Supporting information for article:

Fast analytical evaluation of intermolecular electrostatic interaction energies using the pseudoatom representation of the electron density. II. The Fourier transform method

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S1. Plane wave expansion of \( \exp(\pm i \mathbf{k} \cdot \mathbf{r}) \) in terms of the associated Legendre polynomials

Define vectors \( \mathbf{r} \) and \( \mathbf{k} \) in the spherical coordinate system:

\[
\mathbf{r} \equiv (r, \theta, \phi) \tag{1}
\]
\[
\mathbf{k} \equiv (k, \bar{\theta}, \bar{\phi}) \tag{2}
\]

The plane wave (Rayleigh) expansion for \( \exp(\pm i \mathbf{k} \cdot \mathbf{r}) \) in terms of complex spherical harmonics \( Y_l^m(\theta, \phi) \) is given by (Geller, 1962; Weissbluth, 1978):

\[
\exp(\pm i \mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left( \frac{(-1)^l (l+m)!}{(l-m)!} \right) P_l^{|m|}(\cos \theta) e^{im\phi} \tag{3}
\]

where symbol * denotes the complex-conjugate, and \( j_\lambda(z) \) is the spherical Bessel function of the first kind (Arfken, 1985; Olver et al., 2018). The complex spherical harmonic function \( Y_l^m(\theta, \phi) \) for \( l \geq 0 \) and \(-l \leq m \leq l\) is defined as (Weissbluth, 1978; Weniger & Steinborn, 1982; Homeier & Steinborn, 1996)

\[
Y_l^m(\theta, \phi) = (-1)^{m+|m|} \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi (l+|m|)!}} P_l^{|m|}(\cos \theta) e^{im\phi} \tag{4}
\]

where functions \( P_l^m(x) \) are the associated Legendre polynomials (Press et al, 1992; Tam, 2008; Wolfram Research, 2018),

\[
P_l^{|m|}(x) = (-1)^{|m|} (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{dx^{|m|}} \tag{5}
\]
\[
P_l^{-|m|}(x) = (-1)^{|m|} (l-|m|)! (l+|m|)! \frac{d^{-|m|} P_l(x)}{dx^{-|m|}} \tag{6}
\]

and functions \( P_l(x) \) are the ordinary (unassociated) Legendre polynomials (Press et al, 1992; Tam, 2008; Wolfram Research, 2018). In this study we follow the notation used in Mathematica (Press et al, 1992; Tam, 2008; Wolfram Research, 2018) according to which the associated Legendre polynomials include the Condon-Shortley phase \((-1)^{|m|} = (-1)^m\) (Condon & Shortley, 1959). Note that equation (4) is valid for both the positive and negative values of \( m \), and is consistent with Mathematica’s function \texttt{SphericalHarmonicY}[l, m, \theta, \phi] \ (Wolfram Research, 2018).

The associated Legendre polynomials for the positive and negative values of \( m \), equations (5) and (6), are related to each other via the following relationship

\[
P_l^m(x) = (-1)^m \frac{(l+m)!}{(l-m)!} P_l^{-m}(x) \tag{7}
\]

which is valid regardless whether \( m \) is positive or negative. Equations (5), (6) and (7) are consistent with Mathematica’s function \texttt{LegendreP}[l, m, x] \ (Wolfram Research, 2018).

Expanding the complex-conjugate spherical harmonic function \( Y_l^m(\bar{\theta}, \bar{\phi}) \) in terms of \( P_l^{-m}(\cos \theta) \).
\[ Y_{\lambda}^{\nu} (\theta, \phi) = (-1)^{\mu + |\nu|} \sqrt{\frac{(2\lambda + 1)(\lambda - \mu)!}{4\pi (\lambda + \mu)!}} \frac{(-1)^{|\mu|} (\lambda + \mu)!}{(\lambda - \mu)!} P_{\lambda}^{-\mu}(\cos \theta) e^{-i\mu\phi} \]  

(8)

and substituting it into the product \( Y_{\lambda}^{\mu}(\theta, \phi)Y_{\lambda}^{\nu}(\bar{\theta}, \bar{\phi}) \) we get

\[ Y_{\lambda}^{\mu}(\theta, \phi)Y_{\lambda}^{\nu}(\bar{\theta}, \bar{\phi}) = \]

\[ (-1)^{\mu + |\nu|} \frac{(2\lambda + 1)(\lambda - \mu)!}{4\pi (\lambda + \mu)!} P_{\lambda}^{\mu}(\cos \theta) e^{-i\mu\phi} \]

\[ \times (-1)^{|\nu|} \frac{(2\lambda + 1)(\lambda - \mu)!}{4\pi (\lambda + \mu)!} (-1)^{|\mu|} \frac{(-1)^{|\mu|} (\lambda + \mu)!}{(\lambda - \mu)!} P_{\lambda}^{-\mu}(\cos \bar{\theta}) e^{-i\mu\bar{\phi}} = \]

\[ (-1)^{|\nu|} \frac{(2\lambda + 1)(\lambda - \mu)!}{4\pi (\lambda + \mu)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) e^{i\mu(\phi - \bar{\phi})} \]

(9)

Inserting this result into the expansion for \( \exp(\pm i\mathbf{k} \cdot \mathbf{r}) \) gives

\[ \exp(\pm i\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{\lambda=0}^{\infty} \left( \sum_{\mu=-\lambda}^{\lambda} \left( \frac{(-1)^{|\mu|} (\lambda + \mu)!}{4\pi (\lambda + \mu)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) e^{i\mu(\phi - \bar{\phi})} \right) \right) \]

(10)

Cancelling out the two \( 4\pi \) factors, moving the \( \mu \)-independent terms out of the inner sum, and applying Euler’s formula \( e^{ix} = \cos x + i \sin x \) results in

\[ \exp(\pm i\mathbf{k} \cdot \mathbf{r}) = \sum_{\lambda=0}^{\infty} \left( 2\lambda + 1 \right) \frac{(-1)^{|\nu|} (\lambda + \mu)!}{4\pi (\lambda + \mu)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \left( \cos(\mu(\phi - \bar{\phi})) + i \sin(\mu(\phi - \bar{\phi})) \right) \]

(11)

Consider the expanded inner sum, and note that terms with both the positive and negative \( \mu \) are present:

\[ \sum_{\mu=-\lambda}^{\lambda} \left( \frac{(-1)^{|\mu|} (\lambda + \mu)!}{4\pi (\lambda + \mu)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \cos(\mu(\phi - \bar{\phi})) + i P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \sin(\mu(\phi - \bar{\phi})) \right) \]

(12)

Using the well-known trigonometric identities \( \sin(-x) = -\sin(x) \) and \( \cos(-x) = \cos(x) \), and expressing the associated Legendre polynomial with \( \mu < 0 \) in terms of that with \( \mu > 0 \) via equation (6),

\[ P_{\lambda}^{-|\mu|}(\cos \theta) = (-1)^{|\mu|} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{\mu}(\cos \theta) \]

(13)

we get for the \( \sin(\ldots) \) terms:

\( \mu > 0 \):

\[ iP_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \sin(\mu(\phi - \bar{\phi})) = (-1)^{|\mu|} \frac{(\lambda + |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \sin(\mu(\phi - \bar{\phi})) \]

\( \mu < 0 \):

\[ -iP_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \sin(\mu(\phi - \bar{\phi})) = (-1)^{|\mu|} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{\mu}(\cos \theta) P_{\lambda}^{-\mu}(\cos \bar{\theta}) \sin(\mu(\phi - \bar{\phi})) \]

\( \mu = 0 \):

\[ iP_{\lambda}^{0}(\cos \theta) P_{\lambda}^{0}(\cos \bar{\theta}) \sin(0(\phi - \bar{\phi})) = 0 \]
It follows that the sum of all the sin(...) terms in equation (12) is zero, and thus they can be safely eliminated from the summation. For the cos(...) terms,

\[
\mu > 0 : P_{\lambda}^{\lambda|\mu|}(\cos \theta)P_{\lambda}^{-|\mu|}(\cos \tilde{\theta}) \cos(\mu\lambda(\phi - \tilde{\phi})) = (-1)^{|\mu|} \frac{(\lambda - |\mu|)l!}{(\lambda + |\mu|)!} P_{\lambda}^{|\mu|}(\cos \theta)P_{\lambda}^{-|\mu|}(\cos \tilde{\theta}) \cos(\mu\lambda(\phi - \tilde{\phi}))
\]

\[
\mu < 0 : P_{\lambda}^{-|\mu|}(\cos \theta)P_{\lambda}^{\lambda|\mu|}(\cos \tilde{\theta}) \cos(-\mu\lambda(\phi - \tilde{\phi})) = (-1)^{|\mu|} \frac{(\lambda - |\mu|)l!}{(\lambda + |\mu|)!} P_{\lambda}^{\lambda|\mu|}(\cos \theta)P_{\lambda}^{-|\mu|}(\cos \tilde{\theta}) \cos(-\mu\lambda(\phi - \tilde{\phi}))
\]

\[
\mu = 0 : P_{\lambda}^{0}(\cos \theta)P_{\lambda}^{0}(\cos \tilde{\theta}) \cos(0(\phi - \tilde{\phi})) = P_{\lambda}^{0}(\cos \theta)P_{\lambda}^{0}(\cos \tilde{\theta})
\]

Because terms for the positive and negative \(\mu\) are the same, we can limit the summation over \(\mu\) to the non-negative values only:

\[
\exp(\pm ik \cdot r) = \sum_{\lambda=0}^{\infty} (2\lambda + 1)(\pm i)^{\lambda} j_{\lambda}(kr) \\
\times \sum_{\mu=0}^{l} \epsilon_{\mu}(-1)^{|\mu|} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{|\mu|}(\cos \theta)P_{\lambda}^{-|\mu|}(\cos \tilde{\theta}) \cos(\mu\lambda(\phi - \tilde{\phi}))
\]

(14)

where \(\epsilon_{\mu}\) is defined as in Morse & Feshbach (1953) and Geller (1963)

\[
\epsilon_{0} = 1 \quad \text{for} \quad \mu = 0, \quad \text{and} \quad \epsilon_{\mu} = 2 \quad \text{for} \quad \mu > 0, \quad \text{or simply} \quad \epsilon_{\mu} = 2 - \delta_{\mu,0}
\]

Note that there is only one \(\mu = 0\) term, while all the \(\mu > 0\) terms need to be counted twice. Finally, since \((-1)^{|\mu|}(-1)^{|\mu|} = 1\), the desired expression for \(\exp(\pm ik \cdot r)\) becomes

\[
\exp(\pm ik \cdot r) = \sum_{\lambda=0}^{\infty} (2\lambda + 1)(\pm i)^{\lambda} j_{\lambda}(kr) \\
\times \sum_{\mu=0}^{l} \epsilon_{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{|\mu|}(\cos \theta)P_{\lambda}^{-|\mu|}(\cos \tilde{\theta}) \cos(\mu\lambda(\phi - \tilde{\phi}))
\]

(15)

which agrees with the expression given for example in Morse & Feshbach (1953), Geller (1963) and Coppens (1997). Note that since \(\cos(\mu\lambda(\phi - \tilde{\phi})) = \cos(-\mu\lambda(\phi - \tilde{\phi})) = \cos(\mu\lambda(\tilde{\phi} - \phi))\), it is clear that the complex conjugation can be freely exchanged between the two spherical harmonic functions.
S2. Fourier transform of Slater-type function with real spherical harmonics

The unnormalized Slater-type function (Slater, 1932) is given by

\[ \chi(r, \theta, \phi) = r^{n-1} e^{-\epsilon r} y_n^m(\theta, \phi) \]  

where all the terms are as defined in the main body of the manuscript. The Fourier transform of \( \chi(r) \), \( F(k) \), is (Geller, 1963)

\[ F(k) = \int \exp(i k \cdot r) \chi(r) \, dr \]  

Expanding the \( \exp(i k \cdot r) \) term as described in Section S1, defining \( y_n^m(\theta, \phi) \) in terms of the associated Legendre polynomials (see equations (3) and (4) in the main body of the manuscript), and switching to the spherical coordinate system we get:

\[ F(k) = \int_0^{2\pi} \int_0^\infty \int_0^\infty (2\lambda + 1) i^\lambda j_\lambda(kr) \sum_{\mu=0}^\lambda \epsilon_\mu (\lambda - |\mu|)! (\lambda + |\mu|)! P_\lambda^{i|\mu|}(\cos \theta) P_\lambda^{j|\mu|}(\cos \theta) \cos(|\mu|(\phi - \tilde{\phi})) \times r^{-1} e^{-\epsilon r} j_\lambda(kr) \, dr \]

Rearranging the integrals and the sums gives

\[ F(k) = (-1)^{|m|} N_{l,m} \sum_{\lambda=0}^\infty (2\lambda + 1) i^\lambda \sum_{\mu=0}^\lambda \epsilon_\mu (\lambda - |\mu|)! (\lambda + |\mu|)! P_\lambda^{i|\mu|}(\cos \theta) P_\lambda^{j|\mu|}(\cos \theta) \int_0^\infty r^{-2} e^{-\epsilon r} j_\lambda(kr) \, dr \]

The radial integral can be simplified to

\[ \int_0^\infty r^{-2} e^{-\epsilon r} j_\lambda(kr) \, dr = \int_0^\infty r^{n+1} e^{-\epsilon r} j_\lambda(kr) \, dr \]

The angular integral over \( \phi \) is (Geller, 1963)

\[ \int_0^{2\pi} \cos(|\mu|(\phi - \tilde{\phi})) \frac{\cos(|m|\phi)}{\sin(|m|\phi)} \, d\phi = \frac{2\pi}{\epsilon_\mu} \cos(|m|\tilde{\phi}) \sin(|m|\phi) \delta_{|\mu|,|m|} \]

where \( \epsilon_\mu \) is defined as in Morse & Feshbach (1953) and Geller (1963)

\[ \epsilon_0 = 1 \text{ for } \mu = 0, \text{ and } \epsilon_\mu = 2 \text{ for } \mu > 0, \text{ or simply } \epsilon_\mu = 2 - \delta_{\mu,0} \]

Since the \( \phi \) integral is non-zero only if \( m = |\mu| \), the \( \theta \) integral simplifies to (Geller, 1963):

\[ \int_0^\pi P_\lambda^{i|\mu|}(\cos \theta) P_\lambda^{j|\mu|}(\cos \theta) \sin \theta \, d\theta = \frac{2}{2l + 1} \frac{(l + |m|)!}{(l - |m|)!} \delta_{\lambda,l} \]
Thus, the only term that survives in the double sum is the one with $\lambda = l$ and $|\mu| = |m|$. As such, the integral $F_{nlm}(k)$ becomes:

$$ F(k) = (-1)^{|m|} N_{l,m} f_{l}^{(m)}(\cos \theta) \left\{ \frac{\cos(|m|\phi)}{\sin(|m|\phi)} \right\} 4\pi i l \int_{0}^{\infty} r^{n+1} e^{-\zeta r j_{l}(kr)} dr $$

(23)

Because

$$ y_{l}^{m}(\theta, \phi) = (-1)^{|m|} N_{l,m} f_{l}^{(m)}(\cos \theta) \left\{ \frac{\cos(|m|\phi)}{\sin(|m|\phi)} \right\} $$

(24)

the final expression for $F(k)$ is

$$ F(k) = y_{l}^{m}(\theta, \phi) 4\pi i l \int_{0}^{\infty} r^{n+1} e^{-\zeta r j_{l}(kr)} dr = f_{nl}(k) y_{l}^{m}(\theta, \phi) $$

(25)

where

$$ f_{nl}(k) = 4\pi i l \int_{0}^{\infty} r^{n+1} e^{-\zeta r j_{l}(kr)} dr $$

(26)

which agrees with expressions given by Geller (1963), Silverstone (1966), Coppens (1997) and others.

S3. The angular integral $d_{abl}(\theta, \phi)$

The total angular integral $d_{abl}(\theta, \phi)$ is defined as:

$$ d_{abl}(\theta, \phi) = \frac{(-1)^{l}(2\lambda + 1)}{4\pi} \times \sum_{\mu=0}^{2\lambda} e_{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{l}^{(\lambda)}(\cos \theta) \int_{0}^{2\pi} \int_{0}^{\pi} y_{l}^{m_{a}}(\theta, \phi) y_{l}^{m_{b}}(\theta, \phi) P_{l}^{(\lambda)}(\cos \theta) \cos(|\mu|/\phi - \phi)) \sin \theta \, d\theta 
\d\phi $$

(27)

Introduction of the auxiliary angular integral $\Omega_{l_{a},m_{a},l_{b},m_{b},\lambda,\mu}(\phi)$.

$$ \Omega_{l_{a},m_{a},l_{b},m_{b},\lambda,\mu}(\phi) = \sum_{\mu=0}^{2\lambda} e_{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{l}^{(\lambda)}(\cos \theta) \sin \theta \, d\theta 
\d\phi $$

(28)

simplifies equation (27) as follows:

$$ d_{abl}(\theta, \phi) = \frac{(-1)^{l}(2\lambda + 1)}{4\pi} \sum_{\mu=0}^{2\lambda} e_{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{l}^{(\lambda)}(\cos \theta) \Omega_{l_{a},m_{a},l_{b},m_{b},\lambda,\mu}(\phi) $$

(29)

Thus, the problem is reduced to evaluation of the integral $\Omega_{l_{a},m_{a},l_{b},m_{b},\lambda,\mu}(\phi)$. Expanding the real spherical harmonic functions in terms of the associated Legendre polynomials, we get:

$$ \Omega_{l_{a},m_{a},l_{b},m_{b},\lambda,\mu}(\phi) = \frac{(-1)^{l}|m_{a}|+|m_{b}|}{N_{l_{a},m_{a}} N_{l_{b},m_{b}}} \int_{0}^{\pi} p_{l_{a}}^{m_{a}}(\cos \theta) p_{l_{b}}^{m_{b}}(\cos \theta) p_{l}^{(\lambda)}(\cos \theta) \sin \theta \, d\theta $$

(30)
where the normalization factors \( N_{t,\lambda} \) and \( N_{b,\mu} \) are defined via equation (4) in the main body of the manuscript. Representing the integrals over \( \Phi \) and \( \tilde{\Phi} \) as

\[
\Phi_{m_a,m_b,|\lambda|}(\phi) = \int_0^{2\pi} \left( \frac{\cos(|m_a|\Phi)}{\sin(|m_a|\Phi)} \right) \left( \frac{\cos(|m_b|\Phi)}{\sin(|m_b|\Phi)} \right) \cos(|\lambda|(\phi - \Phi)) \, d\Phi
\]

and

\[
\Theta_{t,\lambda,m_a,l_b,m_b,\lambda,|\mu|} = \int_0^{\pi} p_1^{m_a} |\cos \theta| p_2^{m_b} |\cos \theta| p_3^{|\mu|} |\cos \theta| \sin \theta \, d\theta,
\]

the expressions for \( \Omega_{t,\lambda,m_a,l_b,m_b,\lambda,|\mu|} \) and \( d_{ab\lambda}(\theta, \phi) \) become:

\[
\Omega_{t,\lambda,m_a,l_b,m_b,\lambda,|\mu|} = (-1)^{|m_a|+|m_b|} N_{t,\lambda} N_{b,\mu} \Phi_{m_a,m_b,|\lambda|}(\phi) \Theta_{t,\lambda,m_a,l_b,m_b,\lambda,|\mu|}
\]

\[
d_{ab\lambda}(\theta, \phi) = \frac{(-1)^{|m_a|+|m_b|+\lambda+1}}{4\pi} N_{t,\lambda} N_{b,\mu} \sum_{\mu=0}^{\lambda} \epsilon_{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} p_1^{m_a} |\cos \theta| p_2^{m_b} |\cos \theta| p_3^{\lambda} |\cos \theta| \sin (|\mu|\theta) \Phi_{m_a,m_b,|\lambda|}(\phi) \Theta_{t,\lambda,m_a,l_b,m_b,\lambda,|\mu|}
\]

### S3.1. The integral \( \Phi_{m_a,m_b,|\lambda|}(\phi) \)

The integral over \( \tilde{\Phi} \), \( \Phi_{m_a,m_b,|\lambda|}(\phi) \),

\[
\Phi_{m_a,m_b,|\lambda|}(\phi) = \int_0^{2\pi} \left( \frac{\cos(|m_a|\Phi)}{\sin(|m_a|\Phi)} \right) \left( \frac{\cos(|m_b|\Phi)}{\sin(|m_b|\Phi)} \right) \cos(|\lambda|(\phi - \Phi)) \, d\Phi
\]

can be evaluated by expanding \( \cos(|\lambda|(\phi - \Phi)) \) as

\[
\cos(|\lambda|(\phi - \Phi)) = \cos(|\lambda\phi - |\lambda|\Phi) = \cos(|\lambda\phi|) \cos(|\lambda|\Phi) + \sin(|\lambda\phi|) \sin(|\lambda|\Phi)
\]

This separates the integral \( \Phi_{m_a,m_b,|\lambda|}(\phi) \) into two terms:

\[
\Phi_{m_a,m_b,|\lambda|}(\phi) = \cos(|\lambda\phi|) \Phi_{m_a,m_b,|\lambda|}^c(\phi) + \sin(|\lambda\phi|) \Phi_{m_a,m_b,|\lambda|}^s(\phi)
\]

where

\[
\Phi_{m_a,m_b,|\lambda|}^c(\phi) = \int_0^{2\pi} \left( \frac{\cos(|m_a|\Phi)}{\sin(|m_a|\Phi)} \right) \left( \frac{\cos(|m_b|\Phi)}{\sin(|m_b|\Phi)} \right) \cos(|\lambda\phi|) \, d\Phi
\]

\[
\Phi_{m_a,m_b,|\lambda|}^s(\phi) = \int_0^{2\pi} \left( \frac{\cos(|m_a|\Phi)}{\sin(|m_a|\Phi)} \right) \left( \frac{\cos(|m_b|\Phi)}{\sin(|m_b|\Phi)} \right) \sin(|\lambda\phi|) \, d\Phi
\]
The two integrals are very similar, and can be described by the general integral $\Phi'_{m_1,m_2,m_3}$:

$$
\Phi'_{m_a,m_b,m_c} = \int_0^{2\pi} \left( \frac{\cos(|m_a|\phi)}{\sin(|m_a|\phi)} \right) \left( \frac{\cos(|m_b|\phi)}{\sin(|m_b|\phi)} \right) \left( \frac{\cos(|m_c|\phi)}{\sin(|m_c|\phi)} \right) d\phi
$$

(40)

The integral $\Phi'_{m_a,m_b,m_c}$ is non-zero only if the following two conditions are met:

$$
|m_c| \in \{|m_a| - |m_b|, |m_a| + |m_b|\}
$$

(41)

$$
\varsigma_c = s_a s_b
$$

(42)

where

$$
s_a = \begin{cases} +1 & \text{if } m_a \geq 0 \\ -1 & \text{if } m_a < 0 \end{cases} \quad s_b = \begin{cases} +1 & \text{if } m_b \geq 0 \\ -1 & \text{if } m_b < 0 \end{cases} \quad s_c = \begin{cases} +1 & \text{if } m_c \geq 0 \\ -1 & \text{if } m_c < 0 \end{cases}
$$

(43)

Thus, the summation over $\mu$ in expressions (27), (29) and (34) for a given $\lambda$ is limited to

$$
|\mu| \in \{|m_a| - |m_b|, |m_a| + |m_b|\} \quad \text{and} \quad |\mu| \leq \lambda
$$

(44)

The final expression for integral $\Phi_{m_a,m_b,|\lambda|}(\phi)$ is

$$
\Phi_{m_a,m_b,|\lambda|}(\phi) = \cos(|\mu|\phi) \Phi'_{m_a,m_b,|\lambda|} + \sin(|\mu|\phi) \Phi'_{m_a,m_b,|\lambda|}
$$

(45)

where the numerical values of integral $\Phi'_{m_a,m_b,m_c}$ for the allowed values of $m_a$, $m_b$, and $m_c$ are:

1) If $m_a = m_b = m_c = 0$, $\Phi'_{m_a,m_b,m_c} = 2\pi$

2) If ( $m_a = 0$ and $s_b s_c > 0$ ) or ( $m_b = 0$ and $s_a s_c > 0$ ) or ( $m_c = 0$ and $s_a s_b > 0$ ),

$$
\Phi'_{m_a,m_b,m_c} = \pi
$$

3) Define $\eta_1 = \delta_{|m_a| - |m_b| - |m_c|,0} \frac{\pi}{2}$, $\eta_2 = \delta_{|m_a| + |m_b| - |m_c|,0} \frac{\pi}{2}$, $\eta_3 = \delta_{|m_a| - |m_b| + |m_c|,0} \frac{\pi}{2}$, and $\eta_4 = \delta_{|m_a| + |m_b| + |m_c|,0} \frac{\pi}{2}$.

a) If $m_a > 0$ and $m_b > 0$ and $m_c > 0$, $\Phi'_{m_a,m_b,m_c} = \eta_1 + \eta_2 + \eta_3 + \eta_4$

b) If $m_a > 0$ and $m_b < 0$ and $m_c < 0$, $\Phi'_{m_a,m_b,m_c} = -\eta_1 + \eta_2 + \eta_3 - \eta_4$

c) If $m_a < 0$ and $m_b > 0$ and $m_c < 0$, $\Phi'_{m_a,m_b,m_c} = \eta_1 + \eta_2 - \eta_3 - \eta_4$

d) If $m_a < 0$ and $m_b < 0$ and $m_c > 0$, $\Phi'_{m_a,m_b,m_c} = \eta_1 - \eta_2 + \eta_3 - \eta_4$
S3.2. The integral $\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}$

The integral over $\bar{\theta}$,

$$\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = \int_0^\pi p_{l_a}^{|m_a|}(\cos \bar{\theta})p_{l_b}^{|m_b|}(\cos \bar{\theta})P_\lambda^{|\mu|}(\cos \bar{\theta}) \sin \bar{\theta} \, d\bar{\theta}$$

(46)

is an overlap integral over three associated Legendre polynomials. It is known in quantum mechanics as the “Gaunt integral”. Solutions for this integral haven been given by Gaunt (1929), Racah (1942), Condon & Shortley (1959), Slater (1960), and recently by Dong & Lemus (2002). The Gaunt integral must satisfy the following conditions (Slater, 1960):

a) $l_a$, $l_b$, and $\lambda$ satisfy the so-called “triangular condition”, i.e.

$$|l_a - l_b| \leq \lambda \leq l_a + l_b$$

(47)

b) the sum of $l_a$, $l_b$, and $\lambda$ is an even number

$$l_a + l_b + \lambda = 2n$$

(48)

where $n$ is an integer.

c) the largest of $|m_a|$, $|m_b|$ and $|\mu|$ is the sum of the other two values; note that this condition is automatically satisfied for all non-zero values of the integral $\Phi_{m_a,m_b,|\mu|}(\phi)$.

It follows that the summation over $\lambda$ in the expression for $I^{(N)}(r)$ (equation 28 in the main body of the manuscript) is limited to the following terms:

$$\lambda \in \{l_a + l_b, l_a + l_b - 2, \ldots , |l_a - l_b|\}$$

(49)

When the non-zero conditions are satisfied, the solutions for integral $\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}$ are (Dong & Lemus, 2002):

1) If $|\mu|=|m_a| + |m_b|$,

$$\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = 2(-1)^{|\mu|} \left( \frac{(l_a+|m_a|)(l_b+|m_b|)(\lambda+|\mu|)!}{(l_a-|m_a|)(l_b-|m_b|)(\lambda-|\mu|)!} \right)^{1/2} \binom{\lambda}{|\mu|} \Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|}$$

(50)

where $\binom{\lambda}{|\mu|}$ and $\binom{l_a}{|m_a|}$ are the 3-j symbols (Edmonds, 1957). Denoting

$$\Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = 2(-1)^{|\mu|} \binom{l_a}{|m_a|} \binom{l_b}{|m_b|} \binom{\lambda}{|\mu|}$$

(51)

we get for $\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}$:

$$\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = \frac{(l_a + |m_a|)! (l_b + |m_b|)! (\lambda + |\mu|)!}{(l_a - |m_a|)! (l_b - |m_b|)! (\lambda - |\mu|)!}^{1/2} \Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|}$$

(52)
2) If \( |\mu| = |m_a| - |m_b| \),

\[
\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = 2(-1)^{\xi-|m_a|+|m_b|} \binom{l_a + |m_a|}{l_a - |m_a|} \binom{l_b + |m_b|}{l_b - |m_b|} \frac{1}{(l_a + |m_a|)! (l_b + |m_b|)! (\lambda + |\mu|)! (\lambda - |\mu|)!} \frac{l_a}{0} \frac{l_b}{0} \frac{\lambda}{0} \frac{|m_a|}{|m_b|} \frac{|m_b|}{|m_a|} \frac{\lambda}{\lambda}
\]

(53)

where \((\text{Dong} \& \text{Lemus}, 2002)\)

\[
\xi = \begin{cases} 
|m_a| & \text{if } |m_b| \geq |m_a| \\
|m_b| & \text{if } |m_b| < |m_a| 
\end{cases}
\]

(54)

Denoting

\[
\Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = 2(-1)^{\xi-|m_a|+|m_b|} \binom{l_a + |m_a|}{l_a - |m_a|} \binom{l_b + |m_b|}{l_b - |m_b|} \frac{1}{(l_a + |m_a|)! (l_b + |m_b|)! (\lambda + |\mu|)! (\lambda - |\mu|)!} \frac{l_a}{0} \frac{l_b}{0} \frac{\lambda}{0} \frac{|m_a|}{|m_b|} \frac{|m_b|}{|m_a|} \frac{\lambda}{\lambda}
\]

(55)

the expression for \(\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}\) becomes identical to that in the first case:

\[
\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = (l_a + |m_a|)! (l_b + |m_b|)! (\lambda + |\mu|)! (\lambda - |\mu|)! (l_a - |m_a|)! (l_b - |m_b|)! \frac{1}{\lambda} \Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|}
\]

(56)

**S3.3. The angular integral \(d_{ab\lambda}(\theta, \phi)\) in terms of the associated Legendre polynomials**

Taking into account the conditions for which the integrals \(\Phi_{m_a,m_b,|\lambda|}\) and \(\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}\) are not zero, the expression for \(d_{ab\lambda}(\theta, \phi)\) can be re-written as

\[
d_{ab\lambda}(\theta, \phi) = \frac{(-1)^{|m_a|+|m_b|+\lambda}(2\lambda + 1)}{4\pi} N_{l_a,m_a} N_{l_b,m_b} \sum_{\mu} \epsilon_{\mu} (\frac{\lambda - |\mu|}{\lambda + |\mu|})^{\lambda} (\cos \theta) \Phi_{m_a,m_b,|\mu|}(\phi) \Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}
\]

(57)

where the conditions for \(\mu\) are defined via equation (44):

\[
\mu \in \{ |m_a| - |m_b|, |m_a| + |m_b| \} \quad \text{and} \quad \mu \leq \lambda
\]

Expanding \(N_{l_a,m_a}\) and \(N_{l_b,m_b}\) as

\[
N_{l_a,m_a} = \left[ \frac{(2l_a + 1)}{2(1 + \delta_{m_a,0}) \pi} \right]^{1/2} \binom{l_a}{l_a} \binom{l_a + |m_a|}{l_a - |m_a|} \binom{\lambda - |m_a|}{\lambda + |m_a|}
\]

(58)

\[
N_{l_b,m_b} = \left[ \frac{(2l_b + 1)}{2(1 + \delta_{m_b,0}) \pi} \right]^{1/2} \binom{l_b}{l_b} \binom{l_b + |m_b|}{l_b - |m_b|} \binom{\lambda - |m_b|}{\lambda + |m_b|}
\]

(59)

and re-writing \(\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|}\) as

\[
\Theta_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = \left( \frac{(l_a + |m_a|)! (l_b + |m_b|)! (\lambda + |\mu|)! (\lambda - |\mu|)!}{(l_a - |m_a|)! (l_b - |m_b|)! (\lambda - |\mu|)! (\lambda + |\mu|)!} \right)^{1/2} \Theta'_{l_a,m_a,l_b,m_b,\lambda,|\mu|}
\]

we get for \(d_{ab\lambda}(\theta, \phi)\)
\[
d_{ab\ell}(\theta, \phi) = \frac{(-1)^{|m_a|+|m_b|+\lambda}(2\lambda+1)}{4\pi} \frac{(2l_a + 1)}{(1 + \delta_{m_a,0})} \frac{(2l_b + 1)}{(1 + \delta_{m_b,0})} \frac{(l_a - |m_a|)!}{(l_a + |m_a|)!} \frac{(l_b - |m_b|)!}{(l_b + |m_b|)!} \left[ \frac{(2l_b + 1)}{2(1 + \delta_{m_b,0}) \pi (l_b + |m_b|)!} \right]^{1/2} \times \sum_{\mu} \epsilon_\mu \left( \frac{\lambda - |\mu|}{\lambda + |\mu|} \right) \! p^{\mu}_{\lambda}(\cos \theta) \Phi_{m_a,m_b,\mu}(\phi) \left( \frac{(l_a + |m_a|)!}{(l_a - |m_a|)!} \right) \left( \frac{(l_b + |m_b|)!}{(l_b - |m_b|)!} \right) \left( \frac{(\lambda + |\mu|)!}{(\lambda - |\mu|)!} \right) \frac{1}{\sqrt{2\pi}} \right]^{1/2} \times \sum_{\mu} \epsilon_\mu \left( \frac{\lambda - |\mu|}{\lambda + |\mu|} \right) \! p^{\mu}_{\lambda}(\cos \theta) \Phi_{m_a,m_b,\mu}(\phi) \theta_{\ell,\mu,m_a,l_a,m_b,l_b}\]  

(60)

After cancelling out the identical terms in numerator and denominator, the final expression for \(d_{ab\ell}(\theta, \phi)\) becomes

\[
d_{ab\ell}(\theta, \phi) = (-1)^{|m_a|+|m_b|+\lambda}(2\lambda+1) \frac{1}{8\pi^2} \frac{(2l_a + 1)}{(1 + \delta_{m_a,0})} \frac{(2l_b + 1)}{(1 + \delta_{m_b,0})} \frac{(l_a - |m_a|)!}{(l_a + |m_a|)!} \frac{(l_b - |m_b|)!}{(l_b + |m_b|)!} \left[ \frac{(2l_b + 1)}{2(1 + \delta_{m_b,0}) \pi (l_b + |m_b|)!} \right]^{1/2} \times \sum_{\mu} \epsilon_\mu \left( \frac{\lambda - |\mu|}{\lambda + |\mu|} \right) \! p^{\mu}_{\lambda}(\cos \theta) \Phi_{m_a,m_b,\mu}(\phi) \theta_{\ell,\mu,m_a,l_a,m_b,l_b} \]  

(61)

where \(\epsilon_\mu\) and \(\mu\) are defined as:

\[
\epsilon_0 = 1 \text{ for } \mu = 0, \text{ and } \epsilon_\mu = 2 \text{ for } \mu > 0, \text{ or simply } \epsilon_\mu = 2 - \delta_{\mu,0} \\
\mu \in \{|m_a| - |m_b|, |m_a| + |m_b|\} \text{ and } \mu \leq \lambda
\]

S3.4. The angular integral \(d_{ab\ell}(\theta, \phi)\) in terms of the R-Gaunt coefficients

Equation (61), while not very elegant, is computationally efficient because only two 3-j symbols need to be evaluated for each allowed value of \(\mu\). Alternatively, the integral \(d_{ab\ell}(\theta, \phi)\) can be expressed in a more aesthetically pleasing form in terms of overlap integrals over three real spherical harmonics (Coppens, 1997), a.k.a. real spherical harmonics coupling coefficients (Homeier & Steinborn, 1996; Coppens, 1997) and R-Gaunt coefficients (Homeier & Steinborn, 1996;). We start by considering the integral \(\Omega(\phi)\)

\[
\Omega_{\ell_a,m_{a},l_{b},m_{b},\lambda,\mu}(\phi) = \int_0^{2\pi} \int_0^\pi y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) \cos(|\mu| \phi - \bar{\phi}) \sin(\theta) \sin(\theta) d\theta d\bar{\phi} 
\]

Expanding \(\cos(|\mu| \phi - \bar{\phi})\) as

\[
\cos(|\mu| \phi - \bar{\phi}) = \cos(|\mu| \phi) \cos(|\mu| \phi) + \sin(|\mu| \phi) \sin(|\mu| \phi) 
\]

separates the integral \(\Omega_{\ell_a,m_{a},l_{b},m_{b},\lambda,\mu}(\phi)\) into two integrals:

\[
\Omega_{\ell_a,m_{a},l_{b},m_{b},\lambda,\mu}(\phi) = \cos(|\mu| \phi) \int_0^{2\pi} \int_0^\pi y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) \cos(|\mu| \phi) \sin(\theta) d\theta d\bar{\phi} 
\]

(62)

+ \sin(|\mu| \phi) \int_0^{2\pi} \int_0^\pi y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) \sin(|\mu| \phi) \sin(\theta) d\theta d\bar{\phi}

Because the real spherical harmonics are defined as
\[ y_l^m(\theta, \phi) = (-1)^{|m|} N_{l,m} p_l^{|m|}(\cos \theta) \begin{cases} \cos(m \phi), m > 0 \\ \sin(m \phi), m < 0 \end{cases} \quad (l > 0) \]  

(63)

with

\[ N_{l,m} = \left( \frac{(2l + 1)(l - |m|)!}{2(1 + \delta_{m,0})\pi (l + |m|)!} \right)^{1/2} \]

(64)

the associated Legendre functions in the integrals can be combined with the sine and cosine functions to give the “unnormalized” real spherical harmonics:

\[ p_l^{|\mu|}(\cos \theta) \cos(|\mu| \phi) = (-1)^{|\mu|} N_{l,|\mu|}^{-1} y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \]

(65)

\[ p_l^{|\mu|}(\cos \theta) \sin(|\mu| \phi) = (-1)^{|\mu|} N_{l,|\mu|}^{-1} y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \]

(66)

where

\[ N_{l,|\mu|}^{-1} = \left( \frac{2(1 + \delta_{|\mu|,0})\pi (\lambda + |\mu|)!}{(2\lambda + 1)(\lambda - |\mu|)!} \right)^{1/2} \]

(67)

Inserting those into equation (62) gives:

\[ \Omega_{l,m_a,l_b,m_b,|\mu|}(\phi) = \cos(|\mu| \phi) (-1)^{|\mu|} N_{l,|\mu|}^{-1} \int_0^{2\pi} \int_0^{2\pi} y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \sin \theta \, d\theta \, d\phi + \sin(|\mu| \phi) (-1)^{|\mu|} N_{l,|\mu|}^{-1} \int_0^{2\pi} \int_0^{2\pi} y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \sin \theta \, d\theta \, d\phi \]

(68)

Denoting the R-Gaunt coefficients as (Homeier & Steinborn, 1996)

\[ R_{l_a,m_a,l_b,m_b,\lambda,|\mu|} = \int_0^{2\pi} \int_0^{2\pi} y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \sin \theta \, d\theta \, d\phi \]

(69)

\[ R_{l_a,m_a,l_b,m_b,\lambda,-|\mu|} = \int_0^{2\pi} \int_0^{2\pi} y_{l_a}^{m_a}(\theta, \phi) y_{l_b}^{m_b}(\theta, \phi) y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \sin \theta \, d\theta \, d\phi \]

(70)

the expression for \( d_{abl \lambda}(\theta, \phi) \) becomes

\[ d_{abl \lambda}(\theta, \phi) = \frac{(-1)^{\lambda}(2\lambda + 1)}{4\pi} \times \sum_{|\mu|} \epsilon_{\lambda,|\mu|} (\lambda + |\mu|) p_l^{|\mu|}(\cos \theta) (-1)^{|\mu|} N_{l,|\mu|}^{-1} y_{l,|\mu|}^{-|\mu|}(\theta, \phi) R_{l_a,m_a,l_b,m_b,\lambda,|\mu|} + \sin(|\mu| \phi) R_{l_a,m_a,l_b,m_b,\lambda,-|\mu|} \]

(71)

Recognizing again that

\[ p_l^{|\mu|}(\cos \theta) \cos(|\mu| \phi) = (-1)^{|\mu|} N_{l,|\mu|}^{-1} y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \]

\[ p_l^{|\mu|}(\cos \theta) \sin(|\mu| \phi) = (-1)^{|\mu|} N_{l,|\mu|}^{-1} y_{l,|\mu|}^{-|\mu|}(\theta, \phi) \]

expanding the product \( N_{l,|\mu|}^{-1} N_{l,|\mu|}^{-1} = N_{l,|\mu|}^{-2} \), simplifying \( \epsilon_{\lambda,|\mu|}(1 + \delta_{|\mu|,0}) = (2 - \delta_{|\mu|,0})(1 + \delta_{|\mu|,0}) = 2 \) and \( (-1)^{|\mu|}(-1)^{|\mu|} = 1 \), and cancelling out the identical factors in numerator and denominator, gives a very
simple and elegant expression for $d_{ab\lambda}(\theta, \phi)$ in terms of real spherical harmonics and the R-Gaunt coefficients:

$$d_{ab\lambda}(\theta, \phi) = (-1)^{\mu} \sum_{\mu} \left\{ y_\lambda^{\mu}(\theta, \phi) R_{Ga}(m_a, l_a, m_b, l_b, \lambda, \mu) + y_\lambda^{-\mu}(\theta, \phi) R_{Ga}(m_a, l_a, m_b, l_b, \lambda, -\mu) \right\}$$

where $\mu$ is defined as:

$$\mu \in \{|m_a| - |m_b|, |m_a| + |m_b|\} \text{ and } \mu \leq \lambda$$

Note that these conditions are in a perfect agreement with those given in Homeier & Steinborn (1996; equation (34)).
S4. References


