Notes for ddCOSMO/ddPCM

December 21, 2016

1 ddCOSMO

The van der Waals molecular cavity Ω is defined as the union of M spheres Ω_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 ϱ 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 ε_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 Ω, it can be represented by means of an apparent surface charge σ 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 σ 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 Ω_j, it can be represented as

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

for some surface charge σ_j. Each restriction W_j satisfies the following boundary condition:

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

where χ_k is the characteristic function of Ω_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 σ_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_ℓ^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:

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

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 σ_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:

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

where ∇_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 Ψ 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 ϕ be the total electrostatic potential of the solute/solvent system, and Φ 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 ε_s is the macroscopic dielectric permittivity of the solvent. Then the reaction potential satisfies the boundary value problem:

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

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 σ, defined on Γ, that satisfies:

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

Then it can be shown that σ satisfies the integral equation

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

where:

$$
\begin{aligned}
\mathcal{R}_\varepsilon &= 2\pi\frac{\varepsilon+1}{\varepsilon-1}I - \mathcal{D} \\
\mathcal{R}_\infty &= 2\pi I - \mathcal{D} \\
\mathcal{D}\sigma(\boldsymbol{s}) &= \int_\Gamma \nabla\frac{1}{|\boldsymbol{s}-\boldsymbol{s}'|}\cdot\boldsymbol{n}(\boldsymbol{s}')\,\sigma(\boldsymbol{s}')\,d\boldsymbol{s}' \qquad , \qquad \forall\,\boldsymbol{s}\in\Gamma
\end{aligned}
$$

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

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

Those extensions can be more compactly written as

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

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:

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

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

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

and a similar result holds for Φ_ε. 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 α, 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 Φ_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:

$$\begin{pmatrix} A^{\varepsilon}_{11} & \cdots & A^{\varepsilon}_{1M} \\ \vdots & \ddots & \vdots \\ A^{\varepsilon}_{M1} & \cdots & A^{\varepsilon}_{MM} \end{pmatrix} \begin{pmatrix} \Phi^{\varepsilon}_1 \\ \vdots \\ \Phi^{\varepsilon}_M \end{pmatrix} = \begin{pmatrix} A^{\infty}_{11} & \cdots & A^{\infty}_{1M} \\ \vdots & \ddots & \vdots \\ A^{\infty}_{M1} & \cdots & A^{\infty}_{MM} \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \vdots \\ \Phi_M \end{pmatrix}$$

or, in short

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

The entries are given by:

$$[A^{\varepsilon}_{jj}]^{mm'}_{\ell\ell'} = 2\pi \frac{\varepsilon+1}{\varepsilon-1}\, \delta_{\ell\ell'}\delta_{mm'} + \frac{2\pi}{2\ell'+1} \sum_n w_n\, Y^m_\ell(\boldsymbol{s}_n)\, U^n_j\, Y^{m'}_{\ell'}(\boldsymbol{s}_n)$$

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

where, for convenience, we set

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

Let us recall that $L\,X = -\Phi_\varepsilon$, so that the full discretization reads as $A_\varepsilon L\, X = -A_\infty \Phi$. 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

$$F_j = -\langle s, -A'_\infty \Phi - A_\infty \Phi' - A'_\varepsilon L\, X - A_\varepsilon L'\, X \rangle = -\langle s, h \rangle$$

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_ε or, more specifically, their action. To this aim, let us drop the ε-dependency for ease of notation, and refer to the partial derivatives as $\partial_{i,\alpha} = \partial / \partial r_{i,\alpha}$. Since the entries of $[A_{jj}]^{mm'}_{\ell\ell'}$ are functions of $\boldsymbol{r}_j$ only, we obtain:

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

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

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

$$
\begin{aligned}
[(\partial_{i,\alpha} A)\phi_j]_\ell^m = &- \sum_{k\neq j} \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n \times \\
&\partial_{i,\alpha}\left[\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1} Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'} \\
= &- \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n \times \\
&\sum_{k\neq j} \partial_{i,\alpha}\left[\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1} Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'} \\
= &- \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, U_j^n \times \\
&\partial_{i,\alpha}\left[\left(\frac{\rho_i}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|}\right)^{\ell'+1} Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_i|}\right)\right][\phi_i]_{\ell'}^{m'}
\end{aligned}
$$

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

$$
\begin{aligned}
[(\partial_{j,\alpha} A)\phi_j]_\ell^m = &- \sum_{k\neq j} \sum_{\ell',m'} \frac{4\pi\ell'}{2\ell'+1} \sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n) \times \\
&\partial_{j,\alpha}\left[U_j^n\left(\frac{\rho_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)^{\ell'+1} Y_{\ell'}^{m'}\left(\frac{\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k}{|\boldsymbol{r}_j+\rho_j\boldsymbol{s}_n-\boldsymbol{r}_k|}\right)\right][\phi_k]_{\ell'}^{m'} + \\
&+ \sum_{\ell',m'} \frac{2\pi}{2\ell'+1} \sum_n w_n\, Y_\ell^m(\boldsymbol{s}_n)\, \partial_{j,\alpha} U_j^n\, Y_{\ell'}^{m'}(\boldsymbol{s}_n)\, [\phi_j]_{\ell'}^{m'}
\end{aligned}
$$

Notice that:

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

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

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

Let us remark that summation occurs over six indices, namely j, ℓ, m, ℓ', 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 $j = i$:

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

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 ℓ, m, k, ℓ', 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

$$\begin{aligned} f_2(k,n) &= \sum_{\ell'} \frac{4\pi\ell'}{2\ell'+1} \sum_{m'} [\phi_k]_{\ell'}^{m'} \, f_1(k,\ell',m',n) \\ f_3(k,n) &= \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n)[s_j]_\ell^m \end{aligned}$$

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

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

and, by setting

$$\begin{aligned} f_2(n) &= \sum_{\ell'} \frac{2\pi}{2\ell'+1} \sum_{m'} Y_{\ell'}^{m'}(\boldsymbol{s}_n)[\phi_j]_{\ell'}^{m'} \\ f_3(n) &= \left(U_j^n\right)' \sum_{\ell,m} Y_\ell^m(\boldsymbol{s}_n) \, [s_j]_\ell^m \end{aligned}$$

we obtain

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