Supporting Information

Pseudocontact shifts from mobile spin labels

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Here we provide more detailed derivation of the equations (28) and Eq. (33) in the main text starting from Eq. (16).

$$\sigma(\mathbf{r}) = -\frac{1}{3}\left[\frac{\nabla_{\mathbf{r}}^{\mathrm{T}}\cdot\boldsymbol{\chi}\cdot\nabla_{\mathbf{r}}}{\nabla^{\mathrm{T}}\cdot\nabla} - \frac{1}{3}\mathrm{Tr}(\boldsymbol{\chi})\right]\rho(\mathbf{r})$$ * MERGEFORMAT

(1)

In the Fourier space this equation can be written as

$$\hat{\sigma}(\mathbf{k}) = -\frac{1}{3}\left[\frac{\mathbf{k}^{\mathrm{T}}\cdot\boldsymbol{\chi}\cdot\mathbf{k}}{\mathbf{k}\cdot\mathbf{k}^{\mathrm{T}}} - \frac{1}{3}\mathrm{Tr}(\boldsymbol{\chi})\right]\hat{\rho}(\mathbf{k})$$ * MERGEFORMAT

(2)

where $\hat{\rho}(\mathbf{k})$ is the Fourier transform of $\rho(\mathbf{r})$ and $\hat{\sigma}(\mathbf{k})$ is the Fourier transform of $\sigma(\mathbf{r})$.

The easiest way to solve Eq. * MERGEFORMAT **(1)** analytically is to expand the probability density in spherical harmonics:

$$\rho(\mathbf{r}) = \sum_{l,m}\alpha_l^m(r)Y_l^m(\hat{\mathbf{r}})$$ * MERGEFORMAT

(3)

where $\alpha_l^m(r)$ are radial functions serving as expansion coefficients in this angular function series:

$$\alpha_l^m(r) = \int_{\Omega}Y_l^{m*}(\hat{\mathbf{r}})\rho(\mathbf{r})\,\mathrm{d}^2\hat{\mathbf{r}}$$ * MERGEFORMAT

(4)

The Fourier transform $\hat{\rho}(\mathbf{k}) = \int\rho(\mathbf{r})\frac{1}{(2\pi)^{3/2}}e^{-i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}^3\mathbf{r}$ is evaluated using the plane wave expansion in terms of spherical harmonics and spherical Bessel functions of the first kind $j_l(kr)$

$$\frac{1}{(2\pi)^{3/2}}e^{-i\mathbf{k}\cdot\mathbf{r}} = \sqrt{\frac{2}{\pi}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^l j_l(kr)Y_l^{m*}(\hat{\mathbf{r}})Y_l^m(\hat{\mathbf{k}})$$ * MERGEFORMAT (5)

$$\hat{\rho}(\mathbf{k})=\sqrt{\frac{2}{\pi}}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}(-i)^{l'}Y_{l'}^{m'}(\hat{\mathbf{k}})\sum_{l,m}\int_{\Omega}Y_{l'}^{m'*}(\hat{\mathbf{s}})Y_{l}^{m}(\hat{\mathbf{s}})\mathrm{d}^{2}\hat{\mathbf{s}}\int_{0}^{\infty}\alpha_{l}^{m}(s)j_{l'}(ks)s^{2}\mathrm{d}s$$ * MERGEFORMAT (6)

Due to orthogonality of spherical harmonics

$$\int_{\Omega}Y_{l'}^{m'*}(\hat{\mathbf{s}})Y_{l}^{m}(\hat{\mathbf{s}})\mathrm{d}^{2}\hat{\mathbf{s}}=\delta_{l'l}\delta_{m'm}$$ * MERGEFORMAT

(7)

Fourier transformed density has a form

$$\hat{\rho}(\mathbf{k})=\sqrt{\frac{2}{\pi}}\sum_{l,m}(-i)^{l}Y_{l}^{m}(\hat{\mathbf{k}})\int_{0}^{\infty}\alpha_{l}^{m}(s)j_{l}(ks)s^{2}\mathrm{d}s$$ * MERGEFORMAT

(8)

So the Fourier transformed pseudocontact shift in terms of the product of spherical harmonics of susceptibility tensor and angular part of the density has a form

$$\hat{\sigma}(\mathbf{k})=-\frac{1}{3}\sqrt{\frac{2}{\pi}}\sum_{l,m}\sum_{m'=-2}^{2}(-i)^{l}\chi_{m'}\alpha_{lm}Y_{2}^{m'}(\hat{\mathbf{k}})Y_{l}^{m}(\hat{\mathbf{k}})\int_{0}^{\infty}\alpha_{l}^{m}(s)j_{l}(ks)s^{2}\mathrm{d}s$$ * MERGEFORMAT

(9)

The rules for product of spherical harmonics in terms of Clebsch-Gordan coefficients

$$Y_{l}^{m}Y_{l'}^{m'}=\sqrt{\frac{(2l+1)(2l'+1)}{4\pi}}\sum_{L=|l-l'|}^{l+l'}\frac{C_{l,0,l',0}^{L,0}C_{l,m,l',m'}^{L,m+m'}}{\sqrt{2L+1}}Y_{L}^{m+m'}$$ * MERGEFORMAT (10)

gives

$$Y_{l}^{m}Y_{2}^{m'}=\sqrt{\frac{5(2l+1)}{4\pi}}\left(\frac{C_{l,0,2,0}^{l-2,0}C_{l,m,2,m'}^{l-2,m+m'}}{\sqrt{2l-3}}Y_{l-2}^{m+m'}+\frac{C_{l,0,l',0}^{l,0}C_{l,m,l',m'}^{l,m+m'}}{\sqrt{2l+1}}Y_{l}^{m+m'}+\frac{C_{l,0,l',0}^{l+2,0}C_{l,m,2,m'}^{l+2,m+m'}}{\sqrt{2l+5}}Y_{l+2}^{m+m'}\right)$$ * MERGEFORMAT (11)

With this substitution in place, Eq. * MERGEFORMAT **(2)** acquires the following form:

$$\hat{\sigma}(\mathbf{k})=-\frac{\sqrt{10}}{6\pi}\sum_{l,m}(-i)^{l}\sqrt{2l+1}\left[\int_{0}^{\infty}j_{l}(ks)\alpha_{l}^{m}(s)s^{2}\mathrm{d}s\right]\sum_{m'=-2}^{2}\chi_{m'}\left[\begin{array}{l}\frac{C_{l,0,2,0}^{l-2,0}C_{l,m,2,m'}^{l-2,m+m'}}{\sqrt{2l-3}}Y_{l-2}^{m+m'}(\hat{\mathbf{k}})+\\ \frac{C_{l,0,2,0}^{l,0}C_{l,m,2,m'}^{l,m+m'}}{\sqrt{2l+1}}Y_{l}^{m+m'}(\hat{\mathbf{k}})+\\ \frac{C_{l,0,2,0}^{l+2,0}C_{l,m,2,m'}^{l+2,m+m'}}{\sqrt{2l+5}}Y_{l+2}^{m+m'}(\hat{\mathbf{k}})\end{array}\right]$$ * MERGEFORMAT (1

To get the final answer we must take the inverse Fourier transform

$$\sigma(\mathbf{r})=\int\hat{\sigma}(\mathbf{k})\frac{1}{(2\pi)^{3/2}}e^{-i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}^{3}\mathbf{k}$$ * MERGEFORMAT (13)

Using the Eq.* MERGEFORMAT (5) where (-*i*) is substituted by i and the orthogonality of spherical harmonics Eq.* MERGEFORMAT (7) the Fourier transform of Eq. * MERGEFORMAT (12). is

$$-\sqrt{\frac{2}{\pi}}\frac{\sqrt{10}}{6\pi}\sum_{l,m}\sqrt{2l+1}\sum_{m'=-2}^{2}\chi_{m'}\left[\begin{array}{l}(-i)^l(i)^{l-2}\frac{\mathrm{C}_{l,0,2,0}^{l-2,0}\mathrm{C}_{l,m,2,m'}^{l-2,m+m'}}{\sqrt{2l-3}}Y_{l-2}^{m+m'}(\hat{\mathbf{r}})\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l-2}(kr)k^2\mathrm{d}s\mathrm{d}k+\\(-i)^l(i)^{l}\frac{\mathrm{C}_{l,0,2,0}^{l,0}\mathrm{C}_{l,m,2,m'}^{l,m+m'}}{\sqrt{2l+1}}Y_{l}^{m+m'}(\hat{\mathbf{r}})\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l}(kr)k^2\mathrm{d}s\mathrm{d}k+\\(-i)^l(i)^{l+2}\frac{\mathrm{C}_{l,0,2,0}^{l+2,0}\mathrm{C}_{l,m,2,m'}^{l+2,m+m'}}{\sqrt{2l+5}}Y_{l+2}^{m+m'}(\hat{\mathbf{r}})\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l+2}(kr)k^2\mathrm{d}s\mathrm{d}k\end{array}\right]$$

The double integrals that make an appearance are all straightforward. Changing the order of integration and integrating the product of two spherical Bessel function with respect to k gives:

$$\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l-2}(kr)k^2\mathrm{d}s\mathrm{d}k=\pi\left(l-\frac{1}{2}\right)r^{l-2}\int_r^\infty\alpha_l^m(s)s^{-l+1}ds \quad \text{* MERGEFORMAT (14)}$$

$$\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l}(kr)k^2\mathrm{d}s\mathrm{d}k=\frac{\pi}{2r^2}\int_0^\infty\alpha_l^m(s)s^2\delta(r-s)ds=\frac{\pi}{2}\alpha_l^m(r) \quad \text{* MERGEFORMAT (15)}$$

$$\int_0^\infty\int_0^\infty\alpha_l^m(s)s^2j_l(ks)j_{l+2}(kr)k^2\mathrm{d}s\mathrm{d}k=\pi\left(l+\frac{3}{2}\right)r^{-l-3}\int_0^r\alpha_l^m(s)s^{l+2}ds \quad \text{* MERGEFORMAT (16)}$$

Taking everything together we obtain the general analytical solution for Eq. * MERGEFORMAT **(1)**:

$$\sigma(\mathbf{r})=-\frac{\sqrt{20}}{12\sqrt{\pi}}\sum_{l,m}\sqrt{2l+1}\sum_{m'=-2}^{2}\chi_{m'}\left(P_{l,m,m'}^{\mathrm{OUT}}(\mathbf{r})+P_{l,m,m'}^{0}(\mathbf{r})+P_{l,m,m'}^{\mathrm{IN}}(\mathbf{r})\right) \quad \text{* MERGEFORMAT (17)}$$

There are three physically different contributions associated with the three integrals of the radial probability density functions in Eqs. * MERGEFORMAT (14)-* MERGEFORMAT (16). The first one corresponds to the integral of the density weighted with a monotonically decreasing function over the region outside the sphere of radius r:

$$P_{l,m,m'}^{\mathrm{OUT}}(\mathbf{r})=-\frac{2l-1}{\sqrt{2l-3}}\mathrm{C}_{l,0,2,0}^{l-2,0}\mathrm{C}_{l,m,2,m'}^{l-2,m+m'}Y_{l-2}^{m+m'}(\hat{\mathbf{r}})r^{l-2}\int_r^\infty\alpha_l^m(s)s^{-l+1}\mathrm{d}s \quad \text{* MERGEFORMAT (18)}$$

The second contribution is proportional to the probability density at the nucleus itself:

$$P_{l,m,m'}^{0}(\mathbf{r})=\frac{1}{\sqrt{2l+1}}\mathrm{C}_{l,0,2,0}^{l,0}\mathrm{C}_{l,m,2,m'}^{l,m+m'}Y_{l}^{m+m'}(\hat{\mathbf{r}})\alpha_l^m(r) \quad \text{* MERGEFORMAT (19)}$$

the most important contribution that is associated with the part of the density that is inside the sphere of radius r:

$$P_{l,m,m'}^{\mathrm{IN}}(\mathbf{r})=-\frac{2l+3}{\sqrt{2l+5}}\mathrm{C}_{l,0,2,0}^{l+2,0}\mathrm{C}_{l,m,2,m'}^{l+2,m+m'}Y_{l+2}^{m+m'}(\hat{\mathbf{r}})r^{-l-3}\int_0^r\alpha_l^m(s)s^{l+2}\mathrm{d}s \quad \text{* MERGEFORMAT (20)}$$

If we assume that there is no paramagnetic centre density outside that sphere, this would allow us to extend the upper integration limit to infinity and the integrals then correspond to the multipole moments of the probability density of the paramagnetic centre:

$$\int_0^r\alpha_l^m(s)s^{l+2}\mathrm{d}s\xrightarrow[r\to\infty]{}I_l^m=\int_0^\infty\left[\int_\Omega Y_l^{m*}(\hat{s})\rho(\mathbf{s})\mathrm{d}^2\hat{s}\right]s^{l+2}\mathrm{d}s \quad \text{* MERGEFORMAT (21)}$$

Outside the bounding sphere PCS is

$$
\begin{aligned}
\sigma(\mathbf{r}) &= -\frac{\sqrt{20}}{12\sqrt{\pi}} \sum_{l,m} \sqrt{2l+1} \sum_{m'=-2}^{2} \chi_{m'} \overbrace{P_{l,m,m'}^{\mathrm{IN}}(\mathbf{r})}^{r\to\infty} \\
&= \frac{\sqrt{20}}{12\sqrt{\pi}} \sum_{l,m} \sqrt{2l+1} \sum_{m'=-2}^{2} \chi_{m'} \frac{2l+3}{\sqrt{2l+5}} \mathrm{C}_{l,0,2,0}^{l+2,0} \mathrm{C}_{l,m,2,m'}^{l+2,m+m'} Y_{l+2}^{m+m'}(\hat{\mathbf{r}}) r^{-l-3} I_l^m
\end{aligned}
$$

* MERGEFORMAT (22)

So the final expression for PCS outside the bounding sphere is

$$
\sigma(\mathbf{r}) = \frac{\sqrt{20}}{12\sqrt{\pi}} \sum_{l,m} \frac{1}{r^{l+3}} \frac{\sqrt{2l+1}(2l+3)}{\sqrt{2l+5}} I_l^m \mathrm{C}_{l,0,2,0}^{l+2,0} \sum_{m'=-2}^{2} \chi_{m'} \mathrm{C}_{l,m,2,m'}^{l+2,m+m'} Y_{l+2}^{m+m'}(\hat{\mathbf{r}})
$$

* MERGEFORMAT (23)