (\mathbf{E} - \omega_c \mathbf{S})^{-1} \mathbf{C}, \quad (17)$$

and the auxiliary vector

$$\begin{aligned} \mathbf{V}^{\omega_1, \omega_2} = & 2\hat{P}_{12} \{ \langle 0 | [\hat{\mathbf{q}}, [\hat{\kappa}^{\omega_1}, [\hat{\kappa}^{\omega_2}, \hat{H}^{(0)}]]] | 0 \rangle \\ & + \langle 0 | [\hat{\mathbf{q}}, [\hat{\kappa}^{\omega_1}, \omega_2 \hat{\kappa}^{\omega_2}]] | 0 \rangle \\ & + 2 \langle 0 | [\hat{\mathbf{q}}, [\kappa^{\omega_1}, \hat{H}^{\omega_2} + V^{\omega_2}]] | 0 \rangle \\ & + \langle 0 | [\hat{\mathbf{q}}, \hat{H}^{\omega_1, \omega_2}] | 0 \rangle \}. \end{aligned} \quad (18)$$

the origin of which is the equation for the second-order parameters (see [5]), and which only depends on the first-order parameters  $\kappa^\omega$ . The relation between the operator and matrix forms of the response parameters in Eqs. (15)–(18) is

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} (a_{pz}^\dagger a_{qz} + a_{p\beta}^\dagger a_{q\beta}) = \hat{\mathbf{q}}^\dagger \kappa. \quad (19)$$

In Eq. (18),  $\hat{P}_{12}$  symmetrizes indices 1 and 2 and the Hamiltonian operators can be calculated from functional derivatives of the energy functional:

$$\hat{H}^{(0)} = \int d\tau \hat{\rho}(\mathbf{r}) \frac{\delta E}{\delta \rho(\mathbf{r})}, \quad (20)$$

$$\hat{H}^\omega = \int \int d\tau d\tau' \hat{\rho}(\mathbf{r}) \frac{\delta^2 E}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \rho^\omega(\mathbf{r}'), \quad (21)$$

$$\begin{aligned} \hat{H}^{\omega_1, \omega_2} = & \int \int d\tau d\tau'' \hat{\rho}(\mathbf{r}) \frac{\delta^2 E}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \bar{\rho}^{\omega_1, \omega_2}(\mathbf{r}') \\ & + \int \int \int d\tau d\tau'' d\tau''' \hat{\rho}(\mathbf{r}) \\ & \times \frac{\delta^3 E}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \rho^{\omega_1}(\mathbf{r}') \rho^{\omega_2}(\mathbf{r}''). \end{aligned} \quad (22)$$

The first- and second-order densities that occur in these expressions are given by:

$$\rho^\omega(\mathbf{r}) = \langle 0 | [\hat{\kappa}^\omega, \hat{\rho}(\mathbf{r})] | 0 \rangle, \quad (23)$$

$$\bar{\rho}^{\omega_1, \omega_2}(\mathbf{r}) = P_{12} \langle 0 | [\hat{\kappa}^{\omega_1}, [\hat{\kappa}^{\omega_2}, \hat{\rho}(\mathbf{r})]] | 0 \rangle. \quad (24)$$

All things considered, the quadratic response can now be written as

$$\langle\langle \hat{A}; \hat{B}; \hat{C} \rangle\rangle_{\omega_b, \omega_c} = \kappa^A \mathbf{V}^{\omega_b, \omega_c} + \hat{P}_{bc} \langle 0 | [\hat{\kappa}^{\omega_b}, [\hat{\kappa}^{\omega_c}, \hat{A}]] | 0 \rangle. \quad (25)$$

The limiting process affects the terms that contain the  $\kappa^C$  response vector. With the results from linear response in mind, we have that

$$\lim_{\omega_c \rightarrow \omega_f} \kappa^C = \mathbf{X}_f \mathbf{X}_f^\dagger \mathbf{C} = \mathbf{X}_f T_f^C. \quad (26)$$

The induced transition amplitude is then obtained from the quadratic response function by replacing  $\kappa^C$  by the eigenvector  $\mathbf{X}_f$  and removing the terms that are independent of  $\kappa^C$ . Introducing  $\mathbf{X}_f^{\omega_b}$  to satisfy

$$\lim_{\omega_c \rightarrow \omega_f} (\omega_c - \omega_f) \mathbf{V}^{\omega_b, \omega_c} = \mathbf{X}_f^{\omega_b} T_f^C, \quad (27)$$

this finally gives the induced transition amplitude as

$$T_f^{AB} = -\kappa^A \mathbf{X}_f^{\omega_b} - \frac{1}{2} \left[ \langle 0 | [\hat{\kappa}^{-\omega_b}, [\hat{X}_f, \hat{A}]] | 0 \rangle + \langle 0 | [\hat{X}_f, [\hat{\kappa}^{-\omega_b}, \hat{A}]] | 0 \rangle \right]. \quad (28)$$

### 3. Implementation

To compute the transition moments  $T^{AB}$  of Eq. (28), we have to evaluate linear and quadratic response functions to obtain the response vectors  $\mathbf{X}_f$  and  $\mathbf{X}_f^{\omega_b}$ . The first-order transition amplitudes Eq. (13) are evaluated by solving the generalized eigenvalue problem

$$\mathbf{R}\mathbf{X}_f = 0, \quad \mathbf{R} = (\mathbf{E}^{[2]} - \omega_k \mathbf{S}^{[2]}), \quad (29)$$

which is subsequently contracted with the response vectors  $\mathbf{A}^\dagger$  and  $\mathbf{B}$  from the left- and right-hand sides, respectively. Direct solution of this problem is impossible because of the large size of the matrices. Selected eigenvalues and eigenvectors are computed iteratively. The evaluation of two-photon absorption transition moments requires only a single transformation of the Hamiltonian's third derivatives with vectors computed in the linear-response phase  $\sum_{kl} (\mathbf{E}_{kl}^{[3]} + \mathbf{E}_{jlk}^{[3]}) \kappa_k^A \kappa_l^B$ .

#### 3.1. Solution of linear response equations

The algorithm for the determination of the linear response vectors consists of two parts:

- iterative solver of an eigenvalue problem
- direct multiplication of second-order derivatives  $\mathbf{R}$  of Eq. (29) by a trial vector.

There are many variants of iterative eigenvalue solvers. The DALTON quantum-chemistry package uses a type of the Davidson method. Until convergence, the equations are at each iteration

spanned in a reduced space, solved by conventional low-dimension techniques, and then reexpanded in the full space.

We first choose a set of  $l$  trial response vectors  $\mathbf{U} = \{b^{(l)}\}$  and perform the multiplication by  $\mathbf{R}$ , reducing it to a  $l$ -dimensional projected problem

$$\tilde{\mathbf{E}}^{(l)} = \mathbf{U}^{(l)\dagger} \mathbf{E} \mathbf{U}^{(l)}, \quad \tilde{\mathbf{S}}^{(l)} = \mathbf{U}^{(l)\dagger} \mathbf{S} \mathbf{U}^{(l)}. \quad (30)$$

This projected problem is solved by traditional methods for the eigenvectors and eigenvalues  $\tilde{\mathbf{X}}^{(l)}$  and  $\omega^{(l)}$

$$(\tilde{\mathbf{E}}^{(l)} - \omega^{(l)} \tilde{\mathbf{S}}^{(l)}) \tilde{\mathbf{X}}^{(l)} = 0, \quad (31)$$

where  $\tilde{\mathbf{X}}^{(l)}$  approximates the solution in the full, unprojected space  $\mathbf{X}^{(l)} = \mathbf{U} \tilde{\mathbf{X}}^{(l)}$ . Next, we compute the residual vector to estimate the approximation error

$$\mathbf{q}^{(l)} = \mathbf{R} \tilde{\mathbf{X}}^{(l)}. \quad (32)$$

If the residual is not close to zero, we expand the reduced space in a new response vector

$$\mathbf{u}_{l+1} = \text{diag}(\mathbf{E} - \omega \mathbf{S})^{-1} \mathbf{q}^{(l)}, \quad (33)$$

which is subsequently orthonormalized against the original set of trial vectors. The paired structure of the equations is maintained throughout.

#### 3.2. Solution of quadratic response equations

The response vectors obtained from linear-response theory are used to compute the doubly transformed auxiliary vectors  $\mathbf{V}^{\omega_1, \omega_2}$ . The transformations in the quadratic response code are similar to those in the linear-response code except that two indices of the third-derivative matrix  $\mathbf{E}_{lmn}^{[3]}$  are transformed.

#### 3.3. Computation of DFT contribution

The transformation of third derivatives of the functional with respect to orbital rotations is performed as described in [5]. Since the functional derivatives cannot be integrated analytically over space, the integration in Eqs. (20)–(22) is performed numerically. For each point of the numerical grid, three steps are carried out.

First, the orbitals as well as the density and density gradient at the grid point are evaluated.

Next, the second and third derivatives of the functional with respect to the density and the density gradient at the point are computed from analytically derived formulas. The DFT contribution to  $\hat{H}^{\omega_1, \omega_2}$  at this point can be represented as a sum of several matrices with different prefactors, which combine functional derivatives with expectation values of the response vectors  $\kappa^B$  and  $\kappa^C$  that the matrix  $\mathbf{E}^{[3]}$  is being contracted with.

DALTON uses the common method for generating the grid for the numerical integration, namely the one in which grids are generated for all atoms and subsequently the weights in overlapping regions are adjusted using Becke's partitioning scheme [9]. The atomic radial generation scheme follows [10] and utilizes the information about the used basis set to optimally choose the spacing and weights of the points. One should note that integration of higher order properties puts higher requirements on the grid generation and used grids must then be denser than the ones used for energy calculations.

#### 4. Computational details

We have used three exchange-correlation functionals: the local density approximation (LDA),

[7,8] the Becke–Lee–Yang–Parr (BLYP) GGA functional, [11,12] and the three-parameter BLYP (B3LYP) hybrid functional [13,14]. To judge the quality of DFT against coupled-cluster theory for the calculation of TPA cross sections, we have carried out calculations on the three molecules H<sub>2</sub>O, HF and C<sub>2</sub>H<sub>4</sub> in the polarized triple-zeta Sadlej basis [15], commonly used for second-order properties [16]. All calculations have been performed with the DALTON program [17]. Geometry optimization was carried out with DFT/B3LYP using the GAUSSIAN 98 program [18].

#### 5. Results and discussion

The TPA cross sections of the lowest two-photon allowed excited states of each molecule are listed in Tables 1–3. For H<sub>2</sub>O of C<sub>2v</sub> symmetry and for HF of C<sub>∞v</sub> symmetry, all states are two-photon allowed. By contrast, for the C<sub>2</sub>H<sub>4</sub> molecule of C<sub>2h</sub> symmetry, only gerade states are allowed.

We note from the Tables, as expected, that electron correlation has a significant effect on the absolute values of the excitation energies and cross sections. Normally, correlation lowers the excitation energy and increases the TPA cross section.

Table 1  
Excitation energy,  $E$  (in eV), TPA cross sections,  $\delta_{\text{tp}}$  (in  $10^3$  a.u.), of the seven lowest excited states of H<sub>2</sub>O molecule

Basis	States	Ab initio						DFT					
		SCF		CC2		CCSD		LDA		BLYP		B3LYP	
		$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$
Sadlej	1B <sub>1</sub>	8.60	0.07	6.99	0.24	7.35	0.16	6.52	0.25	6.24	0.25	6.86	0.18
	1A <sub>2</sub>	10.26	0.64	8.65	2.27	9.11	1.64	7.90	2.63	7.53	2.82	8.30	1.93
	2A <sub>1</sub>	10.95	0.24	9.44	0.48	9.81	0.33	8.67	0.49	8.42	0.49	9.08	0.39
	2B <sub>1</sub>	11.73	0.72	10.12	2.46	10.52	1.83	9.43	2.70	9.06	2.94	9.76	1.91
	3A <sub>1</sub>	12.49	4.19	10.84	16.8	11.28	11.5	10.32	19.6	10.05	21.1	10.66	12.6
	1B <sub>2</sub>	12.60	0.69	11.08	1.33	11.56	1.10	10.04	1.38	9.71	1.42	10.50	1.16
	2A <sub>2</sub>	12.92	0.27	11.35	0.41	11.66	0.45	10.60	0.22	10.30	0.30	10.93	0.30
daug-cc-pVTZ	1B <sub>1</sub>	8.59	0.07	7.19	0.23	7.56	0.15	6.52	0.24	6.22	0.24	6.86	0.17
	1A <sub>2</sub>	10.26	0.60	8.84	1.69	9.32	1.25	7.60	0.94	7.34	1.48	8.23	1.44
	2A <sub>1</sub>	10.85	0.49	9.37	0.59	9.86	1.58	8.06	0.79	7.77	0.77	8.69	0.62
	2B <sub>1</sub>	11.14	0.64	9.40	1.47	9.99	1.20	7.75	0.13	7.56	0.26	8.61	0.69
	3A <sub>1</sub>	11.42	3.56	9.65	4.32	10.21	6.21	8.63	0.94	8.39	0.99	9.09	1.56
	2A <sub>2</sub>	12.08	0.07	10.21	0.01	10.86	0.07	8.08	1.09	7.81	0.82	8.88	0.16
	1B <sub>2</sub>	12.45	0.24	10.47	0.00	11.17	0.00	9.06	0.00	8.73	0.00	9.70	0.00

Table 2

Excitation energy,  $E$  (in eV), TPA cross sections,  $\delta_{\text{tp}}$  (in  $10^3$  a.u.), of the six lowest excited states of HF molecule

States	Ab initio						DFT					
	SCF		CC2		CCSD		LDA		BLYP		B3LYP	
	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$
1 $\Pi$	11.61	0.06	9.65	0.10	10.12	0.12	8.93	0.20	8.58	0.22	9.37	0.14
2 $\Pi$	15.07	0.22	12.96	0.30	13.49	0.46	12.02	0.70	11.61	0.84	12.46	0.54
2 $\Sigma$	15.21	0.19	13.81	0.81	14.20	0.44	12.87	0.26	12.54	0.26	13.27	0.26
1 $\Delta$	15.92	0.94	13.89	2.74	14.34	2.00	13.13	3.72	12.74	4.00	13.51	2.60
3 $\Pi$	16.57	0.18	14.06	0.26	14.70	0.42	13.00	0.82	12.62	0.86	13.57	0.58
3 $\Sigma$	17.21	1.65	14.78	5.35	15.56	4.13	14.22	6.94	13.94	7.38	14.73	4.63

The Sadlej basis set is used.

Table 3

Excitation energy,  $E$  (in eV), TPA cross section,  $\delta_{\text{tp}}$  (in  $10^3$  a.u.), of the nine lowest two-photon allowed excited states of  $\text{C}_2\text{H}_4$  molecule

States	Ab initio						DFT					
	SCF		CC2		CCSD		LDA		BLYP		B3LYP	
	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$	$E$	$\delta_{\text{tp}}$
1B <sub>2g</sub>	7.97	3.67	7.88	3.56	8.05	2.97	7.23	3.63	6.78	4.19	7.20	3.75
1B <sub>3g</sub>	7.80	2.65	7.85	2.77	8.01	2.35	7.25	2.99	6.84	3.65	7.22	3.12
2A <sub>g</sub>	8.61	34.4	8.67	35.0	8.81	30.2	8.27	38.1	7.92	42.0	8.22	38.0
2B <sub>3g</sub>	9.14	0.01	8.62	0.00	8.55	0.02	7.45	0.16	7.66	0.00	7.96	0.00
2B <sub>2g</sub>	10.20	0.04	10.13	0.00	10.13	0.00	9.23	0.00	9.09	0.44	9.50	0.03
3B <sub>3g</sub>	10.37	0.13	10.47	0.00	10.62	0.10	9.60	0.01	9.23	0.07	9.62	0.09
1B <sub>1g</sub>	10.46	1.94	9.48	1.74	9.62	1.54	8.24	2.33	8.17	2.29	8.79	2.00
3B <sub>2g</sub>	10.47	0.85	10.41	0.58	10.62	0.38	9.50	0.78	9.29	0.04	9.58	0.50
4B <sub>2g</sub>	10.73	0.42	10.64	0.19	10.81	0.03	9.94	0.01	9.49	0.00	9.92	0.00

The Sadlej basis set is used.

However, it is noteworthy that the Hartree–Fock method gives the right relative cross sections for the different states in almost all cases, indicating that the general trends predicted by the Hartree–Fock method is reliable.

The water results in Table 1 are displayed for two basis sets, ‘Sadlej’ and ‘daug-cc-pVTZ’, constructed according to different principles, namely as consistent to atomic polarizabilities, respectively, atomic electron correlation. Although being of different character, for the large size employed here both sets must be considered suitable for polarization derived properties like TPA. Indeed the agreement of TPA results between the two basis sets for the water molecule are comforting when choosing only one type for the remaining molecules.

Table 1 also displays a problem in comparing cross sections state by state, namely that the

number and order of states may be different at the different levels of theory. This seems to indeed be the case for the high lying 2A<sub>1</sub> and 3A<sub>1</sub> states of water, for which the order is flipped between going from CCSD to DFT levels of theory. Furthermore, at twice the value of one-photon excitation energies the cross sections are unreliable as they blow up due to resonant effects.

The DFT excitation energies are significantly lower than the coupled-cluster energies, in particular for LDA. Concerning cross sections, we note that the DFT results anticipated to be the best – that is, the B3LYP results – are quite close to the CCSD results for H<sub>2</sub>O and HF but closer to CC2 for C<sub>2</sub>H<sub>4</sub>. However, the differences in absolute values between CC2 and CCSD for C<sub>2</sub>H<sub>4</sub> are quite small. The LDA and BLYP functionals behave in a similar fashion for cross sections as well as for excitation energies. Clearly, the gradient

correction has a minor effect on the optical properties of these molecules. This observation is consistent with previous results for hyperpolarizabilities [5]. It thus seems that the LDA to B3LYP variations are as large as the differences from Hartree–Fock to B3LYP, and that we find a satisfactory agreement between B3LYP and CCSD results. While the latter is the highest coupled-cluster level in this study, a recent investigation of first-order hyperpolarizabilities, a quantity closely related to the TPA cross section, indicates that B3LYP rivals the CCSD results and sometimes approach those of CC3 [19].

In summary, we have presented the first time-dependent DFT calculations for two-photon absorption cross sections of molecules. The results indicate variations in the calculated cross sections that are acceptably small considering the sensitive nature of the property; with some exceptions the Hartree–Fock cross sections agree with the correlated levels of theory roughly within 50%, while coupled-cluster at the CCSD level and DFT at the B3LYP level agree much better than that, within 10–20%. Although these initial calculations on small molecules are promising, the final evaluation of DFT for two-photon excitations can only be made from great many calculations on systems of different size and character.

### Acknowledgements

This work was supported by the Swedish Science Research Council (VR), the Carl Trygger

Foundation (CTS) and by a grant from the photonics project run jointly by the Swedish Materiel Administration (FMV) and the Swedish Defense Institute (FOI).

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