Suppose we have two unpaired electrons. The two-particle Hilbert space spanned by

$$|s_1 m_1\rangle \otimes |s_2 m_2\rangle = |s_1 m_1, s_2 m_2\rangle, \tag{1}$$

the RHS is just a short hand of writing one of the vectors formed from the product $\otimes$. From now on this will be referred to as the *product basis* .

The particles have spin operators denoted $\hat{S}_1$ and $\hat{S}_2$. The product states satisfy
As $m_1 \text{and} m_2 = \pm\frac{1}{2}$, we shall use the further shorthand, e.g., the product state for $s_{1,2} = \frac{1}{2}$, $m_1 = +\frac{1}{2}$ and $m_2 = -\frac{1}{2}$ will be written

$$|+-\rangle = |\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{-1}{2}\rangle \tag{2}$$

$$S_i^2 |s_1 m_1, s_2 m_2\rangle = \hbar^2 s_i(s+1)|s_1 m_1, s_2 m_2\rangle \tag{3}$$

The total angular momentum operator, $\mathbf{S}$, is defined

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \tag{4}$$

We want to find the eigenvalues of S_z and S^2 in this basis. First, look at S_z.

$$S_z|++\rangle = (S_{1z} + S_{2z})|++ = (\frac{\hbar}{2} + \frac{\hbar}{2})|++rangle = |++\rangle \tag{5}$$

$$S_z|++\rangle = (S_{1z} + S_{2z})|++ = (\frac{-\hbar}{2} + \frac{\hbar}{2})|-+rangle = 0 \tag{6}$$

$$S_z|++\rangle = (S_{1z} + S_{2z})|++ = (\frac{\hbar}{2} + \frac{-\hbar}{2})|+-rangle = 0 \tag{7}$$

$$S_z|++\rangle = (S_{1z} + S_{2z})|++ = (\frac{-\hbar}{2} + \frac{-\hbar}{2})|--\rangle = |--\rangle \tag{8}$$

So the representation of $\mathbf{S}_z$ in the product basis is

$$[S_z]_{\{|1,2\rangle\}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{9}$$

where the $\hbar$ has been omitted for convenience.

Now consider the S^2 operator.

$$S^2 = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2) = S_1^2 + S_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{10}$$

Unfortunately, the product states are not eigenfunctions of S^2. This leads us to construct the following basis:

$$\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}$$

$$|++\rangle$$

$$\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}$$
$$|--\rangle$$

I'll refer to this as the "ST basis". The question is now which of these two bases should we use. If we are interested in and operator, $\hat{V}^{(+)}$ of the form,

$$\hat{V}^{(+)} = -(v_1^{(+)}\mathbf{S}_1 + v_2^{(+)}\mathbf{S}_2) \cdot \mathbf{B} \tag{11}$$

this indicates non-interacting spins, hence it makes sense to use the product basis. However, if we have and operator $\hat{V}^{\times}$, corresponding to interacting spins

$$\hat{V}^{\times} = v^{\times}\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{12}$$

then it makes send to use the ST basis.

Soncini provides a basis of matrices which may be used to represent the representation of an operator in the above bases. To understand how this basis is constructed, it is useful to recap the addition of angular momentum, and how bases such as those above can be transformed into one another.

1 Addition of classical angular momentum

Consider adding two angular momenta, and the associated product states. As with spin we have

$$J_z|j_1 m_1\rangle = (m_1 + m_2)|j_1 m_1, j_2 m_2\rangle \tag{13}$$

Note that his is going to be degenrate, as multiple combinations of m_1 and m_2 can result in the same eigenvalue. Within each of these degenerate eigenspaces (which can be thought of corresponding to spin multiplets) we want to chose a basis which consists solely of eigenvectors of J^2.

If $j_1 \geq j_2$, then the value of the total angular momentum j can take on values

$$(j_1 + j_2 - 1), (j_1 + j_2 - 2), ..., (j_1 - j_2) \tag{14}$$

So the total number of states in this basis is $(2j_1 + 1)(2j_2 + 1)$. In fact we can state that the tensor product space $j_1 \otimes j_2$ can be represented as a sum of spaces, each of which is associated with one the eigenvalues stated above, i.e.,

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus ...(j_1 - j_2) \tag{15}$$

The states within each one of these degenerate subspaces are

$$|JM, j_1 j_2\rangle \quad \text{where} \quad (j_1 + j_2) \geq j \geq (j_1 - j_2) \quad \text{and} \quad j \geq m \geq -j \tag{16}$$

Now we can consider which states exist in each one of these degenerate subspaces Or, when applied to the $j_1 = j_2 = \frac{1}{2}$ case we have It must be possible to obtain these states (which have a good value of J^2) via some transformation of the states in the product basis. We can see that for the $|S = 1, M = 1\rangle$ state in the product basis is the same as

	$J = j_1 + j_2$	$J = j_1 + j_2 - 1$	$J = j_1 + j_2 - 2$	$J = j_1 + j_2 - 3$
m=3	$\|3,3\rangle$			
m=2	$\|3,2\rangle$	$\|2,2\rangle$		
m=1	$\|3,1\rangle$	$\|2,1\rangle$	$\|1,1\rangle$	
m=0	$\|3,0\rangle$	$\|2,0\rangle$	$\|1,0\rangle$	$\|0,0\rangle$
M=-1	$\|3,-1\rangle$	$\|2,-1\rangle$	$\|1,-1\rangle$	
M=-2	$\|3,-2\rangle$	$\|2,-2\rangle$		
M=-3	$\|3,-3\rangle$			

	$J = 1$	$J = 0$
m=1	$\|1,1\rangle$	
m=0	$\|1,0\rangle$	$\|0,0\rangle$
M=-1	$\|1,-1\rangle$	

the state in the ST basis. We can now generate the other states via use of the ladder operators on this high spin state, i.e.,

$$\hat{S}_-|1,1\rangle = \frac{1}{\sqrt{2}}|1,0\rangle$$
$$= (\hat{s}_{1-} + \hat{s}_{2-})|1,1\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$$

acting again with the ladder operator yields

$$S_{-1}|S=1,M=0\rangle = |--\rangle \tag{17}$$

Whilst this proeedure is done for the simple case of two similar spins of $\frac{1}{2}$, is it can be applied generally to any angualr momenta, and hence may be applied recursively to build up systems of more than two couple momenta. For example, the appropriate basis for three coupled spins can be obtained by first constructing the ST basis for two coupled spins, and then coupling a further third spin to the states in this ST basis.

A side note is that the choice of phase for these spins can alter the sign resulting from application of the ladder operators. It is important to bear this in mind, but generally, the phase is chose so that the signs yielded are those shown above.

We now need to consider $|S=0,M=0\rangle$. This can be obtained by noting it must be orthogonal to the above defined states. By convention, it is also chosen such that it has real coefficients (I don't know if this convention has any significant ramifications, or requires justificaiton). We also require it to be normalized to 1. Orthogonality to $|++\rangle$ and $|--\rangle$ means the state must be written as some combination

$$|0,0\rangle = \alpha|+-\rangle + \beta|-+\rangle \quad \text{where} \quad \alpha+\beta=0 \quad \text{and} \quad \alpha^2+\beta^2=1 \tag{18}$$

Solving for α and β yields

$$|0,0\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \tag{19}$$

the standard covention is that the coefficient corresponding to the state with $m_1 = j_1$ positive for the $|J=0,M=0\rangle$ state. Again this doesn't truly matter, but is important

if we want our coefficients to match up with everyone elses.

We can now think about extending this to the general problem, i.e., the case where j_1 and j_2 take any value (where we chose the indexes so $j_1 \geq j_2$). As before, the state with the highest angular momenta ($J = j_1 + j_2$) is the same as can be built out of a single product ket

$$|J = (j_1 + j_2), M = (j_1 + j_2)\rangle = |j_1 = j_1, m_1 = j_1; j_2 = j_2, m_2 = j_2\rangle \tag{20}$$

As before we can use the ladder operators to decrease the value of M one step

$$|J = (j_1 + j_2), M = (j_1 + j_2)\rangle = \frac{1}{\hbar} J_- |J = (j_1 + j_2), M = (j_1 + j_2)\rangle \tag{21}$$

hence

$$|j_1 + j_2, j_1 + j_2 - 1\rangle = \sqrt{\frac{1}{2(j_1 + j_2)}}(J_{1-} + J_{2-})|J, M\rangle$$

$$J = |j_1{+}j_2, M = j_1{+}j_2{-}1\rangle = \sqrt{\frac{j_1}{j_1 + j_2}}\left|j_1 = (j_1{-}1), j_2 = j_2\right\rangle + \sqrt{\frac{j_2}{j_1 + j_2}}\left|j_1 = j_1, j_2 = (j_2{-}1)\right\rangle$$

So we can obtain all the states with $J = j_1{+}j_2$, $J \geq m_1 \geq -J$ by successively applying the ladder operator in this manner.

Now we must move onto states where $J = j_1 + j_2 - 1$. There are only two product kets from which we may construct the coupled basis; those with $|j_1 = j_1, m_1 = j_1; j_2 = j_2, m_2 = j_2 - 1\rangle$and $|j_1 = j_1, m_1 = j_1 - 1; j_2 = j_2, m_2 = j_2\rangle$.. By inspection the high M state for $J = j_1 + j_2 - 1$ is

$$|J = j_1{+}j_2{-}1, M = j_1{+}j_2{-}1\rangle = \sqrt{\frac{j_1}{j_1 + j_2}}\left|j_1, j_1; j_2, (j_2{-}1)\right\rangle - \sqrt{\frac{j_2}{j_1 + j_2}}\left|j_1, (j_1{-}1); j_2, j_2\right\rangle \tag{22}$$

To reiterate, the sign is always chosen to be positive for the state with $m_1 = j_1$.

We continue to proceed in this manner; apply various constraints to obtain the maximum possible value of M for each set of states with common J, and obtain all other states in that multiplet through application of the lowering operator.

The above leads to statements such as

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0, \tag{23}$$

i.e., the space necessary to describe two interacting spins with angular momenta 1/2 is equivalent to the space formed from the states of a spin with angular momentum 1, and a spin with angular momentum 0. More generally we can write

$$J_1 \otimes J_2 = \oplus_i j_i' \tag{24}$$

seperating out the space into a sum of a number of other spaces can greatly simplify some of the maths, and allow for the derivation of various selection rules.

2 Clebsch Gordon Coefficients

The product states form a complete basis for representation of the coupled states, hence we can write

$$|J, M\rangle = \sum_{m_1} \sum_{m_2} |j_1 m_1; j_2, m_2\rangle \langle j_1 m_1; j_2, m_2 | j_1 m_1; j_2, m_2\rangle \tag{25}$$

where $\rangle\langle j_1 m_1; j_2, m_2 | j_1 m_1; j_2, m_2\rangle$ are the referred to as the Clebsch-Gordon coefficients, i.e., the coefficients which take us from the product basis to the coupled basis.

These coefficients have a number of important properties

$$\langle j_1, m_1; j_2, m_2 | JM\rangle \neq 0 \qquad \text{iff} \qquad j_1 - j_2 \leq J \leq j_1 + j_2 \tag{26}$$

This is referred to as the triangle inequality, as it requires that we must be able to form a triangle with sides j_1, j_2 and J.

$$\langle j_1, m_1; j_2, m_2 | JM\rangle \neq 0 \qquad \text{iff} \qquad m_1 + m_2 = M \tag{27}$$

There also, by convention, always real, and as stated previously

$$\langle j_1, m_1; j_2, J - j_1 | JM\rangle \geq 0 \tag{28}$$

We can also note that the Clebsch-Gordon coefficients must obey the relation

$$\langle j_1, m_1; j_2, m_2 | JM\rangle = (-1)^{j_1 + j_2 - J} \langle j_1, -m_1; j_2, -m_2 | JM\rangle \tag{29}$$

indicating the matrix whose elements are the Clebsch-Gordon (CG) coefficients is antisymmetry, as we would expect given that it corresponds to a real, unitary transformation.

An illustrative example can be provided by using the CG coefficients determined in the previous section to construct a transformation matrix:

$$\begin{bmatrix} |1,1\rangle \\ |1,0\rangle \\ |0,0\rangle \\ |1,-1\rangle \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} & 0 \\ 0 & \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{bmatrix} \tag{30}$$

With these tools any space constructed from a product of angular momenta, $j_1 \otimes æ_2$ is reducible to to a linear combination of other angular momenta spaces, e.g.,

$$\begin{aligned} \frac{1}{2} \otimes \frac{1}{2} &= 1 \oplus 0 \\ \frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} &= \frac{1}{2} \otimes (1 \oplus 0) = \frac{3}{2} \oplus \frac{1}{2} \oplus \frac{1}{2} \end{aligned} \tag{31}$$

Hence any operator which is defined on a space formed from the product of angular momenta can be similarly decomposed. In the context of magnetic resonance theory this can be accomplished through use of irreducible tensor operators (ITOs)/spherical tensor operators(STOs)/irreducible spherical tensor operators(ISTOs) (sadly, all these various names all seem to be in use, despite the fact that not all irreducible tensor operators are spherical).

3 Cartesian, Irreducible and Spherical Tensor Operators

The most commonly encountered tensor are Cartesian tensors (CTs), ones whose elements transform under rotations in the same way we as a vector. That is, if a vector, $\mathbf{V}$, with elements V_i transforms under a rotation $\mathbf{R}$ between two co-ordinate systems labelled with indexes i and i' as

$$V_{i'} = \sum_i R_{i'i} V \tag{32}$$

then a tensor $\mathbf{T}$ which has components T_i when represented on a space formed from a product of such vectors will transform as

$$T_{i'j'k'....} R_{i'i} R_{j'j} R_{k'k} ... T_{ijk...} \tag{33}$$

not all tensors need to transform in this manner. The magnetic resonance (MR)[1] tensors (as they are usually defined) are generally of this type. However, Soncini's theory takes a different approach, and instead defines the MR tensors as being irreducible spherical tensor operators (ISTO). An irreducible spherical tensor (IST) being one whose elements transform in the same way as spherical harmonics, $\Upsilon_{l,m}(\theta, \phi)$.

Whilst in principle Soncini's definition is just a matter of formalism, it has a number of important differences to previous definitions. The first thing is to clarify the above definition of an IST: An IST of rank l has a $2l + 1$ elements, whose components transform as spherical harmonics $2l + 1$. Hence, only one set of spherical harmonics, those corresponding to angular momentum l, are involved in the definition of a tensor of a given rank. A consequence of this is that isomorphism between ISTs and CTs only exists for tensors of ranks 0 and 1. Hence a Catesian tensor of rank 2 *does not* necessarily correspond to a IST of rank-2, or any linear combination of such ISTs.

To illustrate this consider a real CT of rank 2 with 9 independent elements. Then note that an IST of rank 2 has only $2l + 1 = 5$ elements. However, we can get round this by chosing an appropriate decomposition of the CT tensor, e.g.,

$$\mathbf{T} = \mathbf{A} + \mathbf{B} + \mathbf{C} \tag{34}$$

Here $\mathbf{B}$ is an antisymmetric rank 2 CT whose elements which may be arranged into a 3×3 matrix. This tensor has 3 independent elements. If these elements transform under rotations like spherical harmonics, then $\mathbf{B}$ corresponds to a spherical tensor $S^{(1)}$ of rank 1. $\mathbf{C}$ is a second-rank, traceless symmetric CT. Such a CT has 5-independent elements. If these elements transform as spherical harmonics, then $\mathbf{C}$ corresponds to a spherical tensor,$S^{(2)}$ of rank 2. Finally, $\mathbf{A}$ is a second rank tensor with only one independent element, and is invariant under transformations (usually defined as a function of the trace of $\mathbf{T}$ and the diagonal elements of $\mathbf{C}$). Thus $\mathbf{A}$ will correspond to a ST $S^{(0)}$ of rank 0.

[1] shorthand for EPR/NMR/pNMR

Therefore, even if a CT such as $\mathbf{T}$ cannot itself be represented by an ST of a given rank, it can be represented by a linear combination of STs of varying rank, e.g.,

$$\begin{aligned}\mathbf{T} &= a_0 S_0^{(0)} + \sum_{m=-1}^{1} b_m S_m^{(1)} + \sum_{m=-2}^{2} c_m S_m^{(2)} \\ &= \sum_{l=0}^{2} \sum_{m=-l}^{+l} x_m^{(l)} S_m^{(l)} \end{aligned} \tag{35}$$

where a_0, $\{b_m\}_{m=-1,0,1}$ and $\{c_m\}_{m=-2,-1,0,1,2}\}$ are the coefficients corresponding to the tensors $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$. The coefficients $\{x_m^l\}$ is just a more compact way of writing this, and can be compared to equation A6 in Van den Heuvel & Soncini, J. Chem. Phys. 138, 054113 (2013).

This is directly connected to the preceeding discussion of decomposition of spaces formed from the product of angular momenta into linear combinations of spaces corresponding to a singular angular momenta. The elements of a Cartesian tensor operator (CTO) represented on spaces corresponding to a single angular momenta will transform as spherical harmonics, enabling us to represent these CTOs as a linear combination of spherical tensor operators (STOs).

To see how the coefficients a_0, $\{b_m\}_{m=-1,0,1}$ and $\{c_m\}_{m=-2,-1,0,1,2}\}$ may be obtained we need to consider how to map between a Cartesian basis $\{x, y, z\}$ and spherical harmonics. First note transform from Cartesian co-ordinate to spherical ones;

$$cos\theta = \frac{z}{r} \quad sin\theta = \frac{\sqrt{x^2+y^2}}{r} \quad e^{i\phi} sin\theta = \frac{x+iy}{r} \tag{36}$$

Then use these definitions to rewrite the spherical harmonics for $l = 1$ using Cartesian co-ordinates:

$$\Upsilon_{1,-1} = \sqrt{\frac{3}{4\pi}} \frac{x-iy}{r\sqrt{2}} \quad \Upsilon_{1,0} = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \quad \Upsilon_{1,+1} = \sqrt{\frac{3}{4\pi}} \frac{x+iy}{r\sqrt{2}} \tag{37}$$

and $l = 2$:

$$\begin{aligned} \Upsilon_{2,+2} &= \sqrt{\frac{15}{32\pi}} \frac{(x+iy)^2}{r^2} \quad \Upsilon_{2,-2} = \sqrt{\frac{15}{32\pi}} \frac{(x-iy)^2}{r^2} \\ \Upsilon_{2,+1} &= -2\sqrt{\frac{15}{32\pi}} \frac{x+iy}{r^2} z \quad \Upsilon_{2,-1} = 2\sqrt{\frac{15}{32\pi}} \frac{x-iy}{r^2} z \\ \Upsilon_{2,0} &= \frac{1}{\sqrt{3}} \sqrt{\frac{15}{32\pi}} \left(3\frac{z^2}{-}1 \right) \end{aligned} \tag{38}$$

Without loss of generality we can set $r = 1$ [2]. Furthermore, spherical harmonics of different l do not mix under transformations, therefore, the factors common to all members of a given l can be absorbed into the coefficients, leaving us with the much nicer definitions

$$\Upsilon_{1,-1} = \frac{x-iy}{\sqrt{2}} \quad \Upsilon_{1,0} = z \quad \Upsilon_{1,+1} = \frac{x+iy}{\sqrt{2}} \tag{39}$$

[2] defining the Cartesian basis such that $|\mathbf{x}|^2 + |\mathbf{y}|^2 + |\mathbf{z}|^2$

and $l = 2$:

$$\Upsilon_{2,+2} = (x + iy)^2 \quad \Upsilon_{2,-2} = (x - iy)^2$$
$$\Upsilon_{2,+1} = 2(x + iy)z \quad \Upsilon_{2,-1} = -2(x - iy)z$$
$$\Upsilon_{2,0} = \frac{1}{\sqrt{3}}\left(3\frac{z^2}{-}1\right) \tag{40}$$

It follows directly that the components, u_i of a Cartesian vector $\mathbf{U}$, may be written as:

$$v_{1,-1} = \frac{v_x - iv_y}{\sqrt{2}} \quad v_{1,0} = t_z \quad v_{1,+1} = \frac{v_x + iv_y}{\sqrt{2}} \tag{41}$$

and $l = 2$:

$$v_{2,+2} = (v_x + iv_y)^2 \quad v_{2,-2} = (v_x - iv_y)^2$$
$$v_{2,+1} = 2(v_x + iv_y)v_z \quad v_{2,-1} = -2(v_x - iv_y)v_z$$
$$v_{2,0} = \frac{1}{\sqrt{3}}(3v_z^2 - 1) \tag{42}$$

A vector operator is just one whose components transform as a vector. So the above tells us see how we can define a spherical tensor operator from a Cartesian vector operator $\hat{U}$. Unfortunately, in magnetic resonance we are generally concerned with tensor operators (an operator is one whose components transform as the corresponding tensor). Fortuntealy, these are formed from the dot product of two vector operators, e.g.,

$$\hat{\mathbf{U}} \cdot \hat{\mathbf{V}} = \hat{u}_x\hat{v}_x + \hat{u}_y\hat{v}_y + \hat{u}_z\hat{v}_z \tag{43}$$

Substituting in the definitions in (42) we obtain

$$\frac{U_{1,-1} - U_{1,1})(V_{1,-1} - V_{1,1})}{2} - \frac{(U_{-1,1} + U_{1,1})(V_{1,-1} + V_{1,1})}{2} + U_{1,0}V_{1,0}$$
$$= U_{1,0}V_{1,0} - U_{1,-1}V_{1,1} - U_{1,1}V_{1,-1} \tag{44}$$

Where t_i is the coefficient corresponding to the i-component of the tensor operator when represented in the Cartesian co-ordinate system.

It follows directly that the coefficients, $\{x_m^{(l)}\}_{m=-l,..,+l}^{l=0,2}$, used to weight the spherical tensors of Cartesian tensor $\mathbf{T}$ can be defined as
Tensor operators are essentially higher dimensional analogue of vector operators; they transform as a tensor under transformations, rather than a vector. It's important to note that in the above we only have
We can now connect this to the MR tensors, which are usually defined from vector operators of the form

$$\hat{\mathbf{V}} = \hat{\mathbf{B}} \otimes \hat{\mathbf{S}} = \hat{B}_x(\mathbf{S} \tag{45}$$

where $\hat{\mathbf{B}}$ is some vector (typically an external magnetic field), and $\hat{\mathbf{S}}$ is a magnetic magnetic moment which arises from the molecule[3]. Accordingly, we can treat this as three vectors operators; and represent each one of these as a linear combination of spherical tensor operators:

$$\hat{\mathbf{V}} = \hat{b}_x(\hat{s}_x + \hat{s}_y + \hat{s}_z)$$

[3]I know this looks like the formalism associated with the g-tensor, but it is general.

$$+\hat{b}_y(\hat{s}_x + \hat{s}_y + \hat{s}_z)$$
$$+\hat{b}_z(\hat{s}_x + \hat{s}_y + \hat{s}_z) \tag{46}$$

First, we can directly connect the coefficients associated with and MR tensor in the triplet case with the $l = 1$
($\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$

4 Appendix

First, the spin operators represented in the spin product basis (these are the matrices used by EasySpin).

$$S(x,1) = \begin{bmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{bmatrix} \tag{47}$$

$$S(y,1) = \begin{bmatrix} 0 & \frac{i}{\sqrt{2}} & 0 \\ \frac{-i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{bmatrix} \tag{48}$$

$$S(z,1) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & & 1 \end{bmatrix} \tag{49}$$

Now for the product operators, $\hat{s}_i \otimes \hat{s}_j$, represented in the spin product basis.

$$S_{xx} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix} \tag{50}$$

$$s_{xy} = \begin{bmatrix} \frac{-i}{2} & 0 & \frac{i}{2} \\ 0 & 1 & 0 \\ \frac{-i}{2} & 0 & \frac{i}{2} \end{bmatrix} \tag{51}$$

$$S_{xz} = \begin{bmatrix} 0 & 0 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 0 & 0 \end{bmatrix} \tag{52}$$

$$s_{yx} \begin{bmatrix} \frac{i}{2} & 0 & \frac{i}{2} \\ 0 & 1 & 0 \\ \frac{-i}{2} & 0 & \frac{-i}{2} \end{bmatrix} \tag{53}$$

$$s_{yy} = \begin{bmatrix} 0 & 0 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 0 & 0 \end{bmatrix} \tag{54}$$

$$s_{yz} = \begin{bmatrix} 0 & 0 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 0 & 0 \\ \frac{1}{2} & 0 & \frac{-1}{2} \\ 0 & 1 & 0 \\ \frac{-1}{2} & 0 & \frac{1}{2} \end{bmatrix} \tag{55}$$

$$s_{zx} \begin{bmatrix} \frac{i}{2} & 0 & \frac{i}{2} \\ 0 & 1 & 0 \\ \frac{-i}{2} & 0 & \frac{-i}{2} \end{bmatrix} \tag{56}$$

$$s_{zy} = \begin{bmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \\ 0 & \frac{-i}{\sqrt{2}} & 0 \end{bmatrix} \tag{57}$$

$$s_{zz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{58}$$