

Supplementary Information of Why Local and Non-local Terms are Essential for Second Harmonic Generation Simulation?

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Table S1 Fresnel coefficients used in this work

a_1	a_2	a_3	a_4	a_5
0.1712	-0.1905	0.0953	0.1613	0.1712

Table S2 Coordinates of the ions of the water molecule in gas-phase after the geometrical optimisation for the three considered exchange-correlation functionals.

Functional	Atom	x (Å)	y (Å)	z (Å)
BLYP				
	<i>O</i>	0.0000	0.0000	0.0000
	<i>H</i> ₁	-0.7692	0.0000	0.5919
	<i>H</i> ₂	0.7692	0.0000	0.5919
PBE				
	<i>O</i>	0.0000	0.0000	0.0000
	<i>H</i> ₁	-0.7646	0.0000	0.5948
	<i>H</i> ₂	0.7646	0.0000	0.5948
B3LYP				
	<i>O</i>	0.0000	0.0000	0.0000
	<i>H</i> ₁	-0.7639	0.0000	0.5840
	<i>H</i> ₂	-0.7642	0.0000	0.5840

Functional	Atom	x (Å)	y (Å)	z (Å)
BLYP				
	<i>O</i>	0.0000	0.0000	0.0000
	<i>H</i> ₁	-0.7851	0.0000	0.5901
	<i>H</i> ₂	0.7873	0.0000	0.5901
	<i>O</i>	2.3859	0.0156	1.5686
	<i>H</i> ₁	2.9118	0.7856	1.2955
	<i>H</i> ₂	2.9103	-0.7619	1.3142
	<i>O</i>	0.3985	2.5461	-1.2969
	<i>H</i> ₁	0.2030	2.4889	-2.2444
	<i>H</i> ₂	0.1918	1.6556	-0.9344
	<i>O</i>	0.3515	-2.5071	-1.3522
	<i>H</i> ₁	0.1550	-2.4140	-2.2967
	<i>H</i> ₂	0.1685	-1.6234	-0.9609
	<i>O</i>	-2.3070	0.0109	1.7229
	<i>H</i> ₁	-2.4060	0.7875	2.2968
	<i>H</i> ₂	-2.4183	-0.7609	2.3012
PBE				
	<i>O</i>	0.0000	0.0000	0.0000
	<i>H</i> ₁	-0.7797	0.0000	0.5965
	<i>H</i> ₂	0.7832	0.0000	0.5965
	<i>O</i>	2.3491	0.0072	1.5786
	<i>H</i> ₁	2.8890	0.7651	1.3053
	<i>H</i> ₂	2.8733	-0.7727	1.3386
	<i>O</i>	0.3953	2.5087	-1.3011
	<i>H</i> ₁	0.1876	2.4308	-2.2425
	<i>H</i> ₂	0.1925	1.6223	-0.9262
	<i>O</i>	0.3214	-2.5171	-1.3035
	<i>H</i> ₁	0.1147	-2.4225	-2.2436
	<i>H</i> ₂	0.1530	-1.6271	-0.9202
	<i>O</i>	-2.2292	0.0240	1.7613
	<i>H</i> ₁	-2.3973	0.8066	2.3067
	<i>H</i> ₂	-2.4237	-0.7348	2.3310

<i>continued from previous page</i>				
Functional	Atom	x (Å)	y (Å)	z (Å)
B3LYP				
	O	0.0000	0.0000	0.0000
	H_1	-0.7764	0.0000	0.5854
	H_2	0.7788	0.0000	0.5854
	O	2.3600	0.0107	1.5636
	H_1	2.8913	0.7663	1.2908
	H_2	2.8737	-0.7702	1.3317
	O	0.3932	2.4948	-1.3277
	H_1	0.1847	2.4196	-2.2619
	H_2	0.1942	1.6221	-0.9444
	O	0.3148	-2.5220	-1.3036
	H_1	0.1070	-2.4385	-2.2375
	H_2	0.1511	-1.6422	-0.9203
	O	-2.2228	0.0339	1.7700
	H_1	-2.3923	0.8188	2.2988
	H_2	-2.4202	-0.7217	2.3312

Table S3 Coordinates of the ions of the water molecule in liquid-phase after the geometrical optimisation for the three considered exchange-correlation functionals.

Table S4 External electric fields applied on the system using the Berry phase during the wave function optimisation and the localisation of the Wannier functions. Each of the 25 below-mentioned fields corresponded to a distinct calculation and, therefore, to a distinct value of \mathbf{p} . The collinear fields are in the left part of the table while the non-collinear ones are in the right part of the table.

	E_x (a.u.)	E_y (a.u.)	E_z (a.u.)		E_x (a.u.)	E_y (a.u.)	E_z (a.u.)
1	0.000	0.000	0.000	14	0.000	0.005	0.005
2	0.000	0.000	0.005	15	0.000	-0.005	0.005
3	0.000	0.000	-0.005	16	0.005	0.000	0.005
4	0.000	0.000	0.010	17	-0.005	0.000	0.005
5	0.000	0.000	-0.010	18	0.000	0.005	0.005
6	0.000	0.005	0.000	19	0.000	-0.005	-0.005
7	0.000	-0.005	0.000	20	0.005	0.000	-0.005
8	0.000	0.010	0.000	21	-0.005	0.000	-0.005
9	0.000	-0.010	0.000	22	0.005	0.005	0.000
10	0.005	0.000	0.000	23	-0.005	0.005	0.000
11	-0.005	0.000	0.000	24	-0.005	-0.005	0.000
12	0.010	0.000	0.000	25	0.005	-0.005	0.000
13	-0.010	0.000	0.000				

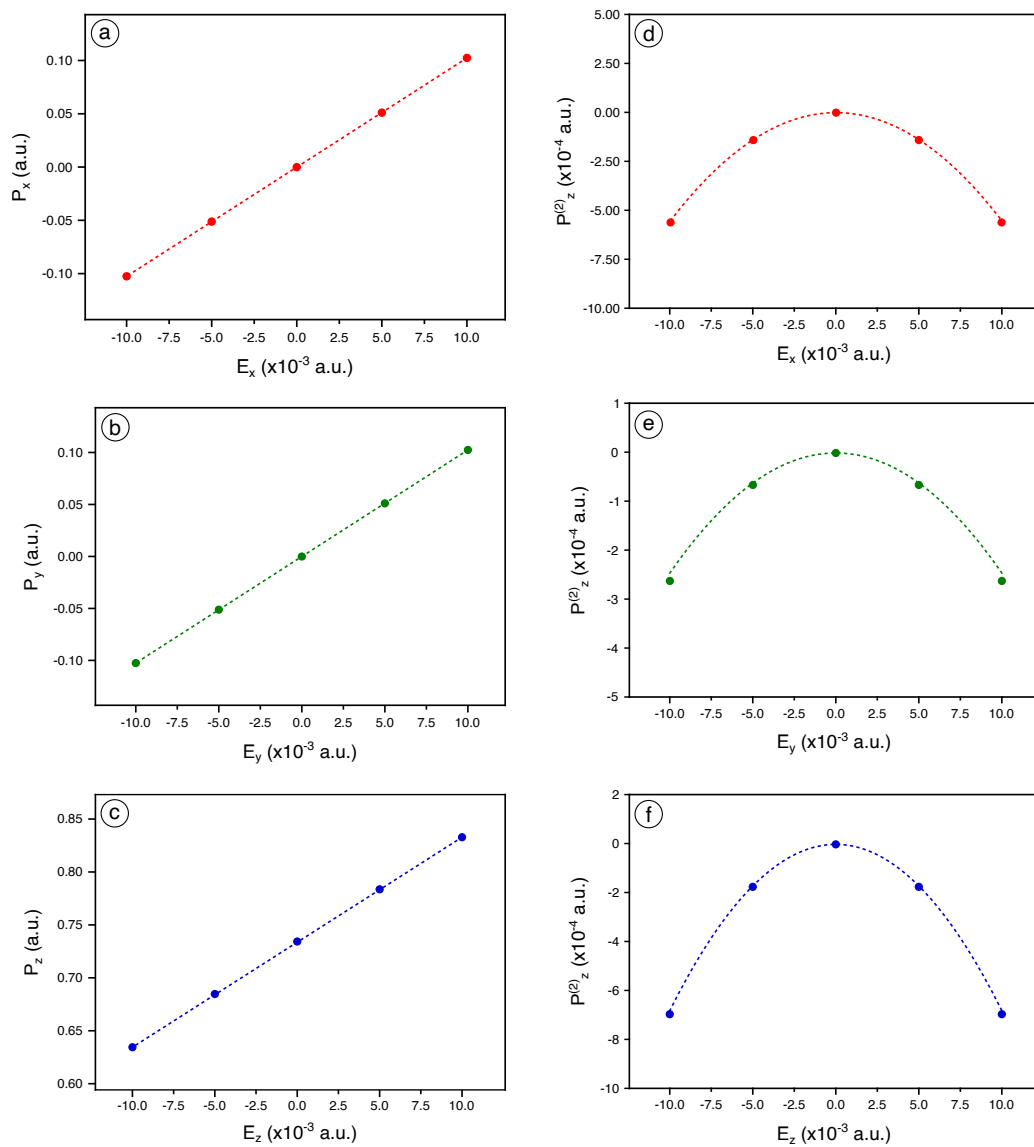


Fig. S1 a-c. Evolution of the x (a), y (b), and z (c) components of the dipole moment of a water molecule *in vacuo* as a function of the x component (a), the y component (b), and the z component (c) of the applied external electric fields. d-f. Evolution of the quadratic term of the z-component of the dipole moment of a water molecule *in vacuo*, i.e., the dipole moment from which the permanent and linear terms have been subtracted, as a function of the x component (d), the y component (e), and the z component (f) of the applied external electric fields.

Table S5 Values of α_{zz} , β_{zzz} , and β_{zxx} as a function of the number and intensities of external electric fields considered in the calculation.

Electric fields (E_x, E_y, E_z) considered in the calculation	α_{zz}	β_{zzz}	β_{zxx}
(0,0,0), (0,0,0.005)	9.9046	-7.2351	-5.2715
(0,0,0), (0,0,0.005), (0,0,-0.005)	9.9026	-7.0125	-5.2666
(0,0,0), (0,0,0.010), (0,0,-0.010)	9.9133	-6.9415	-5.5758
(0,0,0), (0,0,0.005), (0,0,-0.005), (0,0,0.010), (0,0,-0.010)	9.9107	-6.9621	-5.5895

Table S6 Calculated quadrupole hyperpolarizability of a water molecule in a liquid-phase configuration, *i.e.*, surrounded by four water molecules. The calculations were performed using BLYP.

	Liquid-phase	Gas-phase
$Q_{xx}^{(0)}$	2.39	1.84
$Q_{yy}^{(0)}$	-2.57	-1.89
$Q_{zz}^{(0)}$	0.18	0.04
$A_{x,zx}$	2.90	3.32
$A_{x,yy}$	-0.82	0.00
$A_{x,zz}$	0.72	0.00
$A_{y,xy}$	-0.38	0.00
$A_{y,yy}$	0.25	0.02
$A_{y,zy}$	-1.97	1.65
$A_{y,zz}$	-0.14	-0.01
$A_{z,xx}$	6.49	-0.19
$A_{z,xz}$	0.19	-0.01
$A_{z,yy}$	-9.39	-5.82
$A_{z,zz}$	2.89	6.01
$B_{xx,xx}$	-92.99	-71.73
$B_{xz,xx}$	-8.96	0.01
$B_{yy,xx}$	154.41	101.17
$B_{zz,xx}$	73.54	68.94
$B_{xy,xy}$	-28.00	-34.36
$B_{yz,xy}$	-4.37	0.00
$B_{xx,xz}$	-2.41	0.49
$B_{xz,xz}$	-32.35	-29.86
$B_{yy,xz}$	-3.08	0.39
$B_{zz,xz}$	-6.28	0.63
$B_{xx,yy}$	63.69	32.23
$B_{yy,yy}$	-219.65	-189.13
$B_{zz,yy}$	22.70	49.65
$B_{xy,yz}$	-3.97	0.24
$B_{yy,yz}$	-3.60	1.36
$B_{yz,yz}$	-56.60	-37.72
$B_{xx,zz}$	29.29	39.50
$B_{xz,zz}$	-10.70	-0.02
$B_{yy,zz}$	65.25	87.96
$B_{zz,zz}$	-96.24	-118.59