

# Field-Aware Interfaces in Continuum Solvation:

## Supporting Information

Matthew Truscott and Oliviero Andreussi\*

*Department of Physics, University of North Texas, Denton, TX 76207, USA*

E-mail: oliviero.andreussi@unt.edu

### S1 Derivatives of field fluxes

One of the key component of the analytic derivatives of the field-aware interfaces is represented by the derivatives of the field fluxes with respect to the electronic density and the ionic positions. The latter derivative is particularly cumbersome, as the dependence on ionic positions enters both the calculation of the field vector and the direction normal to the soft-sphere interface, which is expressed in terms of the soft-sphere gradient. Moreover, both terms depend explicitly on all the ionic positions, so that all cross terms need to be included, i.e. the partial derivative of the field flux through the soft sphere surrounding atom  $a$  with respect to the change in position of a second atom  $c$  is different from 0.

The derivative that we ought to express is the following

$$\begin{aligned} \nabla_{\mathbf{R}_c} \Phi_a &= \nabla_{\mathbf{R}_c} \int \mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a) \prod_{b \neq a} h_b(r_b) d\mathbf{r} \\ &= \int \nabla_{\mathbf{R}_c} [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] \prod_{b \neq a} h_b(r_b) d\mathbf{r} \\ &\quad + \sum_b (1 - \delta_{ab}) \int [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] \nabla_{\mathbf{R}_c} h_b(r_b) \prod_{d \neq a,b} h_d(r_d) d\mathbf{r} \end{aligned} \tag{1}$$

where the factor  $(1 - \delta_{ab})$  entering the second term is introduced to enforce the fact that the index  $b$  must be different from  $a$ . To semplify the above expression, we can exploit the fact that for central functions we have

$$\nabla_{\mathbf{R}} f(\mathbf{r} - \mathbf{R}) = -\nabla f(\mathbf{r} - \mathbf{R}) \quad (2)$$

or equivalently in this case,

$$\nabla_{\mathbf{R}} h(r) = -\nabla h(r). \quad (3)$$

The summation in the second term can be simplified by noting that the only term different from zero occurs when  $c$  and  $b$  are the same, namely

$$\begin{aligned} \sum_b (1 - \delta_{ab}) \int [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] \nabla_{\mathbf{R}_c} h_b(r_b) \prod_{d \neq a,b} h_d(r_d) d\mathbf{r} = \\ (1 - \delta_{ac}) \int [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] \nabla_{\mathbf{R}_c} h_c(r_c) \prod_{d \neq a,c} h_d(r_d) d\mathbf{r} = \\ (\delta_{ac} - 1) \int [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] \nabla h_c(r_c) \prod_{d \neq a,c} h_d(r_d) d\mathbf{r} \quad (4) \end{aligned}$$

The first integral in Eq. (1), instead, can be simplified by using the vector calculus identity for the differential operator applied to a vector scalar product, namely

$$\begin{aligned} \nabla(\mathbf{A} \cdot \mathbf{B}) &= \nabla(A_x B_x + A_y B_y + A_z B_z) \\ &= (\nabla \otimes \mathbf{A})\mathbf{B} + (\nabla \otimes \mathbf{B})\mathbf{A} \\ &= \mathbf{A} \times (\nabla \times \mathbf{B}) + \mathbf{B} \times (\nabla \times \mathbf{A}) + (\mathbf{A} \cdot \nabla)\mathbf{B} + (\mathbf{B} \cdot \nabla)\mathbf{A} \quad (5) \end{aligned}$$

where the notation  $\mathbf{u} \otimes \mathbf{v}$  is adopted to indicate the outer product between two vectors. By using the above identity, the quantity  $\nabla_{\mathbf{R}_c} [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)]$  can thus be recast into the

following expression

$$\begin{aligned}
\nabla_{\mathbf{R}_c} [\mathbf{E}(\mathbf{r}) \cdot \nabla h_a(r_a)] &= [\nabla_{\mathbf{R}_c} \otimes \mathbf{E}(\mathbf{r})] \nabla h_a(r_a) + [\nabla_{\mathbf{R}_c} \otimes \nabla h_a(r_a)] \mathbf{E}(\mathbf{r}) \\
&= -[\nabla \otimes \nabla \phi(z_c \delta(r_c))] \nabla h_a(r_a) - \delta_{ac} [\nabla \otimes \nabla h_a(r_a)] \mathbf{E}(\mathbf{r}) \\
&= -\mathbf{H}[\phi(z_c \delta(r_c))] \nabla h_a(r_a) - \delta_{ac} \mathbf{H}[h_a(r_a)] \mathbf{E}(\mathbf{r}) \quad (6)
\end{aligned}$$

In the second passage of the above derivation we expressed the electric field originated by the ion  $c$  in terms of the gradient of its electrostatic potential

$$\mathbf{E}_c(\mathbf{r}) = \nabla \phi(z_c \delta(r_c)) \quad (7)$$

while, in the last passage we recast the outer products in terms of the Hessian matrix

$$\nabla \otimes \nabla f = \begin{pmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} & \frac{\partial^2 f}{\partial x \partial z} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} & \frac{\partial^2 f}{\partial y \partial z} \\ \frac{\partial^2 f}{\partial z \partial x} & \frac{\partial^2 f}{\partial z \partial y} & \frac{\partial^2 f}{\partial z^2} \end{pmatrix} = \mathbf{H}[f]. \quad (8)$$

By combining the above relations, the partial derivative of the field flux with respect to the atomic positions can be written as

$$\begin{aligned}
\nabla_{\mathbf{R}_c} \Phi_a &= \\
&- \int (\mathbf{H}[\phi(z_c \delta(r_c))] \nabla h_a(r_a) + \delta_{ac} \mathbf{H}[h_a(r_a)] \mathbf{E}(\mathbf{r})) \prod_{b \neq a, c} h_b(r_b) d\mathbf{r} \\
&+ (\delta_{ac} - 1) \int [\mathbf{E}(\mathbf{r}) \cdot h_a(r_a)] \nabla h_c(r_c) \prod_{b \neq a, c} h_b(r_b) d\mathbf{r} \quad (9)
\end{aligned}$$

## S2 Field fluxes on individual soft spheres

In Table S1 we report the field fluxes computed for each soft sphere for the continuum interfaces of the molecules analyzed in the article. The labels of the atoms are reported in

Figure S1.

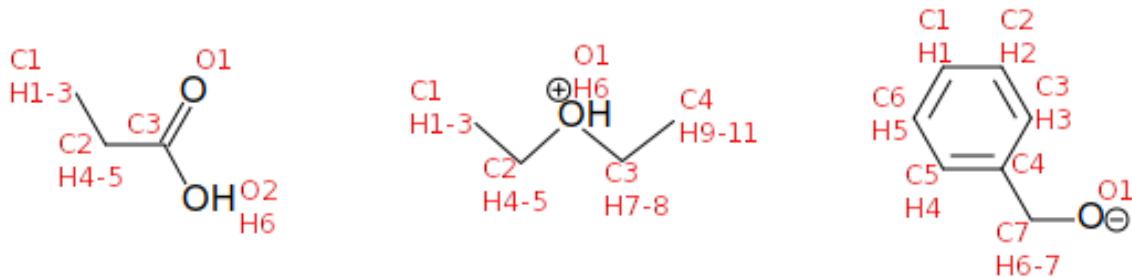


Figure S1: Molecules with labels, can be crossreferenced with Table S1. From left to right, propanoic acid: column 3, diethyl ether cation: column 5, benzyl alcohol anion: column 7. Labels for water are not reported as there is no ambiguity with the assignment of its types.

Table S1: Field fluxes on the different atoms of the molecules considered in the article. Equivalent total charges computed using Gauss's law (bottom row) may not sum up to the total effective charge of the systems due to the presence of electronic charge lying outside of the unscaled soft-sphere interfaces

Label	H <sub>2</sub> O	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	H <sub>3</sub> O	C <sub>4</sub> H <sub>11</sub> O	HO	C <sub>7</sub> H <sub>7</sub> O
O1	-2.3740	-3.7310	7.1193	0.9230	-18.5446	-12.5551
O2		-0.5114				
H1	1.7519	0.6291	6.0156	1.3866	-2.4851	0.5615
H2	1.7520	0.7170	6.0170	1.4833		0.4577
H3		0.6134	6.0154	1.5041		0.2310
H4		1.2208		1.8060		0.2349
H5		1.2129		1.7848		0.4500
H6		2.3360		2.8392		-0.8515
H7				1.8098		-0.8543
H8				1.7796		
H9				1.5112		
H10				1.4105		
H11				1.4969		
C1		0.4364		1.7518		-0.3717
C2		0.6257		1.4125		-0.4218
C3		0.2089		1.4210		-0.5383
C4				1.7228		-0.5285
C5						-0.5389
C6						-0.4322
C7						-1.4890
Total Flux	1.1339	3.7578	25.1673	26.0431	-21.0297	-16.6462
Equivalent Total Charge	0.05	0.15	1.00	1.04	-0.84	-0.66

## S3 Best performing field-aware parameters

In Tables S2-S7 the best performing sets of field-aware parameters are reported for the six molecules considered in the article.

Table S2: Neutral Water

Abs Error	Asymmetry	$\alpha$	$f_0$	Flux Mean	Flux Spread
0.001632	0.5	1.14	0.03	1.5	0.6
0.003574	0.0	1.14	0.07	2.0	0.8
0.003900	-0.5	1.16	0.07	1.5	1.0
0.005944	0.5	1.14	0.03	0.5	0.2
0.005944	0.5	1.14	0.03	0.5	0.4
0.005944	0.5	1.14	0.03	1.0	0.2
0.005944	0.5	1.14	0.03	1.0	0.4
0.005944	0.5	1.14	0.03	1.0	0.6
0.005944	0.5	1.14	0.03	1.0	0.8
0.005944	0.5	1.14	0.03	1.5	0.2

Table S3: Neutral Propanoic Acid

Abs Error	Asymmetry	$\alpha$	$f_0$	Flux Mean	Flux Spread
0.002053	1.0	1.14	0.07	2.0	0.2
0.002722	1.0	1.14	0.06	2.0	0.2
0.003525	1.0	1.16	0.05	2.0	0.2
0.004520	1.0	1.14	0.04	2.0	0.2
0.004969	1.0	1.14	0.07	2.0	0.4
0.005785	1.0	1.14	0.03	2.0	0.2
0.007557	1.0	1.14	0.06	2.0	0.4
0.008959	1.0	1.14	0.03	2.5	0.2
0.008959	1.0	1.14	0.03	2.5	0.4
0.008959	1.0	1.14	0.04	2.5	0.2

Table S4: Cationic Water

Abs Error	$\alpha$	$f_0$	Flux Mean	Flux Spread
0.002199	1.14	0.04	4.5	2.6
0.2112	1.20	0.05	3.5	3.0
0.2268	1.20	0.05	4.5	1.8
0.2950	1.20	0.05	3.5	2.6
0.2950	1.20	0.05	0.5	0.2
0.2950	1.20	0.05	1.5	0.2
0.2950	1.20	0.05	1.5	0.6
0.2950	1.20	0.05	1.5	1.0
0.2950	1.20	0.05	1.5	1.4
0.2950	1.20	0.05	2.5	0.2

Table S5: Cationic Diethyl Ether

Abs Error	$\alpha$	$f_0$	Flux Mean	Flux Spread
0.7991	1.12	0.06	1.5	1.0
1.134	1.20	0.05	0.5	0.2
1.170	1.14	0.07	1.5	1.0
1.236	1.12	0.06	1.5	1.4
1.263	1.12	0.06	1.5	0.6
1.342	1.16	0.07	1.5	1.4
1.351	1.12	0.07	1.5	0.6
1.590	1.16	0.04	0.5	0.2
1.619	1.14	0.04	0.5	0.2
1.718	1.16	0.07	1.5	0.2

Table S6: Anionic Water

Abs Error	$\alpha$	$f_0$	Flux Mean	Flux Spread
0.2847	1.12	0.07	1.0	0.5
0.4813	1.12	0.07	2.0	0.5
1.912	1.14	0.07	1.0	0.5
2.353	1.14	0.07	2.0	0.5
2.925	1.12	0.07	2.0	1.5
3.631	1.16	0.07	1.0	0.5
3.853	1.16	0.07	2.0	0.5
4.430	1.14	0.07	2.0	1.5
5.004	1.18	0.07	1.0	0.5
5.090	1.18	0.07	2.0	0.5

Table S7: Anionic Benzyl Alcohol

Abs Error	$\alpha$	$f_0$	Flux Mean	Flux Spread
8.005	1.14	0.07	1.0	0.5
9.461	1.16	0.07	1.0	0.5
10.56	1.18	0.07	1.0	0.5
10.58	1.12	0.06	1.0	0.5
10.96	1.12	0.07	2.0	1.5
11.39	1.14	0.06	1.0	0.5
11.42	1.20	0.07	1.0	0.5
11.45	1.12	0.07	3.0	2.5
11.55	1.12	0.07	4.0	3.5
11.58	1.12	0.07	5.0	4.5