# Notes for ddCOSMO/ddPCM

December 14, 2016

## 1  ddCOSMO

The van der Waals molecular cavity $\Omega$ is defined as the union of $M$ spheres $\Omega_j$'s with centers $\{\boldsymbol{r}_j\}_{1 \leq j \leq M}$ and radii $\{\rho_j\}_{1 \leq j \leq M}$. The solvation energy $E_s$ of the molecule is defined in terms of the solute's density of charge $\varrho$ and the reaction potential $W$ as:

$$E_s = \frac{1}{2} f(\varepsilon_s) \int_\Omega \varrho(\boldsymbol{r}) \, W(\boldsymbol{r}) \, d\boldsymbol{r}$$

Here $f(\varepsilon_s)$ is a constant depending on the solvent dielectric constant $\varepsilon_s$. If we assume a classical charge distribution, namely

$$\varrho(\boldsymbol{r}) = \sum_{j=1}^{M} q_j \, \delta(\boldsymbol{r} - \boldsymbol{r}_j)$$

the solvation energy reduces to

$$E_s = \frac{1}{2} f(\varepsilon_s) \sum_{j=1}^{M} q_j \, W(\boldsymbol{r}_j) \tag{1}$$

The reaction potential $W$ is the solution to the boundary value problem

$$-\Delta W = 0 \quad \text{in } \Omega \qquad ; \qquad W(\boldsymbol{s}) = -\Phi(\boldsymbol{s}) := -\sum_{j=1}^{m} \frac{q_j}{|\boldsymbol{s} - \boldsymbol{r}_j|} \quad \text{on } \Gamma$$

Since $W$ is harmonic over $\Omega$, it can be represented by means of an apparent surface charge $\sigma$ through the single layer potential $\tilde{\mathcal{S}}$:

$$W(\boldsymbol{r}) = \int_\Gamma \frac{\sigma(\boldsymbol{s})}{|\boldsymbol{r} - \boldsymbol{s}|} \, d\boldsymbol{s} =: \tilde{\mathcal{S}}\sigma(\boldsymbol{r}) \qquad , \qquad \forall \, \boldsymbol{r} \in \Omega$$

The apparent surface charge $\sigma$ satisfies the integral equation:

$$\mathcal{S}\sigma(\boldsymbol{s}) := \int_\Gamma \frac{\sigma(\boldsymbol{s}')}{|\boldsymbol{s} - \boldsymbol{s}'|} \, d\boldsymbol{s}' = -\Phi(\boldsymbol{s}) \qquad , \qquad \forall \, \boldsymbol{s} \in \Gamma$$

where $\mathcal{S}$ is the single layer operator. Let us turn to the domain-decomposition approach. Since the restriction $W_j := W|_{\overline{\Omega}_j}$ is harmonic over $\Omega_j$, it can be represented as

$$W_j(\boldsymbol{r}) = \int_{\Gamma_j} \frac{\sigma_j(\boldsymbol{s})}{|\boldsymbol{r} - \boldsymbol{s}|} \, d\boldsymbol{s} =: \tilde{\mathcal{S}}_j \sigma_j(\boldsymbol{r}) \qquad , \qquad \forall \, \boldsymbol{r} \in \Omega_j$$

$$W_j(\boldsymbol{s}) = \int_{\Gamma_j} \frac{\sigma_j(\boldsymbol{s}')}{|\boldsymbol{s} - \boldsymbol{s}'|} \, d\boldsymbol{s}' =: \mathcal{S}_j \sigma_j(\boldsymbol{s}) \qquad , \qquad \forall \, \boldsymbol{s} \in \Gamma_j$$

for some surface charge $\sigma_j$. Each restriction $W_j$ satisfies the following boundary condition:

$$W_j(\boldsymbol{s}) = -\Phi(\boldsymbol{s}) \left( 1 - \frac{1}{|N_j(\boldsymbol{s})|} \sum_{k \in N_j(\boldsymbol{s})} \chi_k(\boldsymbol{s}) \right) + \frac{1}{|N_j(\boldsymbol{s})|} \sum_{k \in N_j(\boldsymbol{s})} \chi_k(\boldsymbol{s}) W_k(\boldsymbol{s})$$

$$\forall \, \boldsymbol{s} \in \Gamma_j$$

where $\chi_k$ is the characteristic function of $\Omega_k$. If we employ single layer potentials and operators, and define coefficients

$$\omega_{kj}(\boldsymbol{s}) = \frac{\chi_k(\boldsymbol{s})}{|N_j(\boldsymbol{s})|}$$

we can rewrite the previous equation in terms of surface charges $\sigma_j$'s as:

$$\mathcal{S}_j \sigma_j(\boldsymbol{s}) = -\Phi(\boldsymbol{s}) \left( 1 - \sum_{k \in N_j(\boldsymbol{s})} \omega_{kj}(\boldsymbol{s}) \right) + \omega_{kj}(\boldsymbol{s}) \, \tilde{\mathcal{S}}_k \sigma_k(\boldsymbol{s}) \qquad , \qquad \boldsymbol{s} \in \Gamma_j$$

If we now expand each local surface charge in series of spherical harmonics $Y_\ell^m$ as

$$\sigma_j(\boldsymbol{s}) = \sum_{\ell,m} [X_j]_\ell^m \, Y_\ell^m(\boldsymbol{s}) \tag{2}$$

we can discretize the previous equation as:

$$[L_{jj}]_{\ell\ell'}^{mm'} [X_j]_{\ell'}^{m'} = [g_j]_\ell^m - [L_{jk}]_{\ell\ell'}^{mm'} [X_k]_{\ell'}^{m'} \qquad , \qquad \forall \, j$$

2

where summation is understood over repeated indices. Equivalently, we can consider the following linear system

$$
\begin{pmatrix}
L_{11} & \cdots & L_{1M} \\
\vdots & \ddots & \vdots \\
L_{M1} & \cdots & L_{MM}
\end{pmatrix}
\begin{pmatrix}
X_1 \\
\vdots \\
X_M
\end{pmatrix}
=
\begin{pmatrix}
g_1 \\
\vdots \\
g_M
\end{pmatrix}
$$

or $LX = g$ in short. Let us now return to the solvation energy in the presence of a classical charge distribution, i.e., equation (1). Since $W(\boldsymbol{r}_j) = W_j(\boldsymbol{r}_j)$, by means of single layer potentials we obtain that:

$$
E_s = \frac{1}{2} f(\varepsilon_s) \sum_{j=1}^{M} q_j \int_{\Gamma_j} \frac{\sigma_j(\boldsymbol{s})}{|\boldsymbol{r}_j - \boldsymbol{s}|} \, d\boldsymbol{s} = \frac{1}{2} f(\varepsilon_s) \sum_{j=1}^{M} \frac{q_j}{\rho_j} \int_{\Gamma_j} \sigma_j(\boldsymbol{s}) \, d\boldsymbol{s}
$$

Without loss of generality, let us replace $\sigma_j(\boldsymbol{s}) \to \rho_j \sigma_j(\boldsymbol{s}) \to \rho_j \sigma_j(\boldsymbol{r}_j + \rho_j \boldsymbol{s})$, so that we can reduce the computation of the energy to a integrals on the unit sphere $\mathbb{S}^2$:

$$
E_s = \frac{1}{2} f(\varepsilon_s) \sum_{j=1}^{M} q_j \int_{\mathbb{S}^2} \sigma_j(\boldsymbol{s}) \, d\boldsymbol{s}
$$

Let us now expand each surface charge $\sigma_j$ is series of spherical harmonics as in equation (2). Since only the first mode has non-zero average, we obtain:

$$
E_s = \frac{1}{2} f(\varepsilon_s) \sum_{j=1}^{M} q_j [X_j]_0^0
$$

Thus, if we define

$$
[\Psi_j]_\ell^m = \frac{1}{2} f(\varepsilon_s) q_j \delta_{\ell 0} \delta_{m0}
$$

we can write the polarization energy as

$$
E_s = \sum_j \sum_{\ell,m} [\Psi_j]_\ell^m [X_j]_\ell^m =: \langle \Psi, X \rangle
$$

Let us recall that $L = L(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M)$, and $g = g(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M)$, thus the solution vector $X = L^{-1} g$ does depend on $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M$ as well. The force acting on the $j$-th particle can be computed as:

$$
F_j = -\nabla_j \langle \Psi, \sigma \rangle
$$

3

where $\nabla_j$ is the gradient with respect to the position of the $j$-th atom. In the following we should just refer to it with the symbol $\cdot'$. Let $s$ be the solution of the adjoint problem $L^* s = \Psi$. Then, in the case that $\Psi$ is independent of $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_M$, we obtain

$$F_j = -\langle \Psi, X' \rangle = -\langle L^* s, X' \rangle = -\langle s, LX' \rangle$$

Recalling that $LX = g$, Leibnitz formula yields $L'X + LX' = g'$, hence:

$$F_j = -\langle s, g' - L'X \rangle = -\langle s, h \rangle$$

where we set $h = g' - L'X$. Thus, the computation of $F_j$ amounts to the adjoint solve $L^* s = \Psi$ contracted with $h = g' - L'X$.

# 2   ddPCM

Let $\phi$ be the total electrostatic potential of the solute/solvent system, and $\Phi$ be the potential of the solute in vacuum. The reaction potential is $W = \phi - \Phi$. Let us define:

$$\varepsilon = \begin{cases} 1 & \text{in } \Omega \\ \varepsilon_s & \text{on } \mathbb{R}^3 \setminus \Omega \end{cases}$$

where $\varepsilon_s$ is the macroscopic dielectric permittivity of the solvent. Then the reaction potential satisfies the boundary value problem:

$$-\Delta W = 0 \quad \text{in } \mathbb{R}^3 \setminus \Gamma \quad ; \quad [\![W]\!] = 0 \quad , \quad [\![\varepsilon\, \partial_n W]\!] = (\varepsilon_s - 1)\partial_n \Phi \quad \text{on } \Gamma$$

As previously, since $W$ is harmonic over $\mathbb{R}^3 \setminus \Omega$, we can write

$$W(\boldsymbol{r}) = \int_\Gamma \frac{\sigma(\boldsymbol{s})}{|\boldsymbol{r} - \boldsymbol{s}|}\, d\boldsymbol{s} \qquad \forall\, \boldsymbol{r} \in \mathbb{R}^3 \setminus \Gamma$$

for some apparent surface charge $\sigma$, defined on $\Gamma$, that satisfies:

$$\sigma = \frac{1}{4\pi}[\![\partial_n W]\!] \qquad \text{on } \Gamma$$

Then it can be shown that $\sigma$ satisfies the integral equation

$$\mathcal{R}_\varepsilon \mathcal{S} \sigma = -\mathcal{R}_\infty \Phi \qquad \text{on } \Gamma$$

4

where:

$$\mathcal{R}_\varepsilon = 2\pi \frac{\varepsilon + 1}{\varepsilon - 1} I - \mathcal{D}$$

$$\mathcal{R}_\infty = 2\pi I - \mathcal{D}$$

$$\mathcal{D}\sigma(\boldsymbol{s}) = \int_\Gamma \nabla \frac{1}{|\boldsymbol{s} - \boldsymbol{s}'|} \cdot \boldsymbol{n}(\boldsymbol{s}')\, \sigma(\boldsymbol{s}')\, d\boldsymbol{s}' \qquad , \qquad \forall\, \boldsymbol{s} \in \Gamma$$

Here $\mathcal{D}$ is known as the double layer operator. Thus, if we set $\mathcal{S}\sigma = -\Phi_\varepsilon$, namely a ddCOSMO solve, we obtain:

$$\mathcal{R}_\varepsilon \Phi_\varepsilon = \mathcal{R}_\infty \Phi \qquad \text{on } \Gamma \tag{3}$$

In order to treat this integral equation through a domain-decomposition approach, let us define the trivial extensions

$$\Phi_j = \begin{cases} \Phi & \text{on } \Gamma_j \cap \Gamma \\ 0 & \text{otherwise} \end{cases} \quad , \qquad \Phi_{\varepsilon,j} = \begin{cases} \Phi_\varepsilon & \text{on } \Gamma_j \cap \Gamma \\ 0 & \text{otherwise} \end{cases}$$

Those extensions can be more compactly written as

$$\Phi_j = U_j\, \Phi \quad , \quad \Phi_{\varepsilon,j} = U_{\varepsilon,j}\, \Phi_\varepsilon \quad ; \qquad U_j(\,\cdot\,) = 1 - \sum_{k \in N_j(\,\cdot\,)} \omega_{jk}(\,\cdot\,)$$

Notice that $U_j$ is the characteristic function of $\Gamma_j \cap \Gamma$, while $1 - U_j$ is the characteristic function of $\Gamma_j \setminus \Gamma_j \cap \Gamma$. If we define:

$$\mathcal{D}_j\sigma(\boldsymbol{s}) = \int_{\Gamma_j} \nabla \frac{1}{|\boldsymbol{s} - \boldsymbol{s}'|} \cdot \boldsymbol{n}(\boldsymbol{s}')\, \sigma(\boldsymbol{s}')\, d\boldsymbol{s}' \qquad , \qquad \forall\, \boldsymbol{s} \in \Gamma_j$$

$$\tilde{\mathcal{D}}_j\sigma(\boldsymbol{r}) = \int_{\Gamma_j} \nabla \frac{1}{|\boldsymbol{r} - \boldsymbol{s}|} \cdot \boldsymbol{n}(\boldsymbol{s})\, \sigma(\boldsymbol{s})\, d\boldsymbol{s} \qquad , \qquad \forall\, \boldsymbol{r} \in \mathbb{R}^3 \setminus \Gamma_j$$

then, for every $\boldsymbol{s} \in \Gamma_j \cap \Gamma$, we obtain

$$\mathcal{D}\Phi(\boldsymbol{s}) = \int_\Gamma \nabla \frac{1}{|\boldsymbol{s} - \boldsymbol{s}'|} \cdot \boldsymbol{n}(\boldsymbol{s}')\, \Phi(\boldsymbol{s}')\, d\boldsymbol{s}'$$

$$= \sum_k \int_{\Gamma_k} \nabla \frac{1}{|\boldsymbol{s} - \boldsymbol{s}'|} \cdot \boldsymbol{n}(\boldsymbol{s}')\, \Phi_k(\boldsymbol{s}')\, d\boldsymbol{s}' = \mathcal{D}_j\, \Phi_j(\boldsymbol{s}) + \sum_{k \neq j} \tilde{\mathcal{D}}_k\, \Phi_k(\boldsymbol{s})$$

and a similar result holds for $\Phi_\varepsilon$. Thus, for every $\boldsymbol{s} \in \Gamma_j \cap \Gamma$, we can write equation (3) as:

$$2\pi \frac{\varepsilon + 1}{\varepsilon - 1} \Phi_{\varepsilon,j}(\boldsymbol{s}) - \mathcal{D}_j \, \Phi_{\varepsilon,j}(\boldsymbol{s}) - \sum_{k \neq j} \tilde{\mathcal{D}}_k \, \Phi_{\varepsilon,k}(\boldsymbol{s})$$

$$= 2\pi \, \Phi_j(\boldsymbol{s}) - \mathcal{D}_j \, \Phi_j(\boldsymbol{s}) - \sum_{k \neq j} \tilde{\mathcal{D}}_k \, \Phi_k(\boldsymbol{s})$$

By setting

$$\mathcal{R}_{\varepsilon,j} = 2\pi \frac{\varepsilon + 1}{\varepsilon - 1} I - \mathcal{D}_j \qquad , \qquad \tilde{\mathcal{R}}_{\varepsilon,j} = -\tilde{\mathcal{D}}_j$$

with obvious extension to the case $\varepsilon = \infty$, we obtain:

$$\mathcal{R}_{\varepsilon,j} \, \Phi_{\varepsilon,j} + \sum_{k \neq j} \tilde{\mathcal{R}}_{\varepsilon,j} \, \Phi_{\varepsilon,j} = \mathcal{R}_{\infty,j} \, \Phi_j + \sum_{k \neq j} \tilde{\mathcal{R}}_{\infty,j} \, \Phi_j \quad \text{on } \Gamma_j \cap \Gamma$$

which, together with the condition $\Phi_{\varepsilon,j} = 0$ on $\Gamma_j \setminus \Gamma_j \cap \Gamma$ is the local problem. In order to lump those two equations into a single one, we resort to characteristic functions. In fact, we can equivalently write:

$$(1 - U_j)\Phi_{\varepsilon,j} = 0 \quad \text{on } \Gamma_j$$

$$U_j \left( \mathcal{R}_{\varepsilon,j} \, \Phi_{\varepsilon,j} + \sum_{k \neq j} \tilde{\mathcal{R}}_{\varepsilon,j} \, \Phi_{\varepsilon,j} - \mathcal{R}_{\infty,j} \, \Phi_j - \sum_{k \neq j} \tilde{\mathcal{R}}_{\infty,j} \, \Phi_j \right) = 0 \quad \text{on } \Gamma_j$$

and, after premultiplying the first equation by a non-zero constant $\alpha$, side-wise addition yields:

$$\alpha(1 - U_j)\Phi_{\varepsilon,j} + U_j \left( \mathcal{R}_{\varepsilon,j} \, \Phi_{\varepsilon,j} + \sum_{k \neq j} \tilde{\mathcal{R}}_{\varepsilon,j} \, \Phi_{\varepsilon,j} \right) = U_j \left( \mathcal{R}_{\infty,j} \, \Phi_j - \sum_{k \neq j} \tilde{\mathcal{R}}_{\infty,j} \, \Phi_j \right)$$

$$\text{on } \Gamma_j$$

If we choose $\alpha = 2\pi(\varepsilon + 1)/(\varepsilon - 1)$, we obtain:

$$2\pi \frac{\varepsilon + 1}{\varepsilon - 1}\Phi_{\varepsilon,j} - U_j \left( \mathcal{D}_j \Phi_{\varepsilon,j} + \sum_{k \neq j} \tilde{\mathcal{D}}_{\varepsilon,k} \, \Phi_{\varepsilon,k} \right) = 2\pi U_j \Phi_j - U_j \left( \mathcal{D}_j \Phi_j + \sum_{k \neq j} \tilde{\mathcal{D}}_k \, \Phi_k \right)$$

$$\text{on } \Gamma_j \quad (4)$$

Let us recall that the load $\Phi_j$ can be computed as $\Phi_j = U_j\Phi$. In order to define an approximation, we interpret equation (4) in a variational setting, with test functions given by spherical harmonics. We obtain the following linear system:

$$
\begin{pmatrix}
A_{11}^{\varepsilon} & \cdots & A_{1M}^{\varepsilon} \\
\vdots & \ddots & \vdots \\
A_{M1}^{\varepsilon} & \cdots & A_{MM}^{\varepsilon}
\end{pmatrix}
\begin{pmatrix}
\Phi_1^{\varepsilon} \\
\vdots \\
\Phi_M^{\varepsilon}
\end{pmatrix}
=
\begin{pmatrix}
A_{11}^{\infty} & \cdots & A_{1M}^{\infty} \\
\vdots & \ddots & \vdots \\
A_{M1}^{\infty} & \cdots & A_{MM}^{\infty}
\end{pmatrix}
\begin{pmatrix}
\Phi_1 \\
\vdots \\
\Phi_M
\end{pmatrix}
$$

or, in short

$$A_{\varepsilon}\Phi_{\varepsilon} = A_{\infty}\Phi$$

The entries are given by:

$$[A_{jj}^{\varepsilon}]_{\ell\ell'}^{mm'} = 2\pi\frac{\varepsilon+1}{\varepsilon-1}\delta_{\ell\ell'}\delta_{mm'} - \frac{2\pi}{2\ell'+1}\sum_n w_n\, Y_{\ell}^m(\boldsymbol{s}_n)\, U_j^n\, Y_{\ell'}^{m'}(\boldsymbol{s}_n)$$

$$[A_{jk}^{\varepsilon}]_{\ell\ell'}^{mm'} = -\frac{4\pi\ell'}{2\ell'+1}\sum_n w_n\, Y_{\ell}^m(\boldsymbol{s}_n)\, U_j^n \left(\frac{\rho_k}{|\boldsymbol{r}_j + \rho_j\boldsymbol{s}_n - \boldsymbol{r}_k|}\right)^{\ell'+1} Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j + \rho_j\boldsymbol{s}_n - \boldsymbol{r}_k}{|\boldsymbol{r}_j + \rho_j\boldsymbol{s}_n - \boldsymbol{r}_k|}\right)$$

where, for convenience, we set

$$U_j^n = U_j(\boldsymbol{r}_j + \rho_j\boldsymbol{s}_n)$$

Let us recall that $LX = -\Phi_{\varepsilon}$, so that the full discretization reads as $A_{\varepsilon}LX = -A_{\infty}\Phi$. We follow the same approach we used in the ddCOSMO case and set $(A_{\varepsilon}L)^*s = \Psi$. The force acting on the $j$-th particle is computed as:

$$F_j = -\langle\Psi, X'\rangle = -\langle s, A_{\varepsilon}L\,X'\rangle$$

and, using Leibnitz rule, we obtain that

$$F_j = -\langle s, -A_{\infty}'\Phi - A_{\infty}\Phi' - A_{\varepsilon}'LX - A_{\varepsilon}L'X\rangle = -\langle s, h\rangle$$

where we set $h = -A_{\infty}'\Phi - A_{\infty}\Phi' + A_{\varepsilon}'\Phi_{\varepsilon} - A_{\varepsilon}L'X$. Thus we need to compute the analytical derivatives of $A_{\varepsilon}$ or, more specifically, their action. To this aim, let us drop the $\varepsilon$-dependency for ease of notation, and refer to the partial derivatives as $\partial_{i,\alpha} = \partial/\partial r_{i,\alpha}$. Since the entries of $[A_{jj}]_{\ell\ell'}^{mm'}$ are functions of $\boldsymbol{r}_j$ only, we obtain:

$$[(\partial_{i,\alpha}A)\phi_j]_{\ell}^m = \sum_{k\neq j}\sum_{\ell',m'}\partial_{i,\alpha}[A_{jk}]_{\ell\ell'}^{mm'}\,[\phi_k]_{\ell'}^{m'} \qquad\qquad i\neq j$$

$$[(\partial_{j,\alpha}A)\phi_j]_{\ell}^m = \sum_{k\neq j}\sum_{\ell',m'}\partial_{j,\alpha}[A_{jk}]_{\ell\ell'}^{mm'}\,[\phi_k]_{\ell'}^{m'} + \sum_{\ell',m'}\partial_{j,\alpha}[A_{jj}]_{\ell\ell'}^{mm'}\,[\phi_j]_{\ell'}^{m'}$$

7

Then, in the case $i \neq j$, we have:

$$[(\partial_{i,\alpha}A)\phi_j]_\ell^m = -\sum_{k\neq j}\sum_{\ell',m'}\frac{4\pi\ell'}{2\ell'+1}\sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n\times$$

$$\partial_{i,\alpha}\left[\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1}Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'}$$

$$= -\sum_{\ell',m'}\frac{4\pi\ell'}{2\ell'+1}\sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n\times$$

$$\sum_{k\neq j}\partial_{i,\alpha}\left[\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1}Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'}$$

$$= -\sum_{\ell',m'}\frac{4\pi\ell'}{2\ell'+1}\sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n\times$$

$$\partial_{i,\alpha}\left[\left(\frac{\rho_i}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|}\right)^{\ell'+1}Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|}\right)\right][\phi_i]_{\ell'}^{m'}$$

Similarly, when $i = j$, we obtain:

$$[(\partial_{j,\alpha}A)\phi_j]_\ell^m = -\sum_{k\neq j}\sum_{\ell',m'}\frac{4\pi\ell'}{2\ell'+1}\sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\times$$

$$\partial_{j,\alpha}\left[U_j^n\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1}Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'}+$$

$$-\sum_{\ell',m'}\frac{2\pi}{2\ell'+1}\sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\,\partial_{j,\alpha}U_j^n\, Y_{\ell'}^{m'}(\boldsymbol{s}_n)\,[\phi_j]_{\ell'}^{m'}$$

Notice that:

$$\partial_{i,\alpha}\left(\frac{\rho_i}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|}\right)^{\ell'+1} = (\ell'+1)\,(\,\cdot\,)^{\ell'}\rho_i\frac{r_{j,\alpha}+\rho_j s_{n,\alpha}-r_{i,\alpha}}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|^3}$$

$$\partial_{j,\alpha}\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1} = -(\ell'+1)\,(\,\cdot\,)^{\ell'}\rho_k\frac{r_{j,\alpha}+\rho_j s_{n,\alpha}-r_{k,\alpha}}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|^3}$$

8

Let $\boldsymbol{s} = \boldsymbol{r}/|\boldsymbol{r}| \in \mathbb{S}^2$. Using index notation we have that:

$$\partial_{i,\alpha} Y = \frac{\partial Y}{\partial s_\beta} \frac{\partial s_\beta}{\partial r_\gamma} \frac{\partial r_\gamma}{\partial r_{i,\alpha}}$$

and:

$$\frac{\partial s_\beta}{\partial r_\gamma} = \frac{\delta_{\beta\gamma}}{|\boldsymbol{r}|} - \frac{r_\beta r_\gamma}{|\boldsymbol{r}|^3}$$

Finally, we have that:

$$\partial_{i,\alpha} \left[ Y_{\ell'}^{m'} \left( \frac{\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i|} \right) \right] = \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{\delta_{\beta\gamma}}{|\boldsymbol{r}|} - \frac{r_\beta r_\gamma}{|\boldsymbol{r}|^3} \right)(-\delta_{\gamma\alpha}) = \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{r_\beta r_\alpha}{|\boldsymbol{r}|^3} - \frac{\delta_{\beta\alpha}}{|\boldsymbol{r}|} \right) =$$

$$= \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{(r_{j,\beta} + \rho_j s_{n,\beta} - r_{i,\beta})(r_{j,\alpha} + \rho_j s_{n,\alpha} - r_{i,\alpha})}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i|^3} - \frac{\delta_{\alpha\beta}}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i|} \right)$$

and

$$\partial_{j,\alpha} \left[ Y_{\ell'}^{m'} \left( \frac{\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k|} \right) \right] = \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{\delta_{\beta\gamma}}{|\boldsymbol{r}|} - \frac{r_\beta r_\gamma}{|\boldsymbol{r}|^3} \right) \delta_{\gamma\alpha} = \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{\delta_{\beta\alpha}}{|\boldsymbol{r}|} - \frac{r_\beta r_\alpha}{|\boldsymbol{r}|^3} \right) =$$

$$= \frac{\partial Y_{\ell'}^{m'}}{\partial s_\beta} \left( \frac{\delta_{\alpha\beta}}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k|} - \frac{(r_{j,\beta} + \rho_j s_{n,\beta} - r_{k,\beta})(r_{j,\alpha} + \rho_j s_{n,\alpha} - r_{k,\alpha})}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k|^3} \right)$$

Let us now discuss how to efficiently compute the contraction $\langle s, A'\phi \rangle$. To this aim let us split the computation as

$$\langle s, A'\phi \rangle = \sum_j \sum_{\ell,m} [s_j]_\ell^m [A'\phi_j]_\ell^m = \sum_{j \neq i} \sum_{\ell,m} [s_j]_\ell^m [A'\phi_j]_\ell^m + \sum_{\ell,m} [s_i]_\ell^m [A'\phi_i]_\ell^m = I_1 + I_2$$

We shall begin with the case $j \neq i$, and rearrange summations so that the computation is efficient. Let us recall that

$$I_1 = -\sum_{j \neq i} \sum_{\ell,m} \sum_{\ell',m'} \sum_n \frac{4\pi\ell'}{2\ell'+1} \, w_n \, Y_\ell^m(\boldsymbol{s}_n) \, U_j^n \, f_1(j,n,\ell',m') \, [\phi_i]_{\ell'}^{m'} \, [s_j]_\ell^m$$

where, for ease of notation, we set

$$f_1(j,n,\ell',m') = \left[ \left( \frac{\rho_i}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i|} \right)^{\ell'+1} Y_{\ell'}^{m'} \left( \frac{\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_i|} \right) \right]'$$

9

Let us remark that summation occurs over six indices, namely $j, \ell, m, \ell', m', n$. We can rearrange summations as follow

$$I_1 = -\sum_n w_n \sum_{j\neq i} \left( \sum_{\ell'} \frac{4\pi\ell'}{2\ell'+1} \sum_{m'} [\phi_i]_{\ell'}^{m'} f_1(j, n, \ell', m') \right) \left( U_j^n \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) [s_j]_\ell^m \right)$$

If we further define

$$f_2(j, n) = \sum_{\ell'} \frac{4\pi\ell'}{2\ell'+1} \sum_{m'} [\phi_i]_{\ell'}^{m'} f_1(j, n, \ell', m')$$

$$f_3(j, n) = U_j^n \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) [s_j]_\ell^m$$

we can compactly write

$$I_1 = -\sum_n w_n \sum_{j\neq i} f_2(j, n) \, f_3(j, n)$$

Let us recall the bounds on the summation indices:

$$1 \leq n \leq N \quad, \quad 0 \leq \ell, \ell' \leq L \quad, \quad -\ell \leq m \leq \ell \quad, \quad 1 \leq j \leq M$$

Then, provided we can precompute $f_1$, the cost of one evaluation of $f_2$ is $O(L^2)$ and similarly for $f_3$. Thus the total cost of evaluating $I_1$ is $O(M\,N\,L^2)$.

Let us now consider the case $j = i$:

$$I_2 = -\sum_{\ell,m} \left[ \sum_{k\neq j} \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n Y_\ell^m(\boldsymbol{s}_n) f_1(k, \ell', m', n) [\phi_k]_{\ell'}^{m'} + \right.$$

$$\left. -\sum_{\ell',m'} \frac{2\pi}{2\ell'+1} \sum_n w_n Y_\ell^m(\boldsymbol{s}_n) \left( U_j^n \right)' Y_{\ell'}^{m'}(\boldsymbol{s}_n) [\phi_j]_{\ell'}^{m'} \right] [s_j]_\ell^m$$

where, for ease of notation, we set

$$f_1(k, \ell', m', n) = \left[ U_j^n \left( \frac{\rho_k}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k|} \right)^{\ell'+1} Y_{\ell'}^{m'} \left( \frac{\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k}{|\boldsymbol{r}_j + \rho_j \boldsymbol{s}_n - \boldsymbol{r}_k|} \right) \right]'$$

Let us break $I_2$ down into two contributions:

$$I_{2,1} = -\sum_{\ell,m} \sum_{k\neq j} \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n Y_\ell^m(\boldsymbol{s}_n) f_1(k, \ell', m', n) [\phi_k]_{\ell'}^{m'} [s_j]_\ell^m$$

$$I_{2,2} = \sum_{\ell,m} \sum_{\ell',m'} \frac{2\pi}{2\ell'+1} \sum_n w_n Y_\ell^m(\boldsymbol{s}_n) \left( U_j^n \right)' Y_{\ell'}^{m'}(\boldsymbol{s}_n) [\phi_j]_{\ell'}^{m'} [s_j]_\ell^m$$

In the case of $I_{2,1}$, the summation occurs over six indices, namely $\ell, m, k, \ell', m', n$. We can rearrange such summation as

$$I_{2,1} = - \sum_n w_n \sum_{k \neq j} \left( \sum_{\ell'} \frac{4\pi\ell'}{2\ell'+1} \sum_{m'} [\phi_k]_{\ell'}^{m'} f_1(k, \ell', m', n) \right) \left( \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) [s_j]_\ell^m \right)$$

and, by setting

$$f_2(k, n) = \sum_{\ell'} \frac{4\pi\ell'}{2\ell'+1} \sum_{m'} [\phi_k]_{\ell'}^{m'} f_1(k, \ell', m', n)$$

$$f_3(k, n) = \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n)[s_j]_\ell^m$$

we obtain

$$I_{2,1} = - \sum_n w_n \sum_{k \neq j} f_2(k, n) \, f_3(k, n)$$

As before, this quantity can be computed in $O(M\,N\,L^2)$ operations. Finally, for $I_{2,2}$, we can rearrange summations as

$$I_{2,2} = \sum_n w_n \left( \sum_{\ell'} \frac{2\pi}{2\ell'+1} \sum_{m'} Y_{\ell'}^{m'}(\boldsymbol{s}_n)[\phi_j]_{\ell'}^{m'} \right) \left( (U_j^n)' \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) [s_j]_\ell^m \right)$$

and, by setting

$$f_2(n) = \sum_{\ell'} \frac{2\pi}{2\ell'+1} \sum_{m'} Y_{\ell'}^{m'}(\boldsymbol{s}_n)[\phi_j]_{\ell'}^{m'}$$

$$f_3(n) = \left( U_j^n \right)' \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) [s_j]_\ell^m$$

we obtain

$$I_{2,2} = \sum_n w_n \, f_2(n) \, f_3(n)$$