Notes for ddCOSMO/ddPCM

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1 Intro

Let $\{\boldsymbol{r}_j\}_{1\le j\le M}$ be the centers of domains, and $\{\rho_j\}_{1\le j\le M}$ be the radii. Let us set

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

and define:

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

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

Let us set $\partial_{i,\alpha} = \partial/\partial r_{i,\alpha}$. The action of A is obtained as:

$$[A\phi_{\ j}]_\ell^m = \sum_k \sum_{\ell',m'} [A_{jk}]_{\ell\ell'}^{mm'}\,[\phi_k]_{\ell'}^{m'}$$

and its partial derivative is:

$$\partial_{i,\alpha}[A\phi_{\ j}]_l^m = [(\partial_{i,\alpha}A)\phi_{\ j}]_l^m + [(A\,\partial_{i,\alpha}\phi)_{\ j}]_l^m$$

Let us focus on the first term in the sum. Since the entries of $[A_{jj}]_{\ell\ell'}^{mm'}$ are functions of $\boldsymbol{r}_j$ only, we obtain:

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

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

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:

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

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

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

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

A Appendix