The SPINOR object of the CP-PAW code

Peter E. Blöchl

Institute of Theoretical Physics; Clausthal University of Technology;
D-38678 Clausthal Zellerfeld; Germany;
http://www.pt.tu-clausthal.de/atp/

Contents

Chapter 1

SPINOR object

1.1 Spin orbitals

An electron is specified by a position and a spin. We combine position and spin into a pseudo-fourdimensional vector

$$\vec{x} = (\vec{r}, \sigma) \tag{1.1}$$

where $\sigma \in \{\uparrow, \downarrow\}$.

An electron wave function naturally obtains a two-component form

$$\psi(\vec{x}) = \psi(\vec{r}, \sigma) = \langle \vec{r}, \sigma | \psi \rangle = \langle \vec{x} | \psi \rangle \tag{1.2}$$

Similarly, we combine sum over spin indices and integration over position into a quasi-fourdimensional integration

$$\int d^4x \; = \sum_\sigma \int d^3r \tag{1.3}$$

The identity operator has the form

$$\hat{1} = \int d^4x \; |\vec{x}\rangle\langle\vec{x}| \tag{1.4}$$

1.2 Pauli matrices and observables

All hermitean matrices in the two-dimensional spinor space can be represented as a superposition of the unit matrix and the three Pauli matrices. In other words, the Pauli matrices including the unit element are a complete basis in the space of all complex, hermitean 2×2 matrices.

$$\begin{aligned}
\mathbf{1} = \boldsymbol{\sigma}^{(0)} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \text{and} \qquad & \boldsymbol{\sigma}_x = \boldsymbol{\sigma}^{(1)} &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
\boldsymbol{\sigma}_y = \boldsymbol{\sigma}^{(2)} &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \text{and} \qquad & \boldsymbol{\sigma}_z = \boldsymbol{\sigma}^{(3)} &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{aligned} \tag{1.5}$$

The total density can be expressed by the unit matrix as

$$\rho(\vec{r}) = -e^2 \sum_{\sigma,\sigma'} \langle\psi|\vec{r},\sigma\rangle \sigma^{(0)}_{\sigma,\sigma'} \langle\vec{r},\sigma'|\psi\rangle = -e^2 \langle\psi| \Big[|\vec{r}\rangle\langle\vec{r}| \circ \hat{\sigma}^{(0)} \Big] |\psi\rangle$$

where $\hat{\sigma}^{(0)}$ is an operator in the two-dimensional spinor state. with the symbol $\circ$ we denote the product where each operator acts in its own Hilbert space.

Similarly we obtain the spin density in the form

$$S_j(\vec{r}) = \frac{\hbar}{2} \sum_{\sigma,\sigma'} \langle\psi|\vec{r},\sigma\rangle \sigma^{(j)}_{\sigma,\sigma'} \langle\vec{r},\sigma'|\psi\rangle = \frac{\hbar}{2} \sum_{\sigma,\sigma'} \langle\psi| \Big[|\vec{r}\rangle\langle\vec{r}| \circ \hat{\sigma}^{(j)} \Big] |\psi\rangle$$

Eigenvectors of Pauli matrices

The eigenvalue equation is

$$\sigma^{(j)}\xi^{(+j)} = \xi^{(+j)} \qquad \text{and} \qquad \sigma^{(j)}\xi^{(-j)} = -\xi^{(-j)} \tag{1.6}$$

Thus the eigenvalues are $+1$ and -1.

The eigenvectors of the Pauli matrices $\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z$ are

$$\xi^{(\pm x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm z)} = \frac{1}{2} \begin{pmatrix} 1 \pm 1 \\ 1 \mp 1 \end{pmatrix} \tag{1.7}$$

for the eigenvalues ± 1.

More explicitely,

$$\begin{aligned}
\xi^{(+x)} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(+y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ +i \end{pmatrix} \qquad \text{and} \qquad \xi^{(+z)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
\xi^{(-x)} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(-y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \qquad \text{and} \qquad \xi^{(-z)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\end{aligned} \tag{1.8}$$

1.3 Representation of a matrices in terms of Pauli matrices

Definition

Now we introduce a transformation between the two-dimensional matrix representation and the total-spin-vector representation for matrices

TRANSFORMATION OF MATRICES BETWEEN $(\uparrow,\downarrow)$ AND (T,X,Y,Z) REPRESENTATION

$$\underbrace{\rho_{\alpha,\beta,\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3} \bar{\rho}^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}}_{\text{back transform}} \qquad \overset{Eqs.\ A.4, A.7}{\Longleftrightarrow} \qquad \underbrace{\bar{\rho}^{(j)}_{\alpha,\beta} \overset{\text{def}}{=} \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'} \left(\sigma^{(j)}_{\sigma,\sigma'}\right)^*}_{\text{forward transform}} \tag{1.9}$$

Conversion of a matrix from $\uparrow,\downarrow$ into t,x,y,z representation and vice versa

We transform a matrix using to Eq. 1.9, which yields for the forward transformation

$$\begin{aligned}
\rho^{(0)}_{a,b} &= \rho_{a,b,\uparrow,\uparrow} + \rho_{a,b,\downarrow,\downarrow} \\
\rho^{(x)}_{a,b} &= \rho_{a,b,\downarrow,\uparrow} + \rho_{a,b,\uparrow,\downarrow} \\
\rho^{(y)}_{a,b} &= -i\Big(\rho_{a,b,\downarrow,\uparrow} - \rho_{a,b,\uparrow,\downarrow}\Big) \\
\rho^{(z)}_{a,b} &= \rho_{a,b,\uparrow,\uparrow} - \rho_{a,b,\downarrow,\downarrow}
\end{aligned} \tag{1.10}$$

and for the backward transformation

$$\begin{aligned}
\rho_{a,b,\uparrow,\uparrow} &= \frac{1}{2}\Big(\rho^{(0)}_{a,b} + \rho^{(z)}_{a,b}\Big) \\
\rho_{a,b,\downarrow,\uparrow} &= \frac{1}{2}\Big(\rho^{(x)}_{a,b} + i\rho^{(y)}_{a,b}\Big) \\
\rho_{a,b,\uparrow,\downarrow} &= \frac{1}{2}\Big(\rho^{(x)}_{a,b} - i\rho^{(y)}_{a,b}\Big) \\
\rho_{a,b,\downarrow,\downarrow} &= \frac{1}{2}\Big(\rho^{(0)}_{a,b} - \rho^{(z)}_{a,b}\Big)
\end{aligned} \tag{1.11}$$

In practice we distinguish the three cases, namely non spin-polarized, collinear spin-polarized, and non-collinear.

Motivation

The convention to apply the factor 1/2 on the back transformation of Eq. 1.9 is motivated as follows: For a collinear spin density in z-direction, the total density is defined as $n_t = n_{\uparrow,\uparrow} + n_{\downarrow,\downarrow}$ and the spin density is defined as $n_s = n_{\uparrow,\uparrow} - n_{\downarrow,\downarrow}$. In that case, the density matrix would have the form

$$n_{\sigma,\sigma'} = \frac{1}{2}n^{(0)}\sigma^{(0)}_{\sigma,\sigma'} + \frac{1}{2}n^{(4)}\sigma^{(4)}_{\sigma,\sigma'} = \begin{pmatrix} \frac{1}{2}n^{(0)} + \frac{1}{2}n^{(4)} & 0 \\ 0 & \frac{1}{2}n^{(0)} - \frac{1}{2}n^{(4)} \end{pmatrix}$$

which allows to identify $n^{(0)} = n_t$ with the total density and $n^{(4)} = n_s$ with the spin density.

This yields

SPIN DEPENDENCE OF THE DENSITY MATRIX

$$\rho(\vec{x},\vec{x'}) = \sum_{\alpha,\beta} \rho_{\alpha,\beta,\sigma,\sigma'}\bar{\chi}_\alpha(\vec{r})\bar{\chi}_\beta(\vec{r'}) \tag{1.12}$$

$$= \frac{1}{2}\sum_{j=0}^{3}\sum_{\alpha,\beta} \rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}\bar{\chi}_\alpha(\vec{r})\bar{\chi}_\beta(\vec{r'}) \tag{1.13}$$

1.3.1 Identity in a spinor representation

The identity matrix in up-down representation is

$$\begin{pmatrix} \boldsymbol{\rho}_{\uparrow,\uparrow} & \boldsymbol{\rho}_{\uparrow,\downarrow} \\ \boldsymbol{\rho}_{\downarrow,\uparrow} & \boldsymbol{\rho}_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} \mathbf{1}_{\uparrow,\uparrow} & \mathbf{0}_{\uparrow,\downarrow} \\ \mathbf{0}_{\downarrow,\uparrow} & \mathbf{1}_{\downarrow,\downarrow} \end{pmatrix} \tag{1.14}$$

After conversion into the spinor representation we obtain

$$\boldsymbol{\rho}^{(0)} = 2\cdot\mathbf{1}; \qquad \boldsymbol{\rho}^{(1)} = \mathbf{0}; \qquad \boldsymbol{\rho}^{(2)} = \mathbf{0}; \qquad \boldsymbol{\rho}^{(3)} = \mathbf{0} \tag{1.15}$$

1.3.2 Hermitean conjugate in a spinor representation

The identity matrix in up-down representation is

$$\begin{pmatrix} \left(\boldsymbol{\rho}^\dagger\right)_{\uparrow,\uparrow} & \left(\boldsymbol{\rho}^\dagger\right)_{\uparrow,\downarrow} \\ \left(\boldsymbol{\rho}^\dagger\right)_{\downarrow,\uparrow} & \left(\boldsymbol{\rho}^\dagger\right)_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} \left(\boldsymbol{\rho}_{\uparrow,\uparrow}\right)^\dagger & \left(\boldsymbol{\rho}_{\downarrow,\uparrow}\right)^\dagger \\ \left(\boldsymbol{\rho}_{\uparrow,\downarrow}\right)^\dagger & \left(\boldsymbol{\rho}_{\downarrow,\downarrow}\right)^\dagger \end{pmatrix} \tag{1.16}$$

After conversion into the spinor representation we obtain

$$\left(\boldsymbol{\rho}^\dagger\right)^{(0)} = \left(\boldsymbol{\rho}^{(0)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(x)} = \left(\boldsymbol{\rho}^{(x)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(y)} = \left(\boldsymbol{\rho}^{(y)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(z)} = \left(\boldsymbol{\rho}^{(z)}\right)^\dagger \tag{1.17}$$

1.3.3 Multiplication of matrices in a spinor representation

Consider to matrices in spinor representation

$$f_{a,b,\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3} \boldsymbol{f}^{(j)}_{a,b}\sigma^{(j)}_{\sigma,\sigma'}$$

now we wish to perform a matrix multiplication

$$\begin{aligned}
\sum_{c,\sigma''} f_{a,c,\sigma,\sigma''}g_{c,b,\sigma'',\sigma'} &= \left(\frac{1}{2}\sum_{j=0}^{3}\boldsymbol{f}^{(j)}_{a,c}\sigma^{(j)}_{\sigma,\sigma''}\right)\left(\frac{1}{2}\sum_{j=0}^{3}\boldsymbol{g}^{(j')}_{c,b}\sigma^{(j')}_{\sigma'',\sigma'}\right) \\
&= \left(\frac{1}{2}\sum_{i=0}^{3} f^{(i)}_{a,c}\sigma^{(i)}_{\sigma,\sigma''}\right)\left(\frac{1}{2}\sum_{j=0}^{3} g^{(j)}_{c,b}\sigma^{(j)}_{\sigma'',\sigma'}\right) \\
&= \frac{1}{4}\sum_{i,j=0}^{3} f^{(i)}_{a,c}g^{(j)}_{c,b}\left(\sigma^{(i)}_{\sigma,\sigma''}\sigma^{(j)}_{\sigma'',\sigma'}\right) \\
&\overset{\text{Eq. A.9}}{=} \frac{1}{2}\left(\frac{1}{2}\sum_{j=0}^{3} f^{(j)}_{a,c}g^{(j)}_{c,b}\right)\sigma^{(0)}_{\sigma,\sigma'} + \frac{1}{2}\sum_{k=1}^{3}\left(\frac{1}{2}\sum_{i=1}^{3}\left(f^{(0)}_{a,c}g^{(k)}_{c,b} + f^{(k)}_{a,c}g^{(0)}_{c,b}\right) + \frac{i}{2}\sum_{i,j=1}^{3}\epsilon_{i,j,k}f^{(i)}_{a,c}g^{(j)}_{c,b}\right)
\end{aligned}$$

Thus if we denote the multiplication as defined above with the symbol □, we obtain

$$\left(\boldsymbol{f}\Box\boldsymbol{g}\right)^{(0)} = \frac{1}{2}\sum_{j=0}^{3} f^{(j)}_{a,c}g^{(j)}_{c,b} \tag{1.18}$$

$$\left(\boldsymbol{f}\Box\boldsymbol{g}\right)^{(j)} = \frac{1}{2}\sum_{i=1}^{3}\left(f^{(0)}_{a,c}g^{(k)}_{c,b} + f^{(k)}_{a,c}g^{(0)}_{c,b}\right) + \frac{i}{2}\sum_{i,j=1}^{3}\epsilon_{i,j,k}f^{(i)}_{a,c}g^{(j)}_{c,b} \qquad \text{for } j>0 \tag{1.19}$$

This expression requires 16 matrix multiplication in the $a, b, c, \ldots$ space, just as if the operations would be done in the $\uparrow ., \downarrow$ representation.

1.3.4 Inversion of a matrix in a spinor representation

The inversion is done by first bringing the matrix into the $\uparrow, \downarrow$ representation using Eq. 1.9.

The problem can then be formulated as a matrix inversion in the (orbital/spin) space

$$\begin{pmatrix} \boldsymbol{A}_{11} & \boldsymbol{A}_{12} \\ \boldsymbol{A}_{21} & \boldsymbol{A}_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{B}_{11} & \boldsymbol{B}_{12} \\ \boldsymbol{B}_{21} & \boldsymbol{B}_{22} \end{pmatrix} = \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1} \end{pmatrix} \tag{1.20}$$

In components, we obtain

$$\begin{aligned} \boldsymbol{A}_{11}\boldsymbol{B}_{11} + \boldsymbol{A}_{12}\boldsymbol{B}_{21} &= \boldsymbol{1} \\ \boldsymbol{A}_{11}\boldsymbol{B}_{12} + \boldsymbol{A}_{12}\boldsymbol{B}_{22} &= \boldsymbol{0} \\ \boldsymbol{A}_{21}\boldsymbol{B}_{11} + \boldsymbol{A}_{22}\boldsymbol{B}_{21} &= \boldsymbol{0} \\ \boldsymbol{A}_{21}\boldsymbol{B}_{12} + \boldsymbol{A}_{22}\boldsymbol{B}_{22} &= \boldsymbol{1} \end{aligned} \tag{1.21}$$

which leads to

$$\begin{aligned} \boldsymbol{B}_{12} &= \underbrace{-\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12}}_{a_{12}}\boldsymbol{B}_{22} \\ \boldsymbol{B}_{21} &= \underbrace{-\boldsymbol{A}_{22}^{-1}\boldsymbol{A}_{21}}_{a_{21}}\boldsymbol{B}_{11} \\ \boldsymbol{B}_{11} &= \Big(\boldsymbol{A}_{11} - \boldsymbol{A}_{12}\underbrace{\boldsymbol{A}_{22}^{-1}\boldsymbol{A}_{21}}_{-a_{21}}\Big)^{-1} \\ \boldsymbol{B}_{22} &= \Big(\boldsymbol{A}_{22} - \boldsymbol{A}_{21}\underbrace{\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12}}_{a_{12}}\Big)^{-1} \end{aligned}$$

The operations are done in the following order

$$\begin{aligned} &\boldsymbol{C}_{11} = \boldsymbol{A}_{11}^{-1} \\ &\boldsymbol{C}_{12} = -\boldsymbol{C}_{11}\boldsymbol{A}_{12} = -\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12} \\ &\boldsymbol{C}_{22} = \boldsymbol{A}_{22} + \boldsymbol{A}_{21}\boldsymbol{C}_{12} = \boldsymbol{A}_{22} - \boldsymbol{A}_{21}\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12} \\ &\boldsymbol{B}_{22} = \boldsymbol{C}_{22}^{-1} = \Big(\boldsymbol{A}_{22} - \boldsymbol{A}_{21}\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12}\Big)^{-1} \\ &\boldsymbol{B}_{12} = \boldsymbol{C}_{12}\boldsymbol{B}_{22} \\ &\boldsymbol{C}_{22} = \boldsymbol{A}_{22}^{-1} \\ &\boldsymbol{C}_{21} = -\boldsymbol{C}_{22}\boldsymbol{A}_{21} = -\boldsymbol{A}_{22}^{-1}\boldsymbol{A}_{21} \\ &\boldsymbol{C}_{11} = \boldsymbol{A}_{11} + \boldsymbol{A}_{12}\boldsymbol{C}_{21} = \boldsymbol{A}_{11} - \boldsymbol{A}_{12}\boldsymbol{A}_{22}^{-1}\boldsymbol{A}_{21} \\ &\boldsymbol{B}_{11} = \boldsymbol{C}_{11}^{-1} = \Big(\boldsymbol{A}_{11} - \boldsymbol{A}_{12}\boldsymbol{A}_{22}^{-1}\boldsymbol{A}_{21}\Big)^{-1} \\ &\boldsymbol{B}_{21} = \boldsymbol{C}_{21}\boldsymbol{B}_{11} \end{aligned}$$

The matrix $\boldsymbol{A}_{11}^{-1}$ can be overlayed with $\boldsymbol{B}_{11}$, $\boldsymbol{A}_{22}^{-1}$ can be overlayed with $\boldsymbol{B}_{22}$, $\boldsymbol{C}_{12}$ can be overlayed with $\boldsymbol{B}_{12}$, and $\boldsymbol{C}_{21}$ can be overlayed with $\boldsymbol{B}_{21}$.

The operations can be done with 4 matrix inversions and 6 matrix multiplications for a general non-collinear problem. (Operations that scale better than the cube behavior are ignored.)

It may be interestint to analyze the scaling behavior. Consider that the computational effort for an inversion of a matrix with dimension n is an^3. The effort for a matrix multiplication shall be bn^3. Thus the scaling will be

$$a(2n)^3 = 4a^3 + 6bn^3 + cn^2 \qquad \rightarrow \qquad a = \frac{3}{2}b + \frac{c}{4n} \tag{1.22}$$

This implies that a matrix inversion takes about 1.5 times the computational effort of a matrix multiplication.

1.3.5 Hermitean Matrices

A matrix that is hermitean in spin-up-down representation, that is

$$\rho_{a,b,\sigma,\sigma'} = \rho^*_{b,a,\sigma',\sigma} \Leftrightarrow \rho^{(j)}_{a,b} = \left(\rho^{(j)}_{b,a}\right)^* \tag{1.23}$$

has hermitean matrices in total-spin representation, and vice versa

This is derived in the following. First we show that

$$\rho^{(j)}_{a,b} = \left(\rho^{(j)}_{b,a}\right)^* \tag{1.24}$$

can be obtained from the hermitean property in spin space, namely

$$\rho_{a,b,\sigma,\sigma'} = \rho^*_{b,a,\sigma',\sigma} \tag{1.25}$$

This is shown as follows

$$\begin{aligned}\rho^{(j)}_{a,b} &\overset{\text{Eq. 1.9}}{=} \sum_{\sigma\sigma'} \rho_{a,b,\sigma,\sigma'} \left(\sigma^{(j)}_{\sigma,\sigma'}\right)^* \overset{\text{Eq. 1.25}}{=} \sum_{\sigma\sigma'} \rho^*_{b,a,\sigma',\sigma} \left(\sigma^{(j)}_{\sigma,\sigma'}\right)^* \overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=} \sum_{\sigma\sigma'} \rho^*_{b,a,\sigma',\sigma} \left(\sigma^{(j)}_{\sigma',\sigma}\right) \\ &\overset{\text{Eq. 1.9}}{=} \left(\rho^{(j)}_{b,a}\right)^*\end{aligned} \tag{1.26}$$

Now we derive the opposite direction:

$$\begin{aligned}\rho_{a,b,\sigma,\sigma'} &\overset{\text{Eq. 1.9}}{=} \frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{a,b}\sigma^{(j)}_{\sigma,\sigma'} \overset{\text{Eq. 1.24}}{=} \frac{1}{2}\sum_{j=0}^{3}\left(\rho^{(j)}_{b,a}\right)^* \sigma^{(j)}_{\sigma,\sigma'} \overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=} \left(\frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{b,a}\sigma^{(j)}_{\sigma',\sigma}\right)^* \\ &\overset{\text{Eq. 1.9}}{=} \left(\rho_{b,a,\sigma',\sigma}\right)^*\end{aligned} \tag{1.27}$$

1.4 Density matrices and spin orbitals with defined spin

Let us choose a basis set $\{|\chi_\alpha\rangle\}$ with states that are product states of a spatial orbital $\bar{\chi}_\alpha(\vec{r})$ and a spin orbital ξ_α, such as

$$\chi_\alpha(\vec{x}) = \bar{\chi}_\alpha(\vec{r})\xi_\alpha(\sigma) \tag{1.28}$$

Typically, the spin orbitals are eigenstates to $\boldsymbol{\sigma}_z$ so that $\xi_\alpha(\sigma) = \delta_{\sigma,\sigma_\alpha}$ and $\sigma_\alpha \in \{\uparrow,\downarrow\} = \{(1,0),(0,1)\}$.

In that case we can write the density matrix

$$\begin{aligned}\rho(\vec{x},\vec{x'}) &= \sum_{\alpha,\beta}\chi_\alpha(\vec{x})\rho_{\alpha,\beta}\chi^*_\beta(\vec{x'})\\ &= \sum_{\alpha,\beta}\bar{\chi}_\alpha(\vec{r})\underbrace{\xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma')}_{\rho_{\alpha,\beta,\sigma,\sigma'}}\bar{\chi}^*_\beta(\vec{r'})\\ &= \sum_{\alpha,\beta}\bar{\chi}_\alpha(\vec{r})\rho_{\alpha,\beta,\sigma,\sigma'}\bar{\chi}^*_\beta(\vec{r'})\end{aligned} \tag{1.29}$$

Here we have defined the density matrix with explicit spin dependence

$$\rho_{\alpha,\beta,\sigma,\sigma'} \stackrel{\text{def}}{=} \xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma') \tag{1.30}$$

The density matrices $\rho_{\sigma,\sigma'} = \xi(\sigma)\xi^*(\sigma')$ for the spin eigenstates Eq. 1.7 are

$$\boldsymbol{\rho}(\pm x) = \frac{1}{2}\begin{pmatrix}1 & \pm1\\ \pm1 & 1\end{pmatrix} \quad\text{and}\quad \boldsymbol{\rho}(\pm y) = \frac{1}{2}\begin{pmatrix}1 & \mp i\\ \pm i & 1\end{pmatrix} \quad\text{and}\quad \boldsymbol{\rho}(\pm z) = \frac{1}{2}\begin{pmatrix}1\pm1 & 0\\ 0 & 1\mp1\end{pmatrix}$$

They obey $\mathrm{Tr}[\boldsymbol{\rho}(\pm j)\boldsymbol{\sigma}^{(j')}] = \pm\delta_{j,j'}$ for $j,j' \in \{x,y,z\}$ and $\mathrm{Tr}[\boldsymbol{\rho}(\pm j)\boldsymbol{\sigma}^{(0)}] = 1$.

1.5 Potentials and spin orbitals

General definition of a potential for a complex matrix quantity

POTENTIAL AS ENERGY DERIVATIVE

The potential of a matrix quantity must be written in the following form

$$V = \frac{dE}{dn^*}$$

For Hermitean quantities, this yields

$$V_{\alpha,\beta} = \frac{dE}{d\rho^*_{\alpha,\beta}} = \frac{dE}{d\rho_{\beta,\alpha}}$$

This has the following reasons

- The trace formula comes from

$$dE = \mathrm{Tr}[\hat{V}d\hat{\rho}] = \sum_{\alpha,\beta}\langle\alpha|\hat{V}|\beta\rangle\langle\beta|d\hat{\rho}|\alpha\rangle = \sum_{\alpha,\beta}V_{\alpha,\beta}d\rho_{\beta,\alpha} \stackrel{\rho=\rho^\dagger}{=} \sum_{\alpha,\beta}V_{\alpha,\beta}d\rho^*_{\alpha,\beta} \qquad\Rightarrow\qquad \frac{\partial E}{\partial\rho^*_{\alpha,\beta}} = V_{\alpha,\beta}$$

- Another form

$$
\begin{aligned}
E &= F[\underbrace{\sum_{\alpha,\beta}\chi_\alpha(\vec{x})\rho_{\alpha,\beta}\chi^*_\beta(\vec{x'})]}_{\rho(\vec{x},\vec{x'})} \\
V_{\alpha,\beta} = \frac{\partial E}{\partial \rho^*_{\alpha,\beta}} &= \left(\frac{\partial E}{\partial \rho_{\alpha,\beta}}\right)^* \overset{\text{Eq. 1.29}}{=} \left(\int d^4x \int d^4x'\ \frac{\partial E}{\partial \rho(\vec{x},\vec{x'})}\chi_\alpha(\vec{x})\chi^*_\beta(\vec{x'})]\right)^* \\
&= \int d^4x \int d^4x'\ \chi^*_\alpha(\vec{x})\underbrace{\frac{\partial E}{\partial \rho^*(\vec{x},\vec{x'})}}_{v(\vec{x},\vec{x'})}\chi_\beta(\vec{x}) = \int d^4x \int d^4x'\ \chi^*_\alpha(\vec{x})v(\vec{x},\vec{x'})\chi_\beta(\vec{x'}) \\
&= \langle\chi_\alpha|\hat{V}|\chi_\beta\rangle
\end{aligned}
$$

- Similarly, we obtain

$$
\begin{aligned}
E &= F[\sum_n \langle\pi_\alpha|\psi_n\rangle f_n\langle\psi_n|\pi_\beta\rangle] \\
\frac{\partial E}{\partial\langle\psi_n|} &= \sum_{\alpha,\beta}|\pi_\beta\rangle\frac{\partial F}{\partial\rho_{\alpha,\beta}}\langle\pi_\alpha|\psi_n\rangle f_n = \sum_{\alpha,\beta}|\pi_\beta\rangle\frac{\partial F}{\partial\rho^*_{\beta,\alpha}}\langle\pi_\alpha|\psi_n\rangle f_n \\
&= \sum_{\alpha,\beta}|\pi_\beta\rangle V_{\beta,\alpha}\langle\pi_\alpha|\psi_n\rangle f_n
\end{aligned}
$$

- with k-points: The density matrix is defined as

$$
\rho_{\alpha,\beta}(\vec{t}_\beta) = \frac{1}{N_k}\sum_{\vec{k}}\langle\pi_\alpha|\psi_n(\vec{k})\rangle f_n(\vec{k})\langle\psi_n(\vec{k})|\pi_\beta\rangle e^{i\vec{k}\vec{t}_\beta}
$$

The density matrix connects an orbital $|\chi_\alpha\rangle$ at $\vec{R}_\alpha$ with an orbital $|\chi_\beta\rangle$ at $\vec{R}_\beta + \vec{t}_\beta$.

$$
\begin{aligned}
\frac{dF}{d\langle\psi_n(\vec{k})|} &= \sum_{\alpha,\beta,\vec{t}_\beta}\frac{dF}{d\rho_{\alpha,\beta}(\vec{t}_\beta)}\frac{d}{d\langle\psi_n(\vec{k})|}\left[\frac{1}{N_k}\sum_{\vec{k}}\sum_n\langle\pi_\alpha|\psi_n(\vec{k})\rangle f_n(\vec{k})\langle\psi_n(\vec{k})|\pi_\beta\rangle e^{i\vec{k}\vec{t}_\beta}\right] \\
&= \frac{1}{N_k}\sum_{\vec{k}}\sum_{\alpha,\beta,\vec{t}_\beta}|\pi_\beta\rangle\left[\frac{dF}{d\rho_{\alpha,\beta}(\vec{t}_\beta)}e^{i\vec{k}\vec{t}_\beta}\langle\pi_\alpha|\psi_n(\vec{k})\rangle f_n(\vec{k})\right. \\
&= \frac{1}{N_k}\sum_{\vec{k}}\sum_{\beta}|\pi_\beta\rangle\left[\sum_{\alpha,\vec{t}_\beta}\underbrace{\frac{dF}{d\rho_{\alpha,\beta}(\vec{t}_\beta)}}_{=V_{\beta,\alpha(\vec{t}_\alpha)}}e^{i\vec{k}\vec{t}_\beta}\langle\pi_\alpha|\psi_n(\vec{k})\rangle\right]f_n(\vec{k})
\end{aligned}
$$

In the implementation, I am using the variable hamil sometimes as V and sometimes as derivative of the functional. The two are hermitean adjuncts of each other, i.e. $V_{\alpha,\beta}(\vec{t}) = V^*_{\beta,\alpha}(-\vec{t})$.

Spin potentials

Let us now return to the potentials obtained as derivative with respect to the different forms of the density matrix.

$$
\begin{aligned}
\bar{V}^{(j)}_{\alpha,\beta} &= \frac{\partial E}{\partial \bar{\rho}^{(j)*}_{\alpha,\beta}} \\
V_{\alpha,\beta,\sigma,\sigma'} &= \frac{\partial E}{\partial \rho^{*}_{\alpha,\beta,\sigma,\sigma'}} = \sum_j \frac{\partial E}{\partial \bar{\rho}^{(j)*}_{\alpha,\beta}} \frac{\partial \bar{\rho}^{(j)*}_{\alpha,\beta}}{\partial \rho^{*}_{\alpha,\beta,\sigma,\sigma'}} = \sum_j \bar{V}^{(j)}_{\alpha,\beta} \left(\frac{\partial \bar{\rho}^{(j)}_{\alpha,\beta}}{\partial \rho_{\alpha,\beta,\sigma,\sigma'}} \right)^* \\
&\overset{\text{Eq. 1.9}}{=} \sum_j \bar{V}^{(j)}_{\alpha,\beta} \left(\sigma^{(j)}_{\sigma,\sigma'} \right)^*
\end{aligned}
$$

TRANSFORMATION FROM A TOTAL-SPIN TO AN UP-DOWN REPRESENTATION

$$
\begin{aligned}
\rho^{(t)} &= \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow} & \rho_{\uparrow,\uparrow} &= \frac{1}{2}(\rho^{(t)} + \rho^{(z)}) \\
\rho^{(x)} &= \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow} & \rho_{\uparrow,\downarrow} &= \frac{1}{2}(\rho^{(x)} - i\rho^{(y)}) \\
\rho^{(y)} &= i(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow}) & \rho_{\downarrow,\uparrow} &= \frac{1}{2}(\rho^{(x)} + i\rho^{(y)}) \\
\rho^{(z)} &= \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow} & \rho_{\downarrow,\downarrow} &= \frac{1}{2}(\rho^{(t)} - \rho^{(z)})
\end{aligned}
$$

For the potentials $v = \left(\frac{\partial E}{\partial \rho}\right)^*$ we obtain

$$
\begin{aligned}
v^{(t)} &= \frac{1}{2}\Big(v_{\uparrow,\uparrow} + v_{\downarrow,\downarrow}\Big) & v_{\uparrow,\uparrow} &= v^{(t)} + v^{(z)} \\
v^{(x)} &= \frac{1}{2}\Big(v_{\uparrow,\downarrow} + v_{\downarrow,\uparrow}\Big) & v_{\uparrow,\downarrow} &= v^{(x)} - iv^{(y)} \\
v^{(y)} &= \frac{i}{2}\Big(v_{\uparrow,\downarrow} - v_{\downarrow,\uparrow}\Big) & v_{\downarrow,\uparrow} &= v^{(x)} + iv^{(y)} \\
v^{(z)} &= \frac{1}{2}\Big(v_{\uparrow,\uparrow} - v_{\downarrow,\downarrow}\Big) & v_{\downarrow,\downarrow} &= v^{(t)} - v^{(z)}
\end{aligned}
$$

These transformations are used in `LDAPLUSU_edft`, `LDAPLUSU_SPINDENMAT`, `LMTO_NTBODENMAT`, `LMTO_NTBODENMATDER`, `WAVES_DENMAT`, `WAVES_DENSITY`.

1.6 Description of Subroutines

[1]

We consider a Hilbert space of two-component spinor wave functions. A real-space-spin basis is $|\vec{r},\sigma\rangle$. Instead of the real space position we may also use a set of orbitals $|\alpha,\sigma\rangle$, which are spin eigenstates with the spatial dependence defined by α, that is $\langle\vec{r},\sigma|\alpha,\sigma\rangle = \langle\vec{r},\sigma'|\alpha,\sigma'\rangle$ and $\langle\vec{r},\sigma|\alpha,\sigma'\rangle = 0$ for $\sigma \neq \sigma'$.

In this basisset a matrix element has the form

$$
\begin{aligned}
A_{\alpha,\beta,\sigma,\sigma'} &= \langle\alpha,\sigma|\hat{A}|\beta,\sigma'\rangle \\
\hat{A} &= \sum_{\alpha,\beta,\sigma,\sigma'} |\alpha,\sigma\rangle A_{\alpha,\beta,\sigma,\sigma'}\langle\beta,\sigma'|
\end{aligned}
$$

An expectation value is obtained by

$$
\begin{aligned}
\langle A\rangle &= \sum_n f_n\langle\psi_n|\hat{A}|\psi_n\rangle \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \underbrace{\left(\sum_n \langle\beta,\sigma'|\psi_n\rangle f_n\langle\psi_n|\alpha,\sigma\rangle\right)}_{\rho_{\beta,\alpha,\sigma',\sigma}} A_{\alpha,\beta,\sigma,\sigma'} \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \rho_{\beta,\alpha,\sigma',\sigma}A_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{1.31}
$$

This defines the matrix elements of the density matrix as

$$
\rho_{\alpha,\beta,\sigma,\sigma'} = \langle\beta,\sigma'|\psi_n\rangle f_n\langle\psi_n|\alpha,\sigma\rangle \tag{1.32}
$$

(t,x,y,z) representation

Let us transform the matrix elements

$$
\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma} \\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma}
\end{aligned}
\tag{1.33}
$$

The back transformation is correspondingly

$$
\begin{aligned}
A_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} A^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'} \\
\rho_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}
\end{aligned}
\tag{1.34}
$$

Proof:

$$
\begin{aligned}
\frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} \underbrace{\left(\sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''}\sigma^{(j)}_{\sigma''',\sigma''}\right)}_{\rho^{(j)}_{\alpha,\beta}} \sigma^{(j)}_{\sigma,\sigma'} \\
&= \sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''} \underbrace{\left(\frac{1}{2}\sum_{j=0}^{3}\sigma^{(j)}_{\sigma''',\sigma''}(\sigma^{(j)}_{\sigma',\sigma})^*\right)}_{\delta_{\sigma''',\sigma'}\delta_{\sigma'',\sigma}} \\
&= \rho_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{1.35}
$$

Expectation value by trace

Now we need the expression for the expectation value

$$\langle A\rangle = \mathrm{Tr}\Big(\hat\rho\ \hat A\Big) = \sum_{\alpha,\beta,\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'} A_{\beta,\alpha,\sigma',\sigma} = \sum_{\alpha,\beta,\sigma,\sigma'} \underbrace{\frac{1}{2}\sum_{j=0}^{3} \bar\rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}}_{\rho_{\alpha\beta,\sigma,\sigma'}} A_{\beta,\alpha,\sigma',\sigma}$$
$$= \frac{1}{2}\sum_{j=0}^{3}\sum_{\alpha,\beta}\bar\rho^{(j)}_{\alpha,\beta}\underbrace{\Big(\sum_{\sigma,\sigma'} A_{\beta,\alpha,\sigma',\sigma}\sigma^{(j)}_{\sigma,\sigma'}\Big)}_{A^{(j)}_{\beta,\alpha}} = \frac{1}{2}\sum_{j=0}^{3}\sum_{\alpha,\beta}\bar\rho^{(j)}_{\alpha,\beta}A^{(j)}_{\beta,\alpha}$$

Physical

Total density

$$\rho_t = \rho^{(0)} = \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow} \tag{1.36}$$
$$\rho_x = \rho^{(0)} = \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow} \tag{1.37}$$
$$\rho_y = \rho^{(0)} = -i\Big(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow}\Big) \tag{1.38}$$
$$\rho_z = \rho^{(0)} = \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow} \tag{1.39}$$

An expectation value is

$$\begin{aligned}
A_{\uparrow,\uparrow} &= \frac{1}{2}\Big(A^{(t)} + A^{(z)}\Big)\\
A_{\uparrow,\downarrow} &= \frac{1}{2}\Big(A^{(x)} - iA^{(y)}\Big)\\
A_{\downarrow,\uparrow} &= \frac{1}{2}\Big(A^{(x)} + iA^{(y)}\Big)\\
A_{\downarrow,\downarrow} &= \frac{1}{2}\Big(A^{(t)} - A^{(z)}\Big)
\end{aligned} \tag{1.40}$$

$$\begin{aligned}
dE &= \sum_{\alpha,\beta,\sigma,\sigma'} \frac{dE}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma}\\
&= \sum_{\alpha,\beta,\sigma,\sigma'}\sum_{j=0}^{3} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \frac{d\rho^{(j)}_{\beta,\alpha}}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma}\\
&= \sum_{j=0}^{3}\sum_{\alpha,\beta} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \Big(\sum_{\sigma,\sigma'}\sigma^{(j)}_{\sigma,\sigma'} d\rho_{\beta,\alpha,\sigma',\sigma}\Big)\\
&= \sum_{j=0}^{3}\sum_{\alpha,\beta}\Big(\frac{dE}{d\rho^{(j)}_{\beta,\alpha}}\Big) d\rho^{(j)}_{\beta,\alpha}
\end{aligned} \tag{1.41}$$

There is an ambiguity becauae of the trace formula

$$A = \frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}A^{(j)} \tag{1.42}$$

$$dE = \sum_{j=0}^{3}\frac{dE}{d\rho^{(j)}}d\rho^{(j)} \tag{1.43}$$

$$v^{(j)} = 2\frac{dE}{d\rho^{(j)}} \tag{1.44}$$

Using the transformation equation for expectation values

$$v_{\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3}v^{(j)}\sigma^{(j)}_{\sigma,\sigma'} = \sum_{j=0}^{3}\frac{dE}{d\rho^{(j)}}\sigma^{(j)}_{\sigma,\sigma'} \tag{1.45}$$

$$\begin{aligned}
v_{\uparrow,\uparrow} &= \frac{1}{2}(v_t + v_z) \\
v_{\uparrow,\downarrow} &= \frac{1}{2}(v_x - iv_y) \\
v_{\downarrow,\uparrow} &= \frac{1}{2}(v_x + iv_y) \\
v_{\downarrow,\downarrow} &= \frac{1}{2}(v_t - v_z)
\end{aligned} \tag{1.46}$$

1.6.1 SPINOR$CONVERT

Converts a density matrix from the (t,x,y,z) into the (uu,ud,du,dd) representation. Converting a

$$\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \frac{1}{2}\sum_{\sigma,\sigma'}A_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma} \\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'}\rho_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma}
\end{aligned} \tag{1.47}$$

- `ID='FWRD'`: (TOUPDN=.false.) transforms the density matrix from (uu,ud,du,dd)→(t,x,y,z)
- `ID='BACK'`: (TOUPDN=.true.) (t,x,y,z)→ (uu,ud,du,dd)

Appendix A

Vector representation of Pauli matrices

Pauli matrices can be represented as vectors in four dimensions.

$$\boldsymbol{\sigma}^{(j)} \hat{=} \vec{\sigma}^{(j)} := \begin{pmatrix} \sigma_{11}^{(j)} \\ \sigma_{12}^{(j)} \\ \sigma_{21}^{(j)} \\ \sigma_{22}^{(j)} \end{pmatrix} \tag{A.1}$$

The usefullness of this representation is that the scalar project of two such vectors can be related to the trace of the corresponding Pauli matrices

$$\left(\vec{\sigma}^{(j)}\right)^* \cdot \vec{\sigma}^{(j')} = \sum_{\sigma,\sigma'} \left(\sigma_{\sigma,\sigma'}^{(j)}\right)^* \sigma_{\sigma,\sigma'}^{(j')} = \sum_{\sigma,\sigma'} \sigma_{\sigma',\sigma}^{(j)} \sigma_{\sigma,\sigma'}^{(j')} = \mathrm{Tr}\left[\boldsymbol{\sigma}^{(j)} \boldsymbol{\sigma}^{(j')}\right] \tag{A.2}$$

We have exploited that a complex conjugation of the Pauli matrices is identical to a transposition, which follows directly from their being hermitean.

The vector representation of the Pauli matrices is

$$\boldsymbol{\sigma}^{(0)} \hat{=} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \qquad \boldsymbol{\sigma}^{(1)} \hat{=} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \qquad \boldsymbol{\sigma}^{(2)} \hat{=} \begin{pmatrix} 0 \\ -i \\ i \\ 0 \end{pmatrix} \qquad \boldsymbol{\sigma}^{(3)} \hat{=} \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix}$$

These vectors have length $\sqrt{2}$ and they are mutually orthogonal to each other in the sense

$$\frac{1}{2}\left(\vec{\sigma}^{(j)}\right)^* \cdot \vec{\sigma}^{(j')} = \delta_{j,j'} \tag{A.3}$$

The orthonormality Eq. A.3 of these vectors together with the expression Eq. A.2 for their scalar product establishes

$$\boxed{\frac{1}{2}\mathrm{Tr}\left[\boldsymbol{\sigma}^{(j)} \boldsymbol{\sigma}^{(j')}\right] = \delta_{j,j'}} \tag{A.4}$$

The expression for the scalar products can be generalized to dyadic products in the vector representation. Let us consider the Product

$$\sum_{\sigma,\sigma',\bar\sigma,\bar\sigma'} A_{\sigma,\sigma'}\sigma^{(j)}_{\sigma,\sigma'}\left(\sigma^{(j')}_{\bar\sigma,\bar\sigma'}\right)^* B_{\bar\sigma,\bar\sigma'} = \left[\vec A\cdot\vec\sigma^{(j)}\right]\left[\left(\vec\sigma^{(j')}\right)^*\cdot\vec B\right] = \vec A\left[\left(\vec\sigma^{(j)}\right)^*\otimes\vec\sigma^{(j')}\right]\vec B$$

$$\Rightarrow \qquad \sigma^{(j)}_{\sigma,\sigma'}\left(\sigma^{(j')}_{\bar\sigma,\bar\sigma'}\right)^* = \left[\left(\vec\sigma^{(j)}\right)^*\otimes\vec\sigma^{(j')}\right]_{\sigma,\sigma';\bar\sigma,\bar\sigma'} \tag{A.5}$$

The sum of the outer products of the Pauli matrices in the vector representation Eq. A.1 gives the identiy matrix.

$$\frac{1}{2}\sum_{j=0}^{3}\vec\sigma^{(j)}\otimes\left(\vec\sigma^{(j)}\right)^* = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix} \tag{A.6}$$

Together with Eq. A.5, tha above result Eq. A.6 provides the second important relation

$$\boxed{\frac{1}{2}\sum_{j}\sigma^{(j)}_{\sigma,\sigma'}\left(\sigma^{(j)}_{\bar\sigma,\bar\sigma'}\right)^* = \delta_{\sigma,\bar\sigma}\delta_{\sigma',\bar\sigma'}} \tag{A.7}$$

Product table of Pauli matrices

The product table of the Pauli matrices including the unit matrix as element with $j = 0$.

$$\boldsymbol\sigma^{(i)}\boldsymbol\sigma^{(j)} = \begin{pmatrix}\boldsymbol\sigma^{(0)} & \boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(y)} & \boldsymbol\sigma^{(z)}\\ \boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(0)} & i\boldsymbol\sigma^{(z)} & -\boldsymbol\sigma^{(y)}\\ \boldsymbol\sigma^{(y)} & -i\boldsymbol\sigma^{(z)} & \boldsymbol\sigma^{(0)} & -\boldsymbol\sigma^{(x)}\\ \boldsymbol\sigma^{(z)} & i\boldsymbol\sigma^{(y)} & -i\boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(0)}\end{pmatrix}$$

$$= \sum_k\Big(\delta_{i,j}\delta_{k,0}+\delta_{i,0}\delta_{j,k}+\delta_{i,k}\delta_{j,0}-2\delta_{i,0}\delta_{j,0}\delta_{k,0} \tag{A.8}$$

$$+\, i(1-\delta_{i,0})(1-\delta_{j,0})(1-\delta_{k,0})\epsilon_{i,j,k}\Big)\boldsymbol\sigma^{(k)} \tag{A.9}$$

Do not get confused, because i is used as index and as $\sqrt{-1}$.

Bibliography

[1] P. E. Blöchl. Projector augmented-wave method. Phys. Rev. B, 50: 17953–17979, Dec 1994. doi: 10.1103/PhysRevB.50.17953. URL http://link.aps.org/doi/10.1103/PhysRevB.50.17953.