Correction to "Linear and Nonlinear Optical Properties from TDOMP2 Theory"

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An error has been discovered in the equations of motion (EOMs) for the λ_a^i amplitudes of the TDCC2 method, eq 22 in Ref. 1. The contributions arising from the term

$$\sum_{\mu_2} \lambda_{\mu_2} \langle \Phi_{\mu_2} | [[\tilde{V}, \hat{X}_i^a], \hat{T}_2] | \Phi_0 \rangle = -\frac{1}{2} \sum_{jkbc} \left(\tilde{V}_b^i \lambda_{ac}^{jk} \tau_{jk}^{bc} + \tilde{V}_a^j \lambda_{bc}^{ik} \tau_{jk}^{bc} \right), \tag{1}$$

of the TDCC2 Hamilton function, eq 21 in Ref. 1, were erronously left out. Including these

contributions, eq 22 in Ref. 1 becomes

$$
\begin{aligned}
i\dot{\lambda}_a^i = (f_1)_a^i &+ \sum_b (f_1)_a^b \lambda_b^i - \sum_j (f_1)_j^i \lambda_a^j + \sum_{bj} \lambda_b^j \tilde{v}_{aj}^{ib} + \frac{1}{2} \sum_{bjc} \lambda_{bc}^{ij} \tilde{v}_{aj}^{bc} - \frac{1}{2} \sum_{bjk} \lambda_{ab}^{jk} \tilde{v}_{jk}^{ib} \\
&+ \sum_{ck} \left(\lambda_b^j \tau_{jk}^{bc} \tilde{v}_{ac}^{ik} - \frac{1}{2} \lambda_b^i \tau_{jk}^{bc} \tilde{v}_{ac}^{jk} - \frac{1}{2} \lambda_a^j \tau_{jk}^{bc} \tilde{v}_{bc}^{ik} \right) \\
&- \frac{1}{2} \sum_{jkbc} \left(\tilde{V}_b^i \lambda_{ac}^{jk} \tau_{jk}^{bc} + \tilde{V}_a^j \lambda_{bc}^{ik} \tau_{jk}^{bc} \right) . \qquad (2)
\end{aligned}
$$

The missing contributions were also left out in the implementation of the TDCC2 and TDCC2-b methods. We have added the missing contributions to the implementation, which has been verified by comparing expectation values of the electric-dipole operator at non-zero electric-field strengths with those obtained by numerical differentiation (second-order central difference) of total energies. Note that energy derivatives at *non-zero* field strengths are required to detect the error.

The peak positions in the absorption spectra (i.e., the excitation energies) are unaffected by the error since the EOMs for the τ amplitudes are unchanged. The relative intensities deviate from the original results by at most 0.0015, typically much less, for all molecules studied. Errors of this magnitude are not visible in plotted spectra. The maximum error occurs for the water molecule as shown in Figure 1. Hence, the reported TDCC2 and TDCC2-b spectra are practically unaffected.

On the other hand, the computed values of the polarizabilities and first hyperpolarizabilities change. In Table 1 and Table 2 we report updated values for the polarizabilities and first hyperpolarizabilities, respectively. We note that the TDCC2 results are now in much better agreement with the LRCC2 results than originally reported. This is also evident in Fig. 4 (replacing Fig. 4 in the original paper) where we have plotted the dispersion of the isotropic polarizability using the new polarizabilties from TDCC2 and TDCC2-b simulations. Also, in Fig. 2 and Fig. 3 we have plotted the first order dipole response functions for the HF molecule from corrected TDCC2 simulations, which corrects the middle panels of Fig. 2 and

Fig. 3 in Ref. 1, respectively.

Finally, we emphasize that the conclusions of the original paper are unaffected by the error.

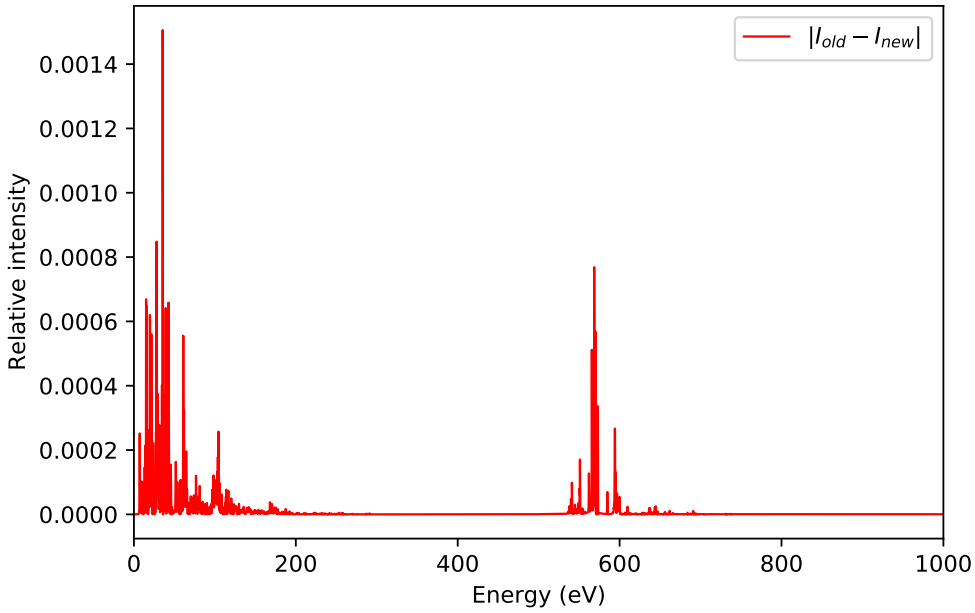

Figure 1: Absolute difference of the TDCC2 absorption spectra of the water molecule before ("old") and after ("new") correcting the EOMs for the λ_a^i amplitudes.

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(2) Larsen, H.; Olsen, J.; Hättig, C.; Jørgensen, P.; Christiansen, O.; Gauss, J. Polarizabilities and first hyperpolarizabilities of HF, Ne, and BH from full configuration interaction and coupled cluster calculations. *J. Chem. Phys.* **1999**, *111*, 1917–1925.

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Table 1: Polarizabilities (a.u.) of Ne, HF, H_2O, NH_3, and CH_4 extracted from LRCC2, TDCC2, and TDCC2-b simulations. The LRCC2 results for Ne and HF are from Ref. 2 and the LRCC2 results are computed with the Dalton quantum chemistry program (Ref. 3). The calculations marked with $*$ refers to the values reported in the original paper.

Ne	ω (a.u.)	0.1	0.2	0.3	0.4	0.5				
	LRCC2*	2.86	2.96	3.18	3.59	4.74				
	TDCC2	2.86	2.96	3.18	3.73	5.27				
	TDCC2*	2.87	2.98	3.19	3.75	5.29				
	TDCC2-b	2.84	2.95	3.16	3.71	5.23				
	TDCC2-b*	2.86	2.97	3.18	3.73	5.26				
HF	ω (a.u.)	0.1		0.2		0.3				
		α_{yy}	α_{zz}	α_{yy}	α_{zz}	α_{yy}	α_{zz}			
	LRCC2*	4.70	6.78	5.20	7.25	7.24	8.29			
	TDCC2	4.71	6.78	5.24	7.28	8.47	8.36			
	TDCC2*	4.75	6.85	5.28	7.36	8.54	8.45			
	TDCC2-b	4.68	6.72	5.20	7.20	8.35	8.27			
	TDCC2-b*	4.72	6.79	5.24	7.28	8.42	8.36			
H_2O	ω (a.u.)	0.0428			0.0656			0.1		
		α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}
	LRCC2*	9.41	10.43	9.63	9.55	10.50	9.71	9.91	10.66	9.92
	TDCC2	9.41	10.43	9.63	9.55	10.50	9.71	9.91	10.67	9.94
	TDCC2*	9.51	10.56	9.74	9.65	10.63	9.83	10.01	10.79	10.06
	TDCC2-b	9.35	10.35	9.55	9.49	10.42	9.63	9.84	10.58	9.86
	TDCC2-b*	9.44	10.47	9.66	9.58	10.54	9.74	9.94	10.71	9.97
NH_3	ω (a.u.)	0.0428		0.0656		0.1				
		α_{yy}	α_{zz}	α_{yy}	α_{zz}	α_{yy}	α_{zz}			
	LRCC2*	13.56	15.86	13.67	16.21	13.92	17.15			
	TDCC2	13.56	15.86	13.67	16.25	13.93	17.21			
	TDCC2*	13.72	16.03	13.83	16.43	14.10	17.40			
	TDCC2-b	13.48	15.76	13.59	16.15	13.84	17.09			
	TDCC2-b*	13.64	15.93	13.75	16.32	14.01	17.28			
CH_4	ω (a.u.)	0.0656	0.1	0.2						
	LRCC2*	17.49	17.84	20.08						
	TDCC2	17.50	17.85	20.12						
	TDCC2*	17.69	18.05	20.34						
	TDCC2-b	17.42	17.77	20.02						
	TDCC2-b*	17.61	17.96	20.25						

Table 2: First hyperpolarizabilities (a.u.) of HF, H_2O, and NH_3 from TDCCSD, TDOMP2, TDCC2, and TDCC2-b simulations. Notation: $\beta_{iii}^{\mathrm{OR}} = \beta_{iii}(0;\omega,-\omega)$ and $\beta_{iii}^{\mathrm{SHG}} = \beta_{iii}(-2\omega;\omega,\omega)$. The LRCCSD and LRCC2 results for HF are taken from Larsen et al. [2]

HF	ω (a.u.)	0.1		0.2		0.3	
		$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$
	LRCC2*	15.52	17.52	18.69	37.67	27.35	−51.78
	TDCC2	15.54	17.53	18.26	34.31	30.57	−60.52
	TDCC2*	16.53	18.63	19.40	36.39	32.11	−61.17
	TDCC2-b	14.73	16.62	17.26	32.34	28.76	−64.06
	TDCC2-b*	15.32	17.26	17.95	33.56	29.76	−64.95
H_2O	ω (a.u.)	0.0428		0.0656		0.1	
		$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$
	LRCC2*	−12.39	−13.12	−12.87	−14.83	−14.11	−20.76
	TDCC2	−12.42	−13.16	−12.93	−14.83	−14.45	−22.02
	TDCC2*	−13.63	−14.42	−14.17	−16.18	−15.75	−23.70
	TDCC2-b	−11.21	−11.88	−11.69	−13.41	−13.10	−20.08
	TDCC2-b*	−11.89	−12.58	−12.38	−14.15	−13.84	−21.01
NH_3	ω (a.u.)	0.0428				0.0656	
		$\beta_{yyy}^{\mathrm{OR}}$	$\beta_{yyy}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$	$\beta_{yyy}^{\mathrm{OR}}$	$\beta_{yyy}^{\mathrm{SHG}}$	$\beta_{zzz}^{\mathrm{OR}}$	$\beta_{zzz}^{\mathrm{SHG}}$
	LRCC2*	−16.69	−17.40	33.80	39.87	−17.16	−19.01	37.72	58.61
	TDCC2	−16.78	−17.58	33.97	39.88	−16.97	−18.59	39.26	63.96
	TDCC2*	−17.32	−18.13	35.80	41.90	−17.51	−19.17	41.24	66.61
	TDCC2-b	−16.59	−17.37	31.53	37.10	−16.77	−18.37	36.62	60.11
	TDCC2-b*	−17.00	−17.79	32.60	38.26	−17.19	−18.81	37.80	61.67

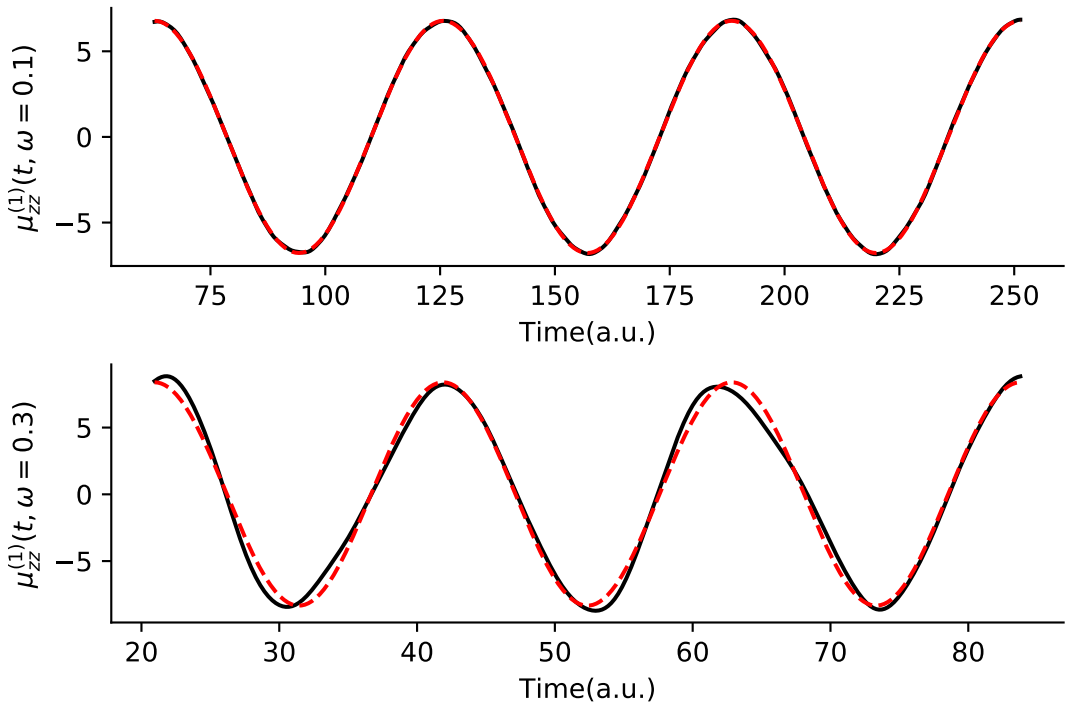

Figure 2: The zz-component of the first-order dipole responses for HF at $\omega = 0.1$ a.u. and $\omega = 0.3$ a.u. from corrected TDCC2 simulations.

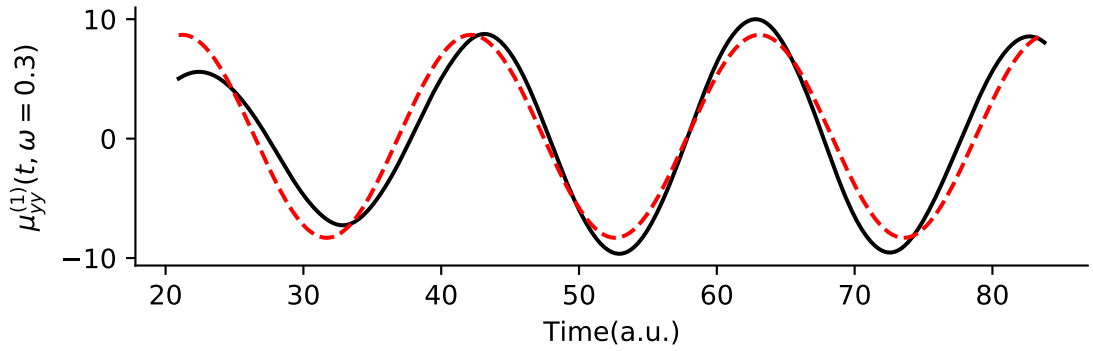

Figure 3: The yy-component of the first-order dipole response for HF at $\omega = 0.3$ a.u. from the corrected TDCC2 simulation.

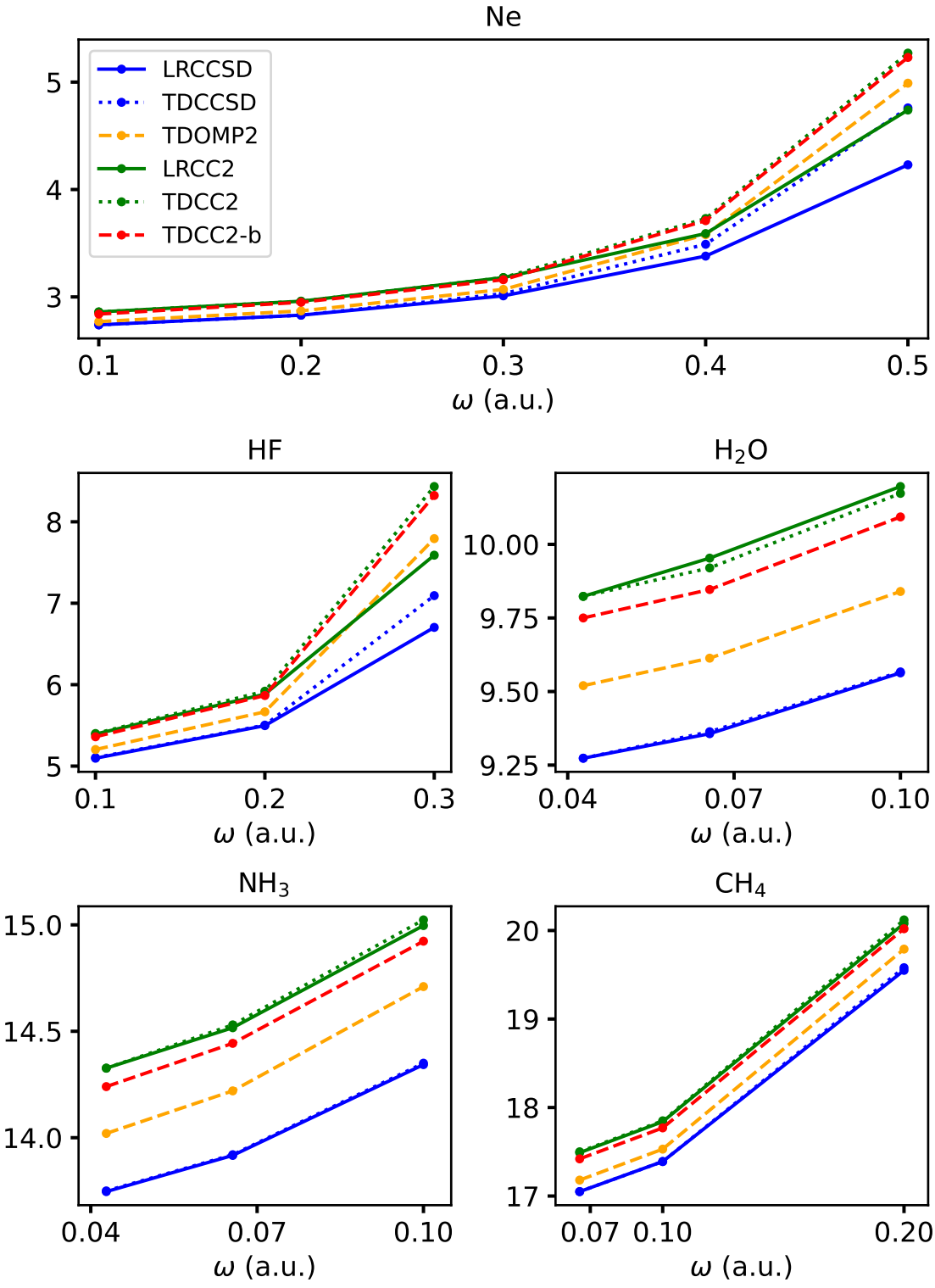

Figure 4: Isotropic polarizabilities extracted from TDCC2, TDOMP2, and TDCCSD simulations, and from LRCC2 and LRCCSD calculations.

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