The expressions for the 2\textsuperscript{nd}-order mixed partial derivatives of Slater-Koster matrix elements at spherical coordinate singularities

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Abstract
In a recent publication it has been shown how to generate derivatives with respect to atom coordinates of Slater-Koster matrix elements for the tight binding (TB) modelling of a system. For the special case of a mixed second partial derivative at coordinate singularities only the results were stated in that publication. In this work, the derivation of these results is given in detail. Though it may seem rather ‘technical’ and only applicable to a very special case, atomic configurations where the connecting vector between the two atoms involved in a two-centre matrix element is aligned along the \textit{z}-axis (in the usual approach) require results for precisely this case. The expressions derived in this work have been implemented in the DINAMO code.

1 Slater-Koster matrix elements
In [1] it was shown how the Slater-Koster matrix element between orbitals localised at two different atoms could be systematically expressed in terms of the distance $R$ between the atoms, and the Euler angles $\alpha$ and $\beta$ describing the orientation of the connecting vector $\vec{R} = (X, Y, Z) = R(\cos \alpha \sin \beta, \sin \alpha \sin \beta, \cos \beta)$ in space and parametrising the rotations of the original coordinate system into a new one necessary for the evaluation of the matrix element. The general expression for a matrix element $\langle l_1m_1| H | l_2m_2 \rangle$, according to [1], with $l_\leq = \min(l_1, l_2)$, is

$$\langle l_1m_1| H | l_2m_2 \rangle(\alpha, \beta, R) = \sum_{m' = 1}^{l_\leq} \left[ S_{m_1m'}^1(\alpha, \beta)S_{m_2m'}^2(\alpha, \beta) + T_{m_1m'}^1(\alpha, \beta)T_{m_2m'}^2(\alpha, \beta) \right] \times (l_1l_2|m'|)(R) + 2A_{m_1}(\alpha)A_{m_2}(\alpha)d_{l_1m_10}^{l_1}(\beta)d_{l_2m_20}^{l_2}(\beta)(l_1l_20)(R)$$

Here $|l_im_i\rangle$ denotes a state whose wavefunction has an angular dependence characterised by a real spherical harmonic $\overline{Y}_{l_im_i}$ on atoms $i = 1, 2$, respectively. The real spherical harmonics are defined as

$$\overline{Y}_{lm} = \delta_{m0}Y_{l0} + (1 - \delta_{m0})\sqrt{2}(-1)^m [\tau(m)\text{Re}Y_{l|m|} + \tau(-m)\text{Im}Y_{l|m|}]$$

with $\tau(m) = 1$ if $m \geq 0$ and $\tau(m) = 0$ if $m < 0$. The $Y_{lm}$ are the ordinary complex valued spherical harmonics, with the phase convention $Y_{lm}^+(\theta, \varphi) = (-1)^mY_{l-m}(\theta, \varphi)$.

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\( H \) in (1) is an operator that is cylindrically symmetric about all possible orientations of the connecting vector \( \vec{R} \); it can be the Hamiltonian, but also the identity, in which case the matrix elements would be overlap integrals between localised states. The other quantities appearing are

\[
A_m(\alpha) := \begin{cases} 
(1)^m \left[ \tau(m) \cos(|m|\alpha) + \tau(-m) \sin(|m|\alpha) \right] & \text{if } m \neq 0 \\
\frac{1}{\sqrt{2}} & \text{if } m = 0
\end{cases}
\]

\[
B_m(\alpha) := \begin{cases} 
(1)^m \left[ \tau(-m) \cos(|m|\alpha) - \tau(m) \sin(|m|\alpha) \right] & \text{if } m \neq 0 \\
0 & \text{if } m = 0
\end{cases}
\]

\[
S^l_{mnm'} := A_m \left[ (-1)^{m'} d^l_{m|m'|} + d^l_{|m|m'} \right]
\]

\[
T^l_{mnm'} := B_m \left[ (-1)^{m'} d^l_{|m|m'} - d^l_{m|m'} \right]
\]

and the Wigner \( d \)-function [3]

\[
d^l_{mm'}(\beta) = 2^{-l} (-1)^{l-m'} \left[ (l+m)! (l-m)! (l+m')! (l-m')! \right]^{1/2} \times \sum_{k=k_<}^{k_>} \frac{(-1)^k \cos \beta}{k! (l-m-k)! (l-m'-k)! (m+m'+k)!} + \frac{\sin \beta}{k! (l-m-k)! (l-m'-k)! (m+m'+k)!}
\]

with \( k_<= \min(l-m,l-m') \), \( k_> \max(0,-m-m') \). The \((l_1 l_2 | m'|)\) are the fundamental matrix elements, which depend only on the distance \( R \) between the two atoms considered; they give the matrix elements \( \langle l_1 m' \mid H \mid l_2 m' \rangle \) when the connecting vector is aligned with the z-axis, \( \vec{R} = R \hat{z} \).

In [2] the approach of [1] has been extended to 1\(^{st}\) and 2\(^{nd}\) order derivatives of the matrix element with respect to the Cartesian coordinates \( X, Y, Z \) of the connecting vector \( \vec{R} \). The approach detailed in [2] can be applied to obtain all first and second partial derivatives for all \( \alpha, \beta, R \), with the exception of \( \partial^2 / \partial X \partial Y \) at the poles \( \beta = 0, \pi \). This is due to a coordinate singularity and for the specific derivative mentioned no way around this problem was found within the approach of [2]; a recourse to a Cartesian description was necessary. The calculations, however, were not detailed in that publication. This will be done in what follows.

The general expression for a Slater-Koster matrix element is a linear combination of \( R \)-dependent functions, the \((l_1 l_2 | m'|)\), where the coefficients are combinations of integer powers of the direction cosines \( X/R, Y/R, Z/R \) of the connecting vector. Therefore, the general form of a matrix element can be expressed as

\[
\mathcal{M} := \langle l_1 m_1 | l_2 m_2 \rangle = \sum_{ijk \geq 0} X^i Y^j Z^k f_{ijk}(R)
\]

where \( f_{ijk} \) is a combination of fundamental matrix elements \((l_1 l_2 | m'|)\) with constant coefficients, divided by \( R^{i+j+k} \). At the poles \( Z = \pm R \), \( X = Y = 0 \) only certain terms from the sum \( \mathcal{M} \) will remain in \( \partial_X \partial_Y \mathcal{M} \). These are precisely those terms where \( X^i Y^j Z^k = XYZ^k \), as we now show:

\[
\partial_X \mathcal{M} = \sum_{ijk \geq 0} \left[ iX^{i-1} Y^j Z^k f_{ijk}(R) + X^{i+1} Y^j Z^k \frac{1}{R} \frac{d}{dR} f_{ijk}(R) \right]
\]
Note that this is also valid if $i = 0$.

\begin{align*}
\partial_Y \partial_X M &= \sum_{ij\geq 0} \left[ ijX^{i-1}Y^{j-1}Z^k f_{ijk}(R) + iX^{i-1}Y^{j+1}Z^k \frac{1}{R} \frac{d}{dR} f_{ijk}(R) + \\
&\quad jX^{i+1}Y^{j-1}Z^k \frac{1}{R} \frac{d}{dR} f_{ijk}(R) + X^{i+1}Y^{j+1}Z^k \left( \frac{1}{R^2} \frac{d^2}{dR^2} f_{ijk}(R) - \frac{1}{R^3} \frac{d}{dR} f_{ijk}(R) \right) \right]
\end{align*}

This is also valid if $j = 0$ and/or $i = 0$. As $i, j \geq 0$ it follows that for $X = Y = 0$, $Z = \pm R$ the 2nd, 3rd and 4th term vanish. The first term is non-zero in this case only if $i = j = 1$. This is the proposition.

2 Intermediate calculations

It is convenient to rewrite the general expression (11) as

\begin{align*}
M = \langle l_1 m_1 | H | l_2 m_2 \rangle &= 2A_{m_1}A_{m_2}d^3_{m_10}d^2_{m_20}(l_1 l_2 0) + \sum_{m''} \left[ A_{m_1}A_{m_2}S^l_{m_1m''}S^l_{m_2m''} + \\
&\quad B_{m_1}B_{m_2}T^l_{m_1m''}T^l_{m_2m''} \right](l_1 l_2 | m'')
\end{align*}

with $S^l_{mm''} = A_mS^l_{mm'}$ and $T^l_{mm''} = B_mT^l_{mm'}$. We have for $|m_1| > 0$ and $|m_2| > 0$:

\begin{align*}
A_{m_1}A_{m_2} &= (-1)^{m_1+m_2} [\tau(m_1) \cos(|m_1| \alpha) + \tau(-m_1) \sin(|m_1| \alpha)] \times \\
&\quad \{\tau(m_2) \cos(|m_2| \alpha) + \tau(-m_2) \sin(|m_2| \alpha)\} = \\
&\quad (-1)^{m_1+m_2} [\tau(m_1)\tau(m_2) \cos(|m_1| \alpha) \cos(|m_2| \alpha) + \tau(-m_1)\tau(-m_2) \sin(|m_1| \alpha) \sin(|m_2| \alpha) + \\
&\quad \tau(-m_1)\tau(m_2) \sin(|m_1| \alpha) \cos(|m_2| \alpha) + \tau(m_1)\tau(-m_2) \cos(|m_1| \alpha) \sin(|m_2| \alpha)]
\end{align*}

and

\begin{align*}
B_{m_1}B_{m_2} &= (-1)^{m_1+m_2} [\tau(-m_1) \cos(|m_1| \alpha) - \tau(m_1) \sin(|m_1| \alpha)] \times \\
&\quad \{\tau(-m_2) \cos(|m_2| \alpha) - \tau(m_2) \sin(|m_2| \alpha)\} = \\
&\quad (-1)^{m_1+m_2} [\tau(-m_1)\tau(-m_2) \cos(|m_1| \alpha) \cos(|m_2| \alpha) + \tau(m_1)\tau(m_2) \sin(|m_1| \alpha) \sin(|m_2| \alpha) - \\
&\quad \tau(-m_1)\tau(m_2) \sin(|m_1| \alpha) \cos(|m_2| \alpha) - \tau(m_1)\tau(-m_2) \cos(|m_1| \alpha) \sin(|m_2| \alpha)]
\end{align*}

For $m \neq 0$ we obtain

\begin{align*}
A_0 A_m &= \frac{(-1)^m}{\sqrt{2}} \{\tau(m) \cos(|m| \alpha) + \tau(-m) \sin(|m| \alpha)\}
\end{align*}

and $B_0 B_m = 0$.

A prefactor $XYZ^k$ in the terms of (13) requires an $\alpha$-dependence that takes the form $\sin(2\alpha) = 2\sin \alpha \cos \alpha$. If we convert the products of two functions $\cos, \sin$ in (10), (11) into sums of two such functions according to the usual trigonometric relations, we obtain $\sin$ functions only for products of the form $\sin \cos$, according two

\begin{align*}
\sin(|m_1| \alpha) \cos(|m_2| \alpha) &= \frac{1}{2} \sin(|m_2| + |m_1|) \alpha - \frac{1}{2} \sin(|m_2| - |m_1|) \alpha
\end{align*}

\begin{align*}
\sin(|m_2| \alpha) \cos(|m_1| \alpha) &= \frac{1}{2} \sin(|m_2| + |m_1|) \alpha + \frac{1}{2} \sin(|m_2| - |m_1|) \alpha
\end{align*}
Henceforth we shall take \(|m_2| \geq |m_1|\); this is no loss of generality, due to the symmetry properties of the inner product. From (13) and (12) we see that we can get the desired \(\sin(2\alpha)\) for

- Case A \(|m_1| = |m_2| = 1\)
- Case B.1 \(|m_2| - |m_1| = 2, m_1 = 0\)
- Case B.2 \(|m_2| - |m_1| = 2, |m_1| > 0\)

The distinction within case B is warranted for by the distinction in the coefficients \(A_m, B_m\) for \(m = 0\) and \(m > 0\). The \(\tau\) functions in (10), (11), (12) further restrict the possible choices of \(m_1\) and \(m_2\). In case A, we must have \(m_1m_2 = -1\), and we can choose, without loss of generality and without violating previous conventions \(m_1 = 1, m_2 = -1\). For B.1 we must have \(m_2 = -2\), and for B.2 \(m_1m_2 < 0\).

The matrix elements that can give contributions to the mixed partial derivative at the poles thus are: \(\langle l_1, 1 | \hat{H} | l_2, -1 \rangle, \langle l_1, 0 | \hat{H} | l_2, -2 \rangle\), and \(\langle l_1, m_1 | \hat{H} | l_2, m_2 \rangle\) with \(|m_1| > 0, |m_2| = |m_1| + 2\), and \(m_1m_2 < 0\).

In order to identify these contributions we note that \(XY = R^2 \sin(\beta) \cos \alpha \sin \alpha\). We can find the required derivatives if we extract from (12) the factor \((\sin \beta)^2 \cos \alpha \sin \alpha\) where possible, evaluate the ‘remainder’ at the poles and divide this result by \(R^2\). This is equivalent to dividing by \(XY\), and for a dependence \(XYZ^k\), the only one giving rise to nonvanishing contributions, is also the same as taking the derivative with respect to \(X\) and \(Y\) at the poles. The \(\beta\)-dependence in the matrix elements stems from products of Wigner \(d\)-functions, as can be seen from (11), (5), (6).

The following relations will be needed:

\[
d^d_{mm'}(\beta) = (-1)^{m-m'}d^d_{m'm}(\beta)
\]
\[
d^d_{mm'}(\pi - \beta) = (-1)^{l+m}d^d_{m-m'}(\beta)
\]

(14)

The \(d\)-functions \(d^d_{mm'}\) occurring in the matrix element all have \(m \geq 0\), and with (13) we can reformulate all expressions such that \(m' \geq 0\) and \(m \leq m'\). We therefore choose to rewrite (7) for \(m, n \geq 0\) as

\[
d^d_{m(m+n)}(\vartheta) = 2^{-l}(-1)^{l-m-n}[(l+m)!(l-m)!(l+m+n)!(l-m-n)!]\frac{1}{2}
\]
\[
\times \sum_{k=0}^{l-m-n} (-1)^k(1 - \cos \vartheta)^{l-m-n-k}(1 + \cos \vartheta)^{k+m+\frac{k}{2}}
\]
\[
\times (1 - \cos \vartheta)^\frac{m-n}{2} \frac{(l+m)!/(l-m-n)!}{(2m+n+k)!}
\]
\[
\times (\sin \vartheta)^n(1 + \cos \vartheta)^m 2^{-l}(-1)^{l-m-n}[(l+m)!(l-m)!(l+m+n)!(l-m-n)!]\frac{1}{2}
\]
\[
\times \sum_{k=0}^{l-m-n} (-1)^k(1 - \cos \vartheta)^{l-m-n-k}(1 + \cos \vartheta)^{k+m}
\]
\[
\times \frac{(l+m)!/(l-m-n)!}{(2m+n+k)!}
\]

(15)

Only the behaviour of these functions at \(\vartheta = 0, \pi\) is important. At \(\vartheta = 0\) only the term with \(k = l - m - n\) contributes, and gives (where we don’t evaluate \(\sin \vartheta\) and \(\cos \vartheta\) outside the sum)

\[
(\sin \vartheta)^n(1 + \cos \vartheta)^m 2^{-(m+n)} \sqrt{(l+m+n)!(l-m)!} \frac{1}{(l+m)!(l-m-n)! n!}
\]

(16)

At \(\vartheta = \pi\) the only contribution comes from \(k = 0\) and reads

\[
(\sin \vartheta)^n(1 + \cos \vartheta)^m 2^{-(m+n)}(-1)^{l-m-n} \sqrt{(l+m)!(l+m+n)!} \frac{1}{(l-m)!(l-m-n)! (2m+n)!}
\]

(17)
We now look separately at the cases A, B.1, B.2, extracting \((\sin \beta)^2 \cos \alpha \sin \alpha\).

### 2.1 Case A : \(m_1 = 1, m_2 = -1\)

The relevant terms are

\[
2A_1 A_{-1} d_{i0}^1 d_{10}^2 (l_1 l_2 0) = 2 \cos \alpha \sin \alpha d_{i0}^1 d_{10}^2 (l_1 l_2 0) = 2 \cos \alpha \sin \alpha d_{01}^1 d_{02}^2 (l_1 l_2 0)
\]  

and

\[
\begin{align*}
\sin \alpha \cos \alpha \sum_{m' = 1}^{l < m} \left[ S_{1m'}^1 S_{-1m'}^2 - T_{1m'}^{l1} T_{-1m'}^{l2} \right](l_1 l_2 | m') &= \\
2 \sin \alpha \cos \alpha \sum_{m' = 1}^{l < m} (-1)^{m'} \left[ d_{1m'}^1(\beta) d_{1m'}^2(\beta) + d_{1m'}^1(\beta) d_{1m'}^2(\beta) \right](l_1 l_2 | m') &= \\
2 \sin \alpha \cos \alpha \sum_{m' = 1}^{l < m} \left[ (-1)^{l_1+m'-1} d_{1m'}^1(\beta) d_{1m'}^2(\pi - \beta) + (-1)^{l_1+m'-1} d_{1m'}^1(\pi - \beta) d_{1m'}^1(\beta) \right](l_1 l_2 | m') &=
\end{align*}
\]  

In the last equation the following relations have been used

\[
S_{1m'}^1 S_{-1m'}^2 = d_{1m'}^1 d_{1m'}^2 + d_{1m'}^1 d_{1m'}^2 + (-1)^{m'} d_{1m'}^1 d_{1m'}^2 + (-1)^{m'} d_{1m'}^1 d_{1m'}^2
\]

\[
T_{1m'}^{l1} T_{-1m'}^{l2} = d_{1m'}^1 d_{1m'}^2 + d_{1m'}^1 d_{1m'}^2 - (-1)^{m'} d_{1m'}^1 d_{1m'}^2 - (-1)^{m'} d_{1m'}^1 d_{1m'}^2
\]

and (14) has been applied.

Using (15) we get at \(\beta = 0\) for (18)

\[
\cos \alpha \sin \alpha (\sin \beta)^2 \frac{1}{2} \sqrt{(l_1 + 1)l_1(l_2 + 1)l_2(l_1 l_2 0)}
\]  

and \((-1)^{l_1+l_2} \times\) this result at \(\beta = \pi\).

For (19) we see from (15) that in the case \(n > 0\) the product \(d_{1m'}^1(\beta) d_{1m'}^2(\pi - \beta)\) contains at least a factor \((\sin \beta)^4\). As we only extract \((\sin \beta)^2\), the remainder vanishes at \(\beta = 0\) and \(\beta = \pi\). So only the case \(m' = 1\) can produce a contributing term; it is

\[
\sin \alpha \cos \alpha (\sin \beta)^2 \left( -\frac{1}{4} \right) [l_2(l_2 + 1) + l_1(l_1 + 1)](l_1 l_2 1)
\]  

at \(\beta = 0\) and \((-1)^{l_1+l_2} \times\) this expression at \(\beta = \pi\).

### 2.2 Case B.1: \(m_1 = 0, m_2 = -2\)

The relevant terms are

\[
2A_0 A_{-2} d_{00}^1 d_{20}^2 (l_1 l_2 0) = 2 \sqrt{2} \sin \alpha \cos \alpha d_{00}^1 d_{02}^2 (l_1 l_2 0)
\]  

(23)
and if \( l_1 > 0 \) also

\[
A_0 A_{-2} \sum_{m' = 1}^{L'_{<}} S_{0 m'} S_{-2 m'} (l_1 l_2 | m') = \sqrt{2} \sin \alpha \cos \alpha \sum_{m' = 1}^{L'_{<}} S_{0 m'} S_{-2 m'} (l_1 l_2 | m') =
\]

\[
\sqrt{2} \sin \alpha \cos \alpha \sum_{m' = 1}^{L'_{<}} \left[ d_{0 m'}^1 (\beta) d_{2 m'}^2 (\beta) + d_{0 - m'}^1 (\beta) d_{-2 m'}^2 (\beta)\right] + \]

\[
(1)^{m'} d_{0 m'}^1 (\beta) d_{2 m'}^2 (\beta) + (1)^{m'} d_{0 - m'}^1 (\beta) d_{-2 m'}^2 (\beta) \right] (l_1 l_2 | m')
\]

\[
\sqrt{2} \sin \alpha \cos \alpha \sum_{m' = 1}^{L'_{<}} \left[ d_{0 m'}^1 (\beta) d_{2 m'}^2 (\beta) + (1)^{l_1 + 1} d_{0 m'}^1 (\beta) d_{2 m'}^2 (\beta) \right] (l_1 l_2 | m')
\]

Equation (23) gives at \( \beta = 0 \)

\[
\sin \alpha \cos \alpha (\sin \beta)^2 \frac{1}{2 \sqrt{2}} \sqrt{(l_2 + 2)(l_2 + 1)(l_2 - 1)(l_1 l_2 0)}
\]

and at \( \beta = \pi \) we obtain this expression \( \times (1)^{l_1 + l_2} \).

Turning to (24) we first note from (15) that for \( m' \geq 3 \) the products \( d_{0 m'}^1 d_{m'}^2 \), contain at least a factor \( (\sin \beta)^4 \) and thus after extraction of \( (\sin \beta)^2 \) still vanish at \( \beta = 0, \pi \). This leaves us with \( m' = 1, 2 \). We find:

\[
d_{01}^1 (\beta) d_{21}^2 (\beta) = -d_{01}^1 (\beta) d_{12}^2 (\beta) = - (\sin \beta)^2 \frac{1}{4} \sqrt{(l_1 + 1) l_1 (l_2 + 2) (l_2 - 1)}
\]

at \( \beta = 0 \), whereas this product vanishes at \( \beta = \pi \) after extraction of \( (\sin \beta)^2 \) due to a factor \( (1 + \cos \beta) \). \( d_{01}^1 (\pi - \beta) d_{21}^2 (\pi - \beta) \) vanishes at \( \beta = 0 \) due to a factor \( (1 - \cos \beta) \), and at \( \beta = \pi \) results in (26).

\[d_{01}^1 (\beta) d_{21}^2 (\pi - \beta)\] vanishes at \( \beta = 0 \) and at \( \beta = \pi \) gives

\[
d_{01}^1 (\beta) d_{21}^2 (\pi - \beta) = -d_{01}^1 d_{12}^2 (\pi - \beta) = - (\sin \beta)^2 \frac{1}{4} \sqrt{(l_1 + 1) l_1 (l_2 + 2) (l_2 - 1)}
\]

at \( \beta = 0 \), whereas this product does not contribute at \( \beta = \pi \); there \( d_{02}^1 (\pi - \beta) d_{22}^2 (\pi - \beta) \) gives the above expression and in turn vanishes at \( \beta = 0 \). At \( \beta = 0 \) \( d_{02}^1 (\beta) d_{22}^2 (\pi - \beta) \) vanishes and at \( \beta = \pi \) yields

\[
(1)^{l_1} \frac{1}{8} (\sin \beta)^2 \sqrt{(l_1 + 2)(l_1 + 1) l_1 (l_1 - 1)}
\]

Vice versa \( d_{02}^1 (\pi - \beta) d_{22}^2 (\beta) \) gives the above expression at \( \beta = 0 \) and vanishes at \( \beta = \pi \). Therefore the \( m' = 2 \) contribution is

\[
\sin \alpha \cos \alpha (\sin \beta)^2 \frac{1}{2 \sqrt{2}} \sqrt{(l_1 + 2)(l_1 + 1) l_1 (l_1 - 1)(l_1 l_2 2)}
\]

and at \( \beta = \pi \) just \( (1)^{l_1 + l_2} \times \) this result.
2.3 Case B.2: $|m_1| > 0, |m_2| = |m_1| + 2$

There will be no contribution from the $(l_1l_20)$ term in (33), because

$$d^i_{0|m_1|d^i_{0|m_2|}} \propto (\sin \beta)^{|m_1|+|m_2|} = (\sin \beta)^{2|m_1|+2}$$

and, because $|m_1| > 0$, the remainder after extraction of $(\sin \beta)^2$ vanishes at $\beta = 0, \pi$. In the sum over $(l_1l_2|m'|)$ for $m' > 0$ only those parts of the prefactors will contribute to the derivative we seek that depend on $\alpha$ like $\cos \alpha \sin \alpha$. If we drop all other terms, this ‘reduced’ sum $\mathcal{M}$ reads in the case $m_1 > 0, m_2 < 0$

$$\mathcal{M} = (-1)^{m_1+m_2} \sin \alpha \cos \alpha \sum_{m'=1}^{l_1} \left[ S_{m_1m'}^l S_{m_2m'}^l + T_{m_1m'}^l T_{m_2m'}^l \right] (l_1l_2|m'|)$$

and in the case $m_1 < 0, m_2 > 0$ it is just the negative of (33). We will be using $m_1 > 0, m_2 < 0$ until stated otherwise. With (14) we can write

$$S_{m_1m'}^l \beta S_{m_2m'}^l (\beta) = d^i_{|m_1|m'}(\beta)d^i_{|m_2|m'}(\beta) +$$

$$(1)^{l_1+l_2}|m_1|+|m_2| d^i_{|m_1|m'}(\pi - \beta)d^i_{|m_2|m'}(\pi - \beta) +$$

$$(1)^{l_1+l_2}|m_2|+m' d^i_{|m_1|m'}(\beta)d^i_{|m_2|m'}(\pi - \beta) +$$

$$(1)^{l_1+l_2}|m_1|+m' d^i_{|m_1|m'}(\beta)d^i_{|m_2|m'}(\pi - \beta)$$

Therefore

$$S_{m_1m'}^l S_{m_2m'}^l + T_{m_1m'}^l T_{m_2m'}^l =$$

$$2d^i_{|m_1|m'}(\beta)d^i_{|m_2|m'}(\beta) + 2(1)^{l_1+l_2} d^i_{|m_1|m'}(\pi - \beta)d^i_{|m_2|m'}(\pi - \beta)$$

Note that $(-1)^{m_1+m_2} = (-1)^{|m_1|+|m_2|} = (-1)^{|m_2|-|m_1|} = 1$ in the present case. The second term in (33) involves the same functions as the first, only evaluated at $\pi - \beta$ instead of $\beta$. In order to evaluate\(^1\) the first term at $\beta = 0$, we have to choose $\vartheta = \beta$ in (17); for $\beta = \pi, \vartheta = \beta$ has to be referred to (17), and we can see that this vanishes ($m \geq 1$). For the second term at $\beta = 0$, the required choice is $\vartheta = \pi - \beta$ in (17). This expression vanishes, as $|1 + \cos(\pi - \beta)|^m = |1 - \cos(\beta)|^m \to 0$ as $\beta \to 0$. At $\beta = \pi$ the second term is evaluated by plugging $\vartheta = \pi - \beta$ into (16). This evidently gives the same result as putting $\beta = 0$ in (16). Looking at (33) as a whole it follows that at $\beta = \pi$ it results in $(-1)^{l_1+l_2}$ times its value at $\beta = 0$, the latter being determined entirely by the first term.

If $m' > |m_2| = |m_1| + 2$ the product $d^i_{|m_1|m'}d^i_{|m_2|m'}$ contains at least a factor $\sin \beta$\(^4\). It therefore does not contribute. If $m' < |m_1| = |m_2| - 2$ then $d^i_{|m_1|m'}d^i_{|m_2|m'} = (-1)^{|m_1|+|m_2|}d^i_{|m_1|m'}d^i_{|m_2|m'}$.

\(^1\)Always explicitly keeping $(\sin \beta)^2$. 

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and this again contains at least $(\sin \beta)^4$. So we have to consider explicitly the cases 
\(m' = |m_2|, \quad m' = |m_1| + 1, \quad m' = |m_1|,\) and only at \(\beta = 0\).

\(m' = |m_2|:\)

\[
d^1_{|m_1||m_2|}(\beta)d^2_{|m_2||m_2|}(\beta) =
\frac{1}{8}(\sin \beta)^2\sqrt{(l_1 + |m_1| + 2)(l_1 + |m_1| + 1)(l_1 - |m_1|)(l_1 - |m_1| - 1)}
\]  
(37)

\(m' = |m_1| + 1 = |m_2| - 1:\)

\[
d^1_{|m_1|+1||m_2|+1}(\beta)d^2_{|m_2|+1||m_2|+1}(\beta) = -d^1_{|m_1|+1||m_2|}(\beta)d^2_{|m_2|+1||m_2|}(\beta) =
- (\sin \beta)^2 \frac{1}{4}\sqrt{(l_1 + |m_1| + 1)(l_1 - |m_1|)(l_2 + |m_1| + 2)(l_2 - |m_1| - 1)}
\]  
(38)

\(m' = |m_1|:\)

\[
d^1_{|m_1||m_1|}(\beta)d^2_{|m_1||m_1|}(\beta) = d^1_{|m_1||m_1|}(\beta)d^2_{|m_1||m_1|}(\beta) =
\frac{1}{8}(\sin \beta)^2\sqrt{(l_2 + |m_1| + 2)(l_2 + |m_1| + 1)(l_2 - |m_1|)(l_2 - |m_1| - 1)}
\]  
(39)

3 Evaluation of \(\frac{\partial^2}{\partial X \partial Y} \langle l_1 m_1 | H | l_2 m_2 \rangle\) at the poles

With the results of the previous section we now compose expressions for the matrix elements at the poles. As explained earlier, dropping \(\cos \alpha \sin \alpha (\sin \beta)^2\) from these expressions and dividing the remainder by \(R^2\) gives the derivative we want. Thus we find at \(\beta = 0\):

Case A:

\[
\partial_X \partial_Y \langle l_1, +1 | H | l_2, -1 \rangle = \frac{1}{R^2} \left\{ \frac{1}{2} \sqrt{l_1(l_1 + 1)l_2(l_2 + 1)} (l_1l_0) \right.
\]

\[
\left. - \frac{1}{4}[l_1(l_1 + 1) + l_2(l_2 + 1)](l_1l_2) \right\}
\]  
(40)

Case B.1:

\[
\partial_X \partial_Y \langle l_1, 0 | H | l_2, -2 \rangle = \frac{1}{2\sqrt{2}R^2} \sqrt{(l_2 + 2)(l_2 + 1)l_2(l_2 - 1)} (l_1l_0)
\]

\[
- (1 - \delta_{l_0}) \frac{1}{\sqrt{2}R^2} \sqrt{l_1(l_1 + 1)(l_2 + 2)(l_2 - 1)} (l_1l_2)
\]

\[
+ (1 - \delta_{l_0})(1 - \delta_{l_1}) \frac{1}{2\sqrt{2}R^2} \sqrt{(l_1 + 2)(l_1 + 1)l_1(l_1 - 1)} (l_1l_2)
\]  
(41)

Case B.2 (\(m_1 > 0, m_2 < 0\), otherwise multiply result below by \(-1\)):

\[
\partial_X \partial_Y \langle l_1, m_1 | H | l_2, m_2 \rangle =
\frac{1}{R^2} \left[ \frac{1}{4} \sqrt{(l_2 + |m_1| + 2)(l_2 + |m_1| + 1)(l_2 - |m_1|)(l_2 - |m_1| - 1)(l_1l_2|m_1|)} \right.
\]

\[
- (1 - \delta_{l_1|m_1}) \frac{1}{2} \sqrt{(l_1 + |m_1| + 1)(l_1 - |m_1|)(l_2 + |m_1| + 2)(l_2 - |m_1| - 1)(l_1l_2|m_1|)}
\]

\[
+ (1 - \delta_{l_1|m_1})(1 - \delta_{l_1|m_1+1}) \frac{1}{4} \sqrt{(l_1 + |m_1| + 2)(l_1 + |m_1| + 1)(l_1 - |m_1|)(l_1 - |m_1| - 1)(l_1l_2|m_2|)}
\]  
(42)
At $\beta = \pi$ we get $(-1)^{l_1 + l_2} \times$ these values. Expressions (40) and (41) were stated in [2]. In this work their derivation has been demonstrated. Result (42) was not mentioned in [2].

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References

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[2] Elena A M, Meister M 2005 cond-mat/0504719

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