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/

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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 2×2 matrices. All hermitean matrices 2×2 matrices are a superposition of Pauli matrices with <u>real</u> coefficients.

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

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 or two operators, 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 for each $j\in\{x,y,z\}$

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

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

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

$$\xi^{(\pm x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm1\end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm y)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm i\end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm z)} = \frac{1}{2}\begin{pmatrix}1\pm1\\ 1\mp1\end{pmatrix} \tag{1.7}$$

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

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

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.

The same in matrix form

$$\begin{aligned}
\begin{pmatrix} \rho^{(0)}_{ab} \\ \rho^{(x)}_{ab} \\ \rho^{(y)}_{ab} \\ \rho^{(z)}_{ab} \end{pmatrix} &= \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \rho_{ab,\uparrow,\uparrow} \\ \rho_{ab,\downarrow,\uparrow} \\ \rho_{ab,\downarrow,\uparrow} \\ \rho_{ab,\downarrow,\downarrow} \end{pmatrix} \\
\begin{pmatrix} \rho_{ab,\uparrow,\uparrow} \\ \rho_{ab,\downarrow,\uparrow} \\ \rho_{ab,\downarrow,\uparrow} \\ \rho_{ab,\downarrow,\downarrow} \end{pmatrix} &= \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & i & 0 \\ 0 & 1 & -i & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \rho^{(0)}_{ab} \\ \rho^{(x)}_{ab} \\ \rho^{(y)}_{ab} \\ \rho^{(z)}_{ab} \end{pmatrix}
\end{aligned} \tag{1.12}$$

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

$$n_{\sigma,\sigma'} \stackrel{\text{Eq. 1.9}}{=} \frac{1}{2}n^{(0)}\sigma^{(0)}_{\sigma,\sigma'} + \frac{1}{2}n^{(4)}\sigma^{(4)}_{\sigma,\sigma'} = \begin{pmatrix} \frac{1}{2}n^{(0)} + \frac{1}{2}n^{(4)} & 0 \\ 0 & \frac{1}{2}n^{(0)} - \frac{1}{2}n^{(4)} \end{pmatrix}$$

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

$$\rho(\vec{x},\vec{x'}) = \sum_{\alpha,\beta} \rho_{\alpha,\beta,\sigma,\sigma'} \bar{\chi}_\alpha(\vec{r})\bar{\chi}_\beta(\vec{r'}) \tag{1.13}$$

$$= \frac{1}{2}\sum_{j=0}^{3}\sum_{\alpha,\beta} \rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'} \bar{\chi}_\alpha(\vec{r})\bar{\chi}_\beta(\vec{r'}) \tag{1.14}$$

where the orbitals $|\bar{\chi}_\alpha\rangle$ are pure spatial orbitals without a spin contribution.

1.3.1 Identity in a spinor representation

The identity matrix in up-down representation[1] is

$$\begin{pmatrix} \boldsymbol{\rho}_{\uparrow,\uparrow} & \boldsymbol{\rho}_{\uparrow,\downarrow} \\ \boldsymbol{\rho}_{\downarrow,\uparrow} & \boldsymbol{\rho}_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} \mathbf{1}_{\uparrow,\uparrow} & \mathbf{0}_{\uparrow,\downarrow} \\ \mathbf{0}_{\downarrow,\uparrow} & \mathbf{1}_{\downarrow,\downarrow} \end{pmatrix} \tag{1.15}$$

After conversion into the spinor representation we obtain

$$\mathbf{1}^{(0)} = 2\cdot\mathbf{1}; \qquad \mathbf{1}^{(1)} = \mathbf{0}; \qquad \mathbf{1}^{(2)} = \mathbf{0}; \qquad \mathbf{1}^{(3)} = \mathbf{0} \tag{1.16}$$

1.3.2 Hermitean conjugate in a spinor representation

The hermitean conjugate of a matrix $\boldsymbol{\rho}$ in up-down representation is

$$\begin{pmatrix} (\boldsymbol{\rho}^\dagger)_{\uparrow,\uparrow} & (\boldsymbol{\rho}^\dagger)_{\uparrow,\downarrow} \\ (\boldsymbol{\rho}^\dagger)_{\downarrow,\uparrow} & (\boldsymbol{\rho}^\dagger)_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} (\boldsymbol{\rho}_{\uparrow,\uparrow})^\dagger & (\boldsymbol{\rho}_{\downarrow,\uparrow})^\dagger \\ (\boldsymbol{\rho}_{\uparrow,\downarrow})^\dagger & (\boldsymbol{\rho}_{\downarrow,\downarrow})^\dagger \end{pmatrix} \tag{1.17}$$

After conversion into the spinor representation we obtain

$$\left(\boldsymbol{\rho}^\dagger\right)^{(0)} = \left(\boldsymbol{\rho}^{(0)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(x)} = \left(\boldsymbol{\rho}^{(x)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(y)} = \left(\boldsymbol{\rho}^{(y)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(z)} = \left(\boldsymbol{\rho}^{(z)}\right)^\dagger \tag{1.18}$$

1.3.3 Multiplication of matrices in a spinor representation

Consider two matrices in spinor representation

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

[1] Here each matrix element is itself considered a matrix in the space of spatial orbitals.

We wish to perform a matrix multiplication

$$
\begin{aligned}
\sum_{c,\sigma''} f_{a,c,\sigma,\sigma''} g_{c,b,\sigma'',\sigma'} &= \sum_{c,\sigma''}\left(\frac{1}{2}\sum_{j=0}^{3} f^{(i)}_{a,c}\sigma^{(i)}_{\sigma,\sigma''}\right)\left(\frac{1}{2}\sum_{j=0}^{3} g^{(j)}_{c,b}\sigma^{(j)}_{\sigma'',\sigma'}\right)\\
&= \frac{1}{4}\sum_{i,j=0}^{3}\left(\sum_{c} f^{(i)}_{a,c} g^{(j)}_{c,b}\right)\left(\sum_{\sigma''}\sigma^{(i)}_{\sigma,\sigma''}\sigma^{(j)}_{\sigma'',\sigma'}\right)\\
&\overset{\text{Eq. A.11}}{=} \frac{1}{2}\left[\frac{1}{2}\sum_{j=0}^{3}\left(\boldsymbol{f}^{(j)}\boldsymbol{g}^{(j)}\right)_{a,b}\right]\sigma^{(0)}_{\sigma,\sigma'}\\
&\quad +\frac{1}{2}\sum_{k=1}^{3}\left\{\frac{1}{2}\left(\boldsymbol{f}^{(0)}\boldsymbol{g}^{(k)}\right)_{a,b}+\frac{1}{2}\left(\boldsymbol{f}^{(k)}\boldsymbol{g}^{(0)}\right)_{a,b}\right.\\
&\qquad\left. +\frac{i}{2}\sum_{i,j=1}^{3}\epsilon_{i,j,k}\left(\boldsymbol{f}^{(i)}\boldsymbol{g}^{(j)}\right)_{a,b}\right\}\sigma^{(k)}_{\sigma,\sigma'}
\end{aligned}
$$

Thus, if we denote the multiplication as defined above with the symbol $\square$, we obtain

$$
\left(\boldsymbol{f}\square\boldsymbol{g}\right)^{(0)}_{a,b} = \frac{1}{2}\sum_{j=0}^{3}\left(\boldsymbol{f}^{(j)}\boldsymbol{g}^{(j)}\right)_{a,b} \tag{1.19}
$$

$$
\left(\boldsymbol{f}\square\boldsymbol{g}\right)^{(k)}_{a,b} = \frac{1}{2}\left(\boldsymbol{f}^{(0)}\boldsymbol{g}^{(k)}\right)_{a,b}+\frac{1}{2}\left(\boldsymbol{f}^{(k)}\boldsymbol{g}^{(0)}\right)_{a,b}+\frac{i}{2}\sum_{i,j=1}^{3}\epsilon_{i,j,k}\left(\boldsymbol{f}^{(i)}\boldsymbol{g}^{(j)}\right)_{a,b} \quad \text{for } j>0 \tag{1.20}
$$

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

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

In components, we obtain

$$
\begin{aligned}
\boldsymbol{A}_{11}\boldsymbol{B}_{11}+\boldsymbol{A}_{12}\boldsymbol{B}_{21} &= \boldsymbol{1}\\
\boldsymbol{A}_{11}\boldsymbol{B}_{12}+\boldsymbol{A}_{12}\boldsymbol{B}_{22} &= \boldsymbol{0}\\
\boldsymbol{A}_{21}\boldsymbol{B}_{11}+\boldsymbol{A}_{22}\boldsymbol{B}_{21} &= \boldsymbol{0}\\
\boldsymbol{A}_{21}\boldsymbol{B}_{12}+\boldsymbol{A}_{22}\boldsymbol{B}_{22} &= \boldsymbol{1}
\end{aligned} \tag{1.22}
$$

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 interesting 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

$$a(2n)^3 = 4a^3 + 6bn^3 + cn^2 \qquad \rightarrow \qquad a = \frac{3}{2}b + \frac{c}{4n} \tag{1.23}$$

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

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

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

This is derived in the following. First we show that

$$\rho^{(j)}_{a,b}=\left(\rho^{(j)}_{b,a}\right)^* \tag{1.25}$$

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

$$\rho_{a,b,\sigma,\sigma'}=\rho^*_{b,a,\sigma',\sigma} \tag{1.26}$$

This is shown as follows

$$\begin{aligned}\rho^{(j)}_{a,b}&\overset{\text{Eq. 1.9}}{=}\sum_{\sigma\sigma'}\rho_{a,b,\sigma,\sigma'}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^*\overset{\text{Eq. 1.26}}{=}\sum_{\sigma\sigma'}\rho^*_{b,a,\sigma',\sigma}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^*\overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=}\sum_{\sigma\sigma'}\rho^*_{b,a,\sigma',\sigma}\left(\sigma^{(j)}_{\sigma',\sigma}\right)\\&\overset{\text{Eq. 1.9}}{=}\left(\rho^{(j)}_{b,a}\right)^*\end{aligned} \tag{1.27}$$

Now we derive the opposite direction:

$$\begin{aligned}\rho_{a,b,\sigma,\sigma'}&\overset{\text{Eq. 1.9}}{=}\frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}_{a,b}\sigma^{(j)}_{\sigma,\sigma'}\overset{\text{Eq. 1.25}}{=}\frac{1}{2}\sum_{j=0}^{3}\left(\rho^{(j)}_{b,a}\right)^*\sigma^{(j)}_{\sigma,\sigma'}\overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=}\left(\frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}_{b,a}\sigma^{(j)}_{\sigma',\sigma}\right)^*\\&\overset{\text{Eq. 1.9}}{=}\left(\rho_{b,a,\sigma',\sigma}\right)^*\end{aligned} \tag{1.28}$$

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

$$\chi_\alpha(\vec{x})=\bar{\chi}_\alpha(\vec{r})\xi_\alpha(\sigma) \tag{1.29}$$

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

$$\begin{aligned}\rho(\vec{x},\vec{x}')&=\sum_{\alpha,\beta}\chi_\alpha(\vec{x})\rho_{\alpha,\beta}\chi^*_\beta(\vec{x}')\\&=\sum_{\alpha,\beta}\bar{\chi}_\alpha(\vec{r})\underbrace{\xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma')}_{\rho_{\alpha,\beta,\sigma,\sigma'}}\bar{\chi}^*_\beta(\vec{r}')\\&=\sum_{\alpha,\beta}\bar{\chi}_\alpha(\vec{r})\rho_{\alpha,\beta,\sigma,\sigma'}\bar{\chi}^*_\beta(\vec{r}')\end{aligned} \tag{1.30}$$

Here we have defined the density matrix with explicit spin dependence

$$\rho_{\alpha,\beta,\sigma,\sigma'}\overset{\text{def}}{=}\xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma') \tag{1.31}$$

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

$$E = F[\underbrace{\sum_{\alpha,\beta} \chi_\alpha(\vec{x})\rho_{\alpha,\beta}\chi^*_\beta(\vec{x'})}_{\rho(\vec{x},\vec{x'})}]$$

$$\begin{aligned}
V_{\alpha,\beta} &= \frac{\partial E}{\partial \rho^*_{\alpha,\beta}} = \left(\frac{\partial E}{\partial \rho_{\alpha,\beta}}\right)^* \stackrel{\text{Eq. 1.30}}{=} \left(\int d^4x \int d^4x' \; \frac{\partial E}{\partial \rho(\vec{x},\vec{x'})} \chi_\alpha(\vec{x})\chi^*_\beta(\vec{x'})]\right)^* \\
&= \int d^4x \int d^4x' \; \chi^*_\alpha(\vec{x}) \underbrace{\frac{\partial E}{\partial \rho^*(\vec{x},\vec{x'})}}_{v(\vec{x},\vec{x'})} \chi_\beta(\vec{x}) = \int d^4x \int d^4x' \; \chi^*_\alpha(\vec{x}) v(\vec{x},\vec{x'}) \chi_\beta(\vec{x'}) \\
&= \langle \chi_\alpha|\hat{V}|\chi_\beta\rangle
\end{aligned}$$

- 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

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

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

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

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.

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

$$
\begin{aligned}
dE &= \sum_{a,b,\sigma,\sigma'} \frac{\delta E}{\delta \rho_{a,b,\sigma,\sigma'}} \delta\rho_{a,b,\sigma,\sigma'} = \sum_{a,b,\sigma,\sigma'} V_{b,a,\sigma',\sigma} \delta\rho_{a,b,\sigma,\sigma'} \\
&\overset{\text{Eq. 1.10}}{=} \sum_{a,b} \Bigg\{ \underbrace{\frac{\delta E}{\delta\rho_{a,b,\uparrow,\uparrow}}}_{V_{b,a,\uparrow,\uparrow}} \underbrace{\frac{1}{2}\left(\delta\rho^{(t)}_{a,b} + \delta\rho^{(z)}_{a,b}\right)}_{\delta\rho_{a,b,\uparrow,\uparrow}} + \underbrace{\frac{\delta E}{\delta\rho_{a,b,\downarrow,\uparrow}}}_{V_{b,a,\uparrow,\downarrow}} \underbrace{\frac{1}{2}\left(\delta\rho^{(x)}_{a,b} + i\delta\rho^{(y)}_{a,b}\right)}_{\delta\rho_{a,b,\downarrow,\uparrow}} \\
&\quad + \underbrace{\frac{\delta E}{\delta\rho_{a,b,\uparrow,\downarrow}}}_{V_{b,a,\downarrow,\uparrow}} \underbrace{\frac{1}{2}\left(\delta\rho^{(x)}_{a,b} - i\delta\rho^{(y)}_{a,b}\right)}_{\delta\rho_{a,b,\uparrow,\downarrow}} + \underbrace{\frac{\delta E}{\delta\rho_{a,b,\downarrow,\downarrow}}}_{V_{b,a,\downarrow,\uparrow}} \underbrace{\frac{1}{2}\left(\delta\rho^{(t)}_{a,b} - \delta\rho^{(z)}_{a,b}\right)}_{\delta\rho_{a,b,\downarrow,\downarrow}} \Bigg\} \\
&= \sum_{a,b} \Bigg\{ \underbrace{\frac{1}{2}\left(\frac{\delta E}{\delta\rho_{a,b,\uparrow,\uparrow}} + \frac{\delta E}{\delta\rho_{a,b,\downarrow,\downarrow}}\right)}_{\bar{V}^{(t)}_{b,a}} \delta\rho^{(t)} + \underbrace{\frac{1}{2}\left(\frac{\delta E}{\delta\rho_{a,b,\downarrow,\uparrow}} + \frac{\delta E}{\delta\rho_{a,b,\uparrow,\downarrow}}\right)}_{\bar{V}^{(x)}_{b,a}} \delta\rho^{(x)}_{a,b} \\
&\quad + \underbrace{\frac{i}{2}\left(\frac{\delta E}{\delta\rho_{a,b,\downarrow,\uparrow}} + \frac{\delta E}{\delta\rho_{a,b,\uparrow,\downarrow}}\right)}_{\bar{V}^{(y)}_{b,a}} \delta\rho^{(y)}_{a,b} + \underbrace{\frac{1}{2}\left(\frac{\delta E}{\delta\rho_{a,b,\uparrow,\uparrow}} - \frac{\delta E}{\delta\rho_{a,b,\downarrow,\downarrow}}\right)}_{\bar{V}^{(z)}_{b,a}} \delta\rho^{(z)} \Bigg\} \\
&= \sum_{j=0}^{3} \sum_{a,b} \bar{V}^{(j)}_{b,a}\, \delta\rho^{(j)}_{a,b} \qquad (1.32)
\end{aligned}
$$

Thus

$$
\begin{aligned}
\bar{V}^{(t)}_{b,a} &= \frac{1}{2}\left(V_{b,a,\uparrow,\uparrow} + V_{b,a,\downarrow,\downarrow}\right) \\
\bar{V}^{(x)}_{b,a} &= \frac{1}{2}\left(v_{b,a,\uparrow,\downarrow} + V_{b,a,\downarrow,\uparrow}\right) \\
\bar{V}^{(y)}_{b,a} &= \frac{i}{2}\left(V_{b,a,\uparrow,\downarrow} - V_{b,a,\downarrow,\uparrow}\right) \\
\bar{V}^{(z)}_{b,a} &= \frac{1}{2}\left(V_{b,a,\uparrow,\uparrow} - V_{b,a,\downarrow,\downarrow}\right) \qquad (1.33)
\end{aligned}
$$

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

$$\rho^{(t)} = \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow} \qquad \rho_{\uparrow,\uparrow} = \frac{1}{2}(\rho^{(t)} + \rho^{(z)})$$

$$\rho^{(x)} = \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow} \qquad \rho_{\uparrow,\downarrow} = \frac{1}{2}(\rho^{(x)} - i\rho^{(y)})$$

$$\rho^{(y)} = i(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow}) \qquad \rho_{\downarrow,\uparrow} = \frac{1}{2}(\rho^{(x)} + i\rho^{(y)})$$

$$\rho^{(z)} = \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow} \qquad \rho_{\downarrow,\downarrow} = \frac{1}{2}(\rho^{(t)} - \rho^{(z)})$$

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

$$v^{(t)} = \frac{1}{2}\left(v_{\uparrow,\uparrow} + v_{\downarrow,\downarrow}\right) \qquad v_{\uparrow,\uparrow} = v^{(t)} + v^{(z)}$$

$$v^{(x)} = \frac{1}{2}\left(v_{\uparrow,\downarrow} + v_{\downarrow,\uparrow}\right) \qquad v_{\uparrow,\downarrow} = v^{(x)} - iv^{(y)}$$

$$v^{(y)} = \frac{i}{2}\left(v_{\uparrow,\downarrow} - v_{\downarrow,\uparrow}\right) \qquad v_{\downarrow,\uparrow} = v^{(x)} + iv^{(y)}$$

$$v^{(z)} = \frac{1}{2}\left(v_{\uparrow,\uparrow} - v_{\downarrow,\downarrow}\right) \qquad v_{\downarrow,\downarrow} = v^{(t)} - v^{(z)}$$

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

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

An expectation value is obtained by

$$
\begin{aligned}
\langle A\rangle &= \sum_n f_n \langle \psi_n|\hat{A}|\psi_n\rangle \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \underbrace{\Big(\sum_n \langle \beta,\sigma'|\psi_n\rangle f_n \langle \psi_n|\alpha,\sigma\rangle\Big)}_{\rho_{\beta,\alpha,\sigma',\sigma}} A_{\alpha,\beta,\sigma,\sigma'} \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \rho_{\beta,\alpha,\sigma',\sigma} A_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{1.34}
$$

This defines the matrix elements of the density matrix as

$$
\rho_{\alpha,\beta,\sigma,\sigma'} = \langle \beta,\sigma'|\psi_n\rangle f_n \langle \psi_n|\alpha,\sigma\rangle \tag{1.35}
$$

(t,x,y,z) representation

Let us transform the matrix elements

$$
\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'} \sigma^{(j)}_{\sigma',\sigma} \\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'} \sigma^{(j)}_{\sigma',\sigma}
\end{aligned}
\tag{1.36}
$$

The back transformation is correspondingly

$$
\begin{aligned}
A_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} A^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'} \\
\rho_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}
\end{aligned}
\tag{1.37}
$$

Proof:

$$
\begin{aligned}
\frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'} &= \frac{1}{2}\sum_{j=0}^{3} \underbrace{\Big(\sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''}\sigma^{(j)}_{\sigma''',\sigma''}\Big)}_{\rho^{(j)}_{\alpha,\beta}} \sigma^{(j)}_{\sigma,\sigma'} \\
&= \sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''} \underbrace{\Big(\frac{1}{2}\sum_{j=0}^{3} \sigma^{(j)}_{\sigma''',\sigma''}(\sigma^{(j)}_{\sigma',\sigma})^*\Big)}_{\delta_{\sigma''',\sigma'}\delta_{\sigma'',\sigma}} \\
&= \rho_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{1.38}
$$

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

$$\rho_t = \rho^{(0)} = \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow} \tag{1.39}$$
$$\rho_x = \rho^{(0)} = \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow} \tag{1.40}$$
$$\rho_y = \rho^{(0)} = -i\Big(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow}\Big) \tag{1.41}$$
$$\rho_z = \rho^{(0)} = \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow} \tag{1.42}$$

An expectation value is

$$\begin{aligned} A_{\uparrow,\uparrow} &= \frac{1}{2}\Big(A^{(t)} + A^{(z)}\Big)\\ A_{\uparrow,\downarrow} &= \frac{1}{2}\Big(A^{(x)} - iA^{(y)}\Big)\\ A_{\downarrow,\uparrow} &= \frac{1}{2}\Big(A^{(x)} + iA^{(y)}\Big)\\ A_{\downarrow,\downarrow} &= \frac{1}{2}\Big(A^{(t)} - A^{(z)}\Big) \end{aligned} \tag{1.43}$$

$$\begin{aligned} dE &= \sum_{\alpha,\beta,\sigma,\sigma'} \frac{dE}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma}\\ &= \sum_{\alpha,\beta,\sigma,\sigma'}\sum_{j=0}^{3} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \frac{d\rho^{(j)}_{\beta,\alpha}}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma}\\ &= \sum_{j=0}^{3}\sum_{\alpha,\beta} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \Big(\sum_{\sigma,\sigma'} \sigma^{(j)}_{\sigma,\sigma'} d\rho_{\beta,\alpha,\sigma',\sigma}\Big)\\ &= \sum_{j=0}^{3}\sum_{\alpha,\beta} \Big(\frac{dE}{d\rho^{(j)}_{\beta,\alpha}}\Big) d\rho^{(j)}_{\beta,\alpha} \end{aligned} \tag{1.44}$$

There is an ambiguity becauae of the trace formula

$$A = \frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}A^{(j)} \tag{1.45}$$

$$dE = \sum_{j=0}^{3}\frac{dE}{d\rho^{(j)}}d\rho^{(j)} \tag{1.46}$$

$$v^{(j)} = 2\frac{dE}{d\rho^{(j)}} \tag{1.47}$$

Using the transformation equation for expectation values

$$v_{\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3}v^{(j)}\sigma^{(j)}_{\sigma,\sigma'} = \sum_{j=0}^{3}\frac{dE}{d\rho^{(j)}}\sigma^{(j)}_{\sigma,\sigma'} \tag{1.48}$$

$$\begin{aligned}
v_{\uparrow,\uparrow} &= \frac{1}{2}(v_t + v_z)\\
v_{\uparrow,\downarrow} &= \frac{1}{2}(v_x - iv_y)\\
v_{\downarrow,\uparrow} &= \frac{1}{2}(v_x + iv_y)\\
v_{\downarrow,\downarrow} &= \frac{1}{2}(v_t - v_z)
\end{aligned} \tag{1.49}$$

1.6.1 SPINOR$CONVERT

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

$$\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \frac{1}{2}\sum_{\sigma,\sigma'}A_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma}\\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'}\rho_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma}
\end{aligned} \tag{1.50}$$

- `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.

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

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

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

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 $j=0$.

$$\begin{aligned}\boldsymbol\sigma^{(i)}\boldsymbol\sigma^{(j)} &= \begin{pmatrix}\boldsymbol\sigma^{(0)} & \boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(y)} & \boldsymbol\sigma^{(z)}\\ \boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(0)} & i\boldsymbol\sigma^{(z)} & -i\boldsymbol\sigma^{(y)}\\ \boldsymbol\sigma^{(y)} & -i\boldsymbol\sigma^{(z)} & \boldsymbol\sigma^{(0)} & i\boldsymbol\sigma^{(x)}\\ \boldsymbol\sigma^{(z)} & i\boldsymbol\sigma^{(y)} & -i\boldsymbol\sigma^{(x)} & \boldsymbol\sigma^{(0)}\end{pmatrix}\\ &= \sum_k\Big(\delta_{i,j}\delta_{k,0}+\delta_{i,0}\delta_{j,k}+\delta_{i,k}\delta_{j,0}-2\delta_{i,0}\delta_{j,0}\delta_{k,0} \qquad\qquad (A.8)\\ &+ i(1-\delta_{i,0})(1-\delta_{j,0})(1-\delta_{k,0})\epsilon_{i,j,k}\Big)\boldsymbol\sigma^{(k)} \qquad\qquad (A.9)\end{aligned}$$

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

In the more intuitive notation with three-dimensional vectors we obtain

$$\left(\begin{array}{c|c}(\boldsymbol\sigma^{(0)})^2 & \boldsymbol\sigma^{(0)}\vec{\boldsymbol\sigma}\\ \hline \boldsymbol\sigma^{(0)}\vec{\boldsymbol\sigma} & \boldsymbol\sigma^{(i)}\boldsymbol\sigma^{(j)}\end{array}\right) = \left(\begin{array}{c|c}\boldsymbol\sigma^{(0)} & \vec{\boldsymbol\sigma}\\ \hline \vec{\boldsymbol\sigma} & \delta_{i,j}\boldsymbol\sigma^{(0)}+i\sum_{k=1,3}\epsilon_{i,j,k}\boldsymbol\sigma^{(k)}\end{array}\right) \tag{A.10}$$

Thus we obtain

$$\sum_{i,j=0}^{3} A_{i,j}\boldsymbol{\sigma}^{(i)}\boldsymbol{\sigma}^{(j)} = \Big(\sum_{k=0}^{3} A_{k,k}\Big)\boldsymbol{\sigma}^{(0)} + \sum_{j=1,3}\Big(A_{0,j} + A_{j,0} + i\sum_{n,m=1}^{3} \epsilon_{j,k,l}A_{k,l}\Big)\boldsymbol{\sigma}^{(j)} \tag{A.11}$$

Take care of the extent of the sum indices. Some run over $[0, 1, 2, 3]$, others over $[1, 2, 3]$ only.

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.