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

Todo

1.1 Time-inversion symmetry

At the moment, we still describe density matrices as real objects in a (total-density, magnetization-vector-density)-representation. This has been used because it exploits time-inversion symmetry. The plan is to change this to complex matrices, because the method can then be generalized to non-equilibrium problems, such as calculations with a fixed current density.

Regarding time-inversion symmetry there are still a few open questions. Even after lifting the restriction to real density matrices in a (total-density, magnetization-vector-density) representation, it may be convenient to separate (large) equilibrium quantities from (small) non-equilibrium quantities.

The implications of time-inversion symmetry for non-collinear calculations are unclear to me. Back-ground on time-inversion symmetry can be found in P. Böchl, *ΦSX: Advanced topics of theoretical physics II, The electronic structure of matter*.

- Is a non-collinear calculation time-inversion symmetric? In our calculations the magnetic field is replaced by a exchange correlation potential. The exchange correlation potential has the property that it is invariant with respect to a sign-change of the spin density. That is a sign-change of the spin induces a sign change of the spin-dependent potential. Whether this can be exploited for a non-collinear calculation is unclear.
- can time-inversion symmetry be used to relate the wave functions with opposite wave vector with each other?
- How does time-inversion symmetry enter in current-density functional theory?

Chapter 2

SPINOR object

2.1 Spin orbitals

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

$$\vec{x} = (\vec{r}, \sigma) \tag{2.1}$$

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

An electron wave function naturally obtains a two-component form

$$\psi(\vec{x}) = \psi(\vec{r}, \sigma) = \langle \vec{r}, \sigma | \psi \rangle = \langle \vec{x} | \psi \rangle \tag{2.2}$$

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

$$\int d^4x \; = \sum_\sigma \int d^3r \tag{2.3}$$

The identity operator has the form

$$\hat{1} = \int d^4x \; |\vec{x}\rangle\langle\vec{x}| \tag{2.4}$$

2.2 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.

$$\begin{aligned} \mathbf{1} = \boldsymbol{\sigma}^{(0)} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \text{and} \qquad \boldsymbol{\sigma}_x = \boldsymbol{\sigma}^{(1)} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \boldsymbol{\sigma}_y = \boldsymbol{\sigma}^{(2)} &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \text{and} \qquad \boldsymbol{\sigma}_z = \boldsymbol{\sigma}^{(3)} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \tag{2.5}$$

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 $j \in \{x, y, z\}$

$$\sigma^{(j)} \xi^{(+j)} = \xi^{(+j)} \qquad \text{and} \qquad \sigma^{(j)} \xi^{(-j)} = -\xi^{(-j)} \tag{2.6}$$

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

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

$$\xi^{(\pm x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \qquad \text{and} \qquad \xi^{(\pm z)} = \frac{1}{2} \begin{pmatrix} 1 \pm 1 \\ 1 \mp 1 \end{pmatrix} \tag{2.7}$$

for the eigenvalues ± 1.

More explicitely,

$$\begin{aligned} \xi^{(+x)} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(+y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ +i \end{pmatrix} \qquad \text{and} \qquad \xi^{(+z)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \xi^{(-x)} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \text{and} \qquad \xi^{(-y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \qquad \text{and} \qquad \xi^{(-z)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned} \tag{2.8}$$

For the sake of completeness let me work out the spin eigenstates for an arbitrary axis $\vec{e}$, where $\vec{e}$ is a normalized vector in 3-d space.

$$\vec{e}\vec{\boldsymbol{S}} = \frac{\hbar}{2} \boldsymbol{\sigma}_{\vec{e}} = \frac{\hbar}{2} \sum_{i=1}^{3} e_i \boldsymbol{\sigma}_i = \frac{\hbar}{2} \begin{pmatrix} e_z & e_x - i e_y \\ e_x + i e_y & -e_z \end{pmatrix} \tag{2.9}$$

The eigenvalues are $\pm\frac{\hbar}{2}$ and the two-dimensional eigenvectors, denoted by $c^{\pm}$, obey

$$\begin{aligned} \begin{pmatrix} e_z \mp 1 & e_x - i e_y \\ e_x + i e_y & -e_z \mp 1 \end{pmatrix} \begin{pmatrix} c^{\pm}_{\uparrow} \\ c^{\pm}_{\downarrow} \end{pmatrix} &= 0 \\ \Rightarrow \qquad \begin{pmatrix} c^{+}_{\uparrow} \\ c^{+}_{\downarrow} \end{pmatrix} &= \begin{pmatrix} e_z + 1 \\ e_x + i e_y \end{pmatrix} \frac{1}{\sqrt{2(1+e_z)}} \\ \begin{pmatrix} c^{-}_{\uparrow} \\ c^{-}_{\downarrow} \end{pmatrix} &= \begin{pmatrix} e_x - i e_y \\ -(e_z + 1) \end{pmatrix} \frac{1}{\sqrt{2(1+e_z)}} \end{aligned} \tag{2.10}$$

To avoid constructing zero vectors, I extracted the first eigenstate from the second line of the eigenvalue equation and the second eigenvector from the first line.

The second eigenvector for the general direction deviates from the ones given for the x, y, z direction by a phase factor.

2.3 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

$$\underbrace{A_{\alpha,\beta,\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3} \bar{\mathcal{A}}^{(j)}_{\alpha,\beta}\sigma^{(j)}_{\sigma,\sigma'}}_{\text{back transform}} \quad \overset{Eqs.\ A.4,A.7}{\Longleftrightarrow} \quad \underbrace{\mathcal{A}^{(j)}_{\alpha,\beta} \overset{\text{def}}{=} \sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^*}_{\text{forward transform}} \tag{2.11}$$

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

We transform a matrix using to Eq. 2.11, which yields for the forward transformation

$$\begin{aligned}
\mathcal{A}^{(0)}_{a,b} &= A_{a,b,\uparrow,\uparrow} + A_{a,b,\downarrow,\downarrow} \\
\mathcal{A}^{(x)}_{a,b} &= A_{a,b,\downarrow,\uparrow} + A_{a,b,\uparrow,\downarrow} \\
\mathcal{A}^{(y)}_{a,b} &= -i\left(A_{a,b,\downarrow,\uparrow} - A_{a,b,\uparrow,\downarrow}\right) \\
\mathcal{A}^{(z)}_{a,b} &= A_{a,b,\uparrow,\uparrow} - A_{a,b,\downarrow,\downarrow}
\end{aligned} \tag{2.12}$$

and for the backward transformation

$$\begin{aligned}
A_{a,b,\uparrow,\uparrow} &= \frac{1}{2}\left(\mathcal{A}^{(0)}_{a,b} + \mathcal{A}^{(z)}_{a,b}\right) \\
A_{a,b,\downarrow,\uparrow} &= \frac{1}{2}\left(\mathcal{A}^{(x)}_{a,b} + i\mathcal{A}^{(y)}_{a,b}\right) \\
A_{a,b,\uparrow,\downarrow} &= \frac{1}{2}\left(\mathcal{A}^{(x)}_{a,b} - i\mathcal{A}^{(y)}_{a,b}\right) \\
A_{a,b,\downarrow,\downarrow} &= \frac{1}{2}\left(\mathcal{A}^{(0)}_{a,b} - \mathcal{A}^{(z)}_{a,b}\right)
\end{aligned} \tag{2.13}$$

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

The same in matrix form

$$\begin{pmatrix} \mathcal{A}^{(0)}_{ab} \\ \mathcal{A}^{(x)}_{ab} \\ \mathcal{A}^{(y)}_{ab} \\ \mathcal{A}^{(z)}_{ab} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} A_{ab,\uparrow,\uparrow} \\ A_{ab,\downarrow,\uparrow} \\ A_{ab,\downarrow,\uparrow} \\ A_{ab,\downarrow,\downarrow} \end{pmatrix}$$

$$\begin{pmatrix} A_{ab,\uparrow,\uparrow} \\ A_{ab,\downarrow,\uparrow} \\ A_{ab,\downarrow,\uparrow} \\ A_{ab,\downarrow,\downarrow} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & i & 0 \\ 0 & 1 & -i & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \mathcal{A}^{(0)}_{ab} \\ \mathcal{A}^{(x)}_{ab} \\ \mathcal{A}^{(y)}_{ab} \\ \mathcal{A}^{(z)}_{ab} \end{pmatrix} \tag{2.14}$$

2.4 Motivation

The convention to apply the factor 1/2 on the back transformation of Eq. 2.11 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

$$n_{\sigma,\sigma'} \stackrel{\text{Eq. 2.11}}{=} \frac{1}{2} n^{(0)} \sigma^{(0)}_{\sigma,\sigma'} + \frac{1}{2} n^{(4)} \sigma^{(4)}_{\sigma,\sigma'} = \begin{pmatrix} \frac{1}{2} n^{(0)} + \frac{1}{2} n^{(4)} & 0 \\ 0 & \frac{1}{2} n^{(0)} - \frac{1}{2} n^{(4)} \end{pmatrix}$$

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

$$\rho(\vec{x}, \vec{x'}) = \sum_{\alpha,\beta} \rho_{\alpha,\beta,\sigma,\sigma'} \bar{\chi}_\alpha(\vec{r}) \bar{\chi}_\beta(\vec{r'}) \tag{2.15}$$

$$= \frac{1}{2} \sum_{j=0}^{3} \sum_{\alpha,\beta} \rho^{(j)}_{\alpha,\beta} \sigma^{(j)}_{\sigma,\sigma'} \bar{\chi}_\alpha(\vec{r}) \bar{\chi}_\beta(\vec{r'}) \tag{2.16}$$

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

2.5 Operations in the spinor representation

The operations in a spinor representation are defined such that they are identical to the ones in the up-down representation.

2.5.1 Identity in a spinor representation

The identity matrix is implemented in `SPINOR$UNITY`.

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

$$\begin{pmatrix} \boldsymbol{\rho}_{\uparrow,\uparrow} & \boldsymbol{\rho}_{\uparrow,\downarrow} \\ \boldsymbol{\rho}_{\downarrow,\uparrow} & \boldsymbol{\rho}_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} \mathbf{1}_{\uparrow,\uparrow} & \mathbf{0}_{\uparrow,\downarrow} \\ \mathbf{0}_{\downarrow,\uparrow} & \mathbf{1}_{\downarrow,\downarrow} \end{pmatrix} \tag{2.17}$$

After conversion into the spinor representation we obtain

$$\mathbf{1}^{(0)} = 2\cdot\mathbf{1}; \qquad \mathbf{1}^{(1)} = \mathbf{0}; \qquad \mathbf{1}^{(2)} = \mathbf{0}; \qquad \mathbf{1}^{(3)} = \mathbf{0} \tag{2.18}$$

2.5.2 Hermitean conjugate in a spinor representation

The hermitean conjugation of a matrix is implemented in `SPINOR$CONJUGATE`.

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

$$\begin{pmatrix} (\boldsymbol{\rho}^\dagger)_{\uparrow,\uparrow} & (\boldsymbol{\rho}^\dagger)_{\uparrow,\downarrow} \\ (\boldsymbol{\rho}^\dagger)_{\downarrow,\uparrow} & (\boldsymbol{\rho}^\dagger)_{\downarrow,\downarrow} \end{pmatrix} = \begin{pmatrix} (\boldsymbol{\rho}_{\uparrow,\uparrow})^\dagger & (\boldsymbol{\rho}_{\downarrow,\uparrow})^\dagger \\ (\boldsymbol{\rho}_{\uparrow,\downarrow})^\dagger & (\boldsymbol{\rho}_{\downarrow,\downarrow})^\dagger \end{pmatrix} \tag{2.19}$$

After conversion into the spinor representation we obtain

$$\left(\boldsymbol{\rho}^\dagger\right)^{(0)} = \left(\boldsymbol{\rho}^{(0)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(x)} = \left(\boldsymbol{\rho}^{(x)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(y)} = \left(\boldsymbol{\rho}^{(y)}\right)^\dagger; \qquad \left(\boldsymbol{\rho}^\dagger\right)^{(z)} = \left(\boldsymbol{\rho}^{(z)}\right)^\dagger \tag{2.20}$$

Hermitean Matrices

This may be a repetition. Should be cleaned up.

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

$$\rho_{a,b,\sigma,\sigma'} = \rho^*_{b,a,\sigma',\sigma} \Leftrightarrow \rho^{(j)}_{a,b} = \left(\rho^{(j)}_{b,a}\right)^* \tag{2.21}$$

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

This is derived in the following. First we show that

$$\rho^{(j)}_{a,b} = \left(\rho^{(j)}_{b,a}\right)^* \tag{2.22}$$

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

$$\rho_{a,b,\sigma,\sigma'} = \rho^*_{b,a,\sigma',\sigma} \tag{2.23}$$

This is shown as follows

$$\begin{aligned}\rho^{(j)}_{a,b} &\overset{\text{Eq. 2.11}}{=} \sum_{\sigma\sigma'} \rho_{a,b,\sigma,\sigma'}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^* \overset{\text{Eq. 2.23}}{=} \sum_{\sigma\sigma'} \rho^*_{b,a,\sigma',\sigma}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^* \overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=} \sum_{\sigma\sigma'} \rho^*_{b,a,\sigma',\sigma}\left(\sigma^{(j)}_{\sigma',\sigma}\right) \\ &\overset{\text{Eq. 2.11}}{=} \left(\rho^{(j)}_{b,a}\right)^*\end{aligned} \tag{2.24}$$

Now we derive the opposite direction:

$$\begin{aligned}\rho_{a,b,\sigma,\sigma'} &\overset{\text{Eq. 2.11}}{=} \frac{1}{2}\sum_{j=0}^{3} \rho^{(j)}_{a,b}\sigma^{(j)}_{\sigma,\sigma'} \overset{\text{Eq. 2.22}}{=} \frac{1}{2}\sum_{j=0}^{3}\left(\rho^{(j)}_{b,a}\right)^*\sigma^{(j)}_{\sigma,\sigma'} \overset{\boldsymbol{\sigma}^{(j)}=\boldsymbol{\sigma}^{(j),\dagger}}{=} \left(\frac{1}{2}\sum_{j=0}^{3}\rho^{(j)}_{b,a}\sigma^{(j)}_{\sigma',\sigma}\right)^* \\ &\overset{\text{Eq. 2.11}}{=} \left(\rho_{b,a,\sigma',\sigma}\right)^*\end{aligned} \tag{2.25}$$

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

2.5.3 Multiplication of matrices in a spinor representation

The matrix multiplication is implemented in SPINOR$MATMUL.

Consider two matrices in spinor representation

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

We wish to perform a matrix multiplication

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

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

$$\left(\boldsymbol{f}\square\boldsymbol{g}\right)^{(0)}_{a,b} = \frac{1}{2}\sum_{j=0}^{3}\left(\boldsymbol{f}^{(j)}\boldsymbol{g}^{(j)}\right)_{a,b} \tag{2.26}$$

$$\left(\boldsymbol{f}\square\boldsymbol{g}\right)^{(k)}_{a,b} = \frac{1}{2}\left(\boldsymbol{f}^{(0)}\boldsymbol{g}^{(k)}\right)_{a,b} + \frac{1}{2}\left(\boldsymbol{f}^{(k)}\boldsymbol{g}^{(0)}\right)_{a,b} + \frac{i}{2}\sum_{i,j=1}^{3}\epsilon_{i,j,k}\left(\boldsymbol{f}^{(i)}\boldsymbol{g}^{(j)}\right)_{a,b} \qquad \text{for } j>0 \tag{2.27}$$

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.

2.5.4 Inversion of a matrix in a spinor representation

The matrix inversion is implemented in SPINOR$INVERT.

The inversion is done by first bringing the matrix into the $\uparrow,\downarrow$ representation using Eq. 2.11.

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

$$\begin{pmatrix} \boldsymbol{A}_{11} & \boldsymbol{A}_{12} \\ \boldsymbol{A}_{21} & \boldsymbol{A}_{22} \end{pmatrix}\begin{pmatrix} \boldsymbol{B}_{11} & \boldsymbol{B}_{12} \\ \boldsymbol{B}_{21} & \boldsymbol{B}_{22} \end{pmatrix} = \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1} \end{pmatrix} \tag{2.28}$$

In components, we obtain

$$\begin{aligned}
\boldsymbol{A}_{11}\boldsymbol{B}_{11}+\boldsymbol{A}_{12}\boldsymbol{B}_{21}&=\boldsymbol{1}\\
\boldsymbol{A}_{11}\boldsymbol{B}_{12}+\boldsymbol{A}_{12}\boldsymbol{B}_{22}&=\boldsymbol{0}\\
\boldsymbol{A}_{21}\boldsymbol{B}_{11}+\boldsymbol{A}_{22}\boldsymbol{B}_{21}&=\boldsymbol{0}\\
\boldsymbol{A}_{21}\boldsymbol{B}_{12}+\boldsymbol{A}_{22}\boldsymbol{B}_{22}&=\boldsymbol{1}
\end{aligned} \tag{2.29}$$

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

$$a(2n)^3=4a^3+6bn^3+cn^2 \qquad\rightarrow\qquad a=\frac{3}{2}b+\frac{c}{4n} \tag{2.30}$$

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

2.5.5 Trace

The trace is implemented in SPINOR$TRACE

$$\mathrm{Tr}[\boldsymbol{A}] = \mathrm{Tr}\Big[\mathcal{A}^{(0)}\Big] \tag{2.31}$$

Proof:

$$\begin{aligned}
\mathrm{Tr}[\boldsymbol{A}] &= \mathrm{Tr}\Big[\boldsymbol{A}_{\uparrow\uparrow} + \boldsymbol{A}_{\downarrow\downarrow}\Big] \\
&= \mathrm{Tr}\Big[\frac{1}{2}\Big(\mathcal{A}^{(0)} + \mathcal{A}^{(z)}\Big) + \frac{1}{2}\Big(\mathcal{A}^{(0)} - \mathcal{A}^{(z)}\Big)\Big] \\
&= \mathrm{Tr}\Big[\mathcal{A}^{(0)}\Big]
\end{aligned} \tag{2.32}$$

2.5.6 Trace or the product of two matrices

The trace of the product of two matrices is implemented in SPINOR$TRACEAB.

The trace of a product of two matrices is used frequently and is much simpler to evaluate directly rather than by first performing the product and then the trace.

$$\mathrm{Tr}[\boldsymbol{A}\boldsymbol{B}] = \frac{1}{2}\sum_{j=0}^{3}\mathrm{Tr}\Big[\mathcal{A}^{(j)}\mathcal{B}^{(j)}\Big] \tag{2.33}$$

Proof: We use the expression Eq. 2.31 for the trace and then insert the result from the multiplication.

2.5.7 Vector model

In the non-collinear model the vectors have two components, of which the first corresponds to the spin-up and the second to the spin-down component.

In the collinear model, the vectors are treated with one spin component only. However, there is a parameter "ispin", which determines whether this component is to be interpreted as the spin-up (ispin=1) or (ispin=2) the spin-down component.

2.5.8 Matrix-vector multiplication

This operation is implemented in the routine spinor$matvecmul.

In the non-collinear model, the matrix vector multiplication has the form

$$\vec{c}_\sigma = \sum_{\sigma'}\boldsymbol{A}_{\sigma,\sigma'}\vec{b}_{\sigma'} \tag{2.34}$$

Using Eq. 2.13, this is reformulated as

$$\begin{aligned}
\vec{c}_\uparrow &= \frac{1}{2}\left(\boldsymbol{A}^{(0)} + \boldsymbol{A}^{(z)}\right)\vec{b}_\uparrow + \frac{1}{2}\left(\boldsymbol{A}^{(x)} - i\boldsymbol{A}^{(y)}\right)\vec{b}_\downarrow \\
\vec{c}_\downarrow &= \frac{1}{2}\left(\boldsymbol{A}^{(x)} + i\boldsymbol{A}^{(y)}\right)\vec{b}_\uparrow + \frac{1}{2}\left(\boldsymbol{A}^{(0)} - \boldsymbol{A}^{(z)}\right)\vec{b}_\downarrow
\end{aligned} \tag{2.35}$$

This can be rearranged in the form[2]

$$\vec{c}_\sigma = \frac{1}{2}\boldsymbol{A}^{(0)}\vec{b}_\sigma + \frac{\sigma}{2}\boldsymbol{A}^{(z)}\vec{b}_\sigma + \frac{1}{2}\left(\boldsymbol{A}^{(x)} - i\sigma\boldsymbol{A}^{(y)}\right)\vec{b}_{-\sigma} \tag{2.36}$$

which allows to start with the non-spin-polarized model, then add the terms for the collinear spin-polarized model and finally to add the terms from the non-collinear model.

2.6 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

$$\chi_\alpha(\vec{x}) = \bar{\chi}_\alpha(\vec{r})\xi_\alpha(\sigma) \tag{2.37}$$

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

$$\begin{aligned}
\rho(\vec{x},\vec{x'}) &= \sum_{\alpha,\beta} \chi_\alpha(\vec{x})\rho_{\alpha,\beta}\chi^*_\beta(\vec{x'}) \\
&= \sum_{\alpha,\beta} \bar{\chi}_\alpha(\vec{r})\underbrace{\xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma')}_{\rho_{\alpha,\beta,\sigma,\sigma'}}\bar{\chi}^*_\beta(\vec{r'}) \\
&= \sum_{\alpha,\beta} \bar{\chi}_\alpha(\vec{r})\rho_{\alpha,\beta,\sigma,\sigma'}\bar{\chi}^*_\beta(\vec{r'})
\end{aligned} \tag{2.38}$$

Here we have defined the density matrix with explicit spin dependence

$$\rho_{\alpha,\beta,\sigma,\sigma'} \stackrel{\text{def}}{=} \xi_\alpha(\sigma)\rho_{\alpha,\beta}\xi^*_\beta(\sigma') \tag{2.39}$$

The density matrices $\rho_{\sigma,\sigma'} = \xi(\sigma)\xi^*(\sigma')$ for the spin eigenstates Eq. 2.7 are

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

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

[2] $\sigma = 1$ for $\sigma = \uparrow$ and $\sigma = -1$ for $\sigma = \downarrow$. The index $-\sigma$ corresponds to the opposite spin direction than the one described by index σ.

2.7 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

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

- Another form

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

$$\begin{aligned}
V_{\alpha,\beta} &= \frac{\partial E}{\partial \rho^*_{\alpha,\beta}} = \left(\frac{\partial E}{\partial \rho_{\alpha,\beta}}\right)^* \overset{\text{Eq. 2.38}}{=} \left(\int d^4x \int d^4x' \, \frac{\partial E}{\partial \rho(\vec{x},\vec{x'})} \chi_\alpha(\vec{x})\chi^*_\beta(\vec{x'})]\right)^* \\
&= \int d^4x \int d^4x' \, \chi^*_\alpha(\vec{x}) \underbrace{\frac{\partial E}{\partial \rho^*(\vec{x},\vec{x'})}}_{v(\vec{x},\vec{x'})} \chi_\beta(\vec{x}) = \int d^4x \int d^4x' \, \chi^*_\alpha(\vec{x}) v(\vec{x},\vec{x'}) \chi_\beta(\vec{x'}) \\
&= \langle \chi_\alpha|\hat{V}|\chi_\beta\rangle
\end{aligned}$$

- 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 $\vec{R}_\beta + \vec{t}_\beta$.

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

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.

$$
\begin{aligned}
\bar{V}^{(j)}_{\alpha,\beta} &\stackrel{\text{def}}{=} \frac{\partial E}{\partial\bar{\rho}^{(j)*}_{\alpha,\beta}} \\
V_{\alpha,\beta,\sigma,\sigma'} &= \frac{\partial E}{\partial\rho^*_{\alpha,\beta,\sigma,\sigma'}} = \sum_j \frac{\partial E}{\partial\bar{\rho}^{(j)*}_{\alpha,\beta}} \frac{\partial\bar{\rho}^{(j)*}_{\alpha,\beta}}{\partial\rho^*_{\alpha,\beta,\sigma,\sigma'}} = \sum_j \bar{V}^{(j)}_{\alpha,\beta}\left(\frac{\partial\bar{\rho}^{(j)}_{\alpha,\beta}}{\partial\rho_{\alpha,\beta,\sigma,\sigma'}}\right)^* \\
&\stackrel{\text{Eq. 2.11}}{=} \sum_j \bar{V}^{(j)}_{\alpha,\beta}\left(\sigma^{(j)}_{\sigma,\sigma'}\right)^*
\end{aligned}
$$

$$
\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. 2.12}}{=} \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}
\end{aligned}
\tag{2.40}
$$

Thus

$$
\begin{aligned}
\bar{V}^{(t)}_{b,a} &= \frac{1}{2}\left(V_{b,a,\uparrow,\uparrow} + V_{b,a,\downarrow,\downarrow}\right) \\
\bar{V}^{(x)}_{b,a} &= \frac{1}{2}\left(v_{b,a,\uparrow,\downarrow} + V_{b,a,\downarrow,\uparrow}\right) \\
\bar{V}^{(y)}_{b,a} &= \frac{i}{2}\left(V_{b,a,\uparrow,\downarrow} - V_{b,a,\downarrow,\uparrow}\right) \\
\bar{V}^{(z)}_{b,a} &= \frac{1}{2}\left(V_{b,a,\uparrow,\uparrow} - V_{b,a,\downarrow,\downarrow}\right)
\end{aligned}
\tag{2.41}
$$

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`.

2.8 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

$$
\begin{aligned}
\langle A \rangle &= \sum_n f_n \langle \psi_n | \hat{A} | \psi_n \rangle \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \underbrace{\Big(\sum_n \langle \beta, \sigma' | \psi_n \rangle f_n \langle \psi_n | \alpha, \sigma \rangle \Big)}_{\rho_{\beta,\alpha,\sigma',\sigma}} A_{\alpha,\beta,\sigma,\sigma'} \\
&= \sum_{\alpha,\beta,\sigma,\sigma'} \rho_{\beta,\alpha,\sigma',\sigma} A_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{2.42}
$$

This defines the matrix elements of the density matrix as

$$
\rho_{\alpha,\beta,\sigma,\sigma'} = \langle \beta, \sigma' | \psi_n \rangle f_n \langle \psi_n | \alpha, \sigma \rangle \tag{2.43}
$$

(t,x,y,z) representation

Let us transform the matrix elements

$$
\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'} \sigma^{(j)}_{\sigma',\sigma} \\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'} \sigma^{(j)}_{\sigma',\sigma}
\end{aligned}
\tag{2.44}
$$

The back transformation is correspondingly

$$
\begin{aligned}
A_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2} \sum_{j=0}^{3} A^{(j)}_{\alpha,\beta} \sigma^{(j)}_{\sigma,\sigma'} \\
\rho_{\alpha,\beta,\sigma,\sigma'} &= \frac{1}{2} \sum_{j=0}^{3} \rho^{(j)}_{\alpha,\beta} \sigma^{(j)}_{\sigma,\sigma'}
\end{aligned}
\tag{2.45}
$$

Proof:

$$
\begin{aligned}
\frac{1}{2} \sum_{j=0}^{3} \rho^{(j)}_{\alpha,\beta} \sigma^{(j)}_{\sigma,\sigma'} &= \frac{1}{2} \sum_{j=0}^{3} \underbrace{\Big(\sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''} \sigma^{(j)}_{\sigma''',\sigma''} \Big)}_{\rho^{(j)}_{\alpha,\beta}} \sigma^{(j)}_{\sigma,\sigma'} \\
&= \sum_{\sigma'',\sigma'''} \rho_{\alpha,\beta,\sigma'',\sigma'''} \underbrace{\Big(\frac{1}{2} \sum_{j=0}^{3} \sigma^{(j)}_{\sigma''',\sigma''} (\sigma^{(j)}_{\sigma',\sigma})^* \Big)}_{\delta_{\sigma''',\sigma'} \delta_{\sigma'',\sigma}} \\
&= \rho_{\alpha,\beta,\sigma,\sigma'}
\end{aligned}
\tag{2.46}
$$

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

$$\rho_t = \rho^{(0)} = \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow} \tag{2.47}$$
$$\rho_x = \rho^{(1)} = \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow} \tag{2.48}$$
$$\rho_y = \rho^{(2)} = -i\Big(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow}\Big) \tag{2.49}$$
$$\rho_z = \rho^{(3)} = \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow} \tag{2.50}$$

An expectation value is

$$\begin{aligned} A_{\uparrow,\uparrow} &= \frac{1}{2}\Big(A^{(t)} + A^{(z)}\Big) \\ A_{\uparrow,\downarrow} &= \frac{1}{2}\Big(A^{(x)} - iA^{(y)}\Big) \\ A_{\downarrow,\uparrow} &= \frac{1}{2}\Big(A^{(x)} + iA^{(y)}\Big) \\ A_{\downarrow,\downarrow} &= \frac{1}{2}\Big(A^{(t)} - A^{(z)}\Big) \end{aligned} \tag{2.51}$$

$$\begin{aligned} dE &= \sum_{\alpha,\beta,\sigma,\sigma'} \frac{dE}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma} \\ &= \sum_{\alpha,\beta,\sigma,\sigma'}\sum_{j=0}^{3} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \frac{d\rho^{(j)}_{\beta,\alpha}}{d\rho_{\beta,\alpha,\sigma',\sigma}} d\rho_{\beta,\alpha,\sigma',\sigma} \\ &= \sum_{j=0}^{3}\sum_{\alpha,\beta} \frac{dE}{d\rho^{(j)}_{\beta,\alpha}} \Big(\sum_{\sigma,\sigma'} \sigma^{(j)}_{\sigma,\sigma'} d\rho_{\beta,\alpha,\sigma',\sigma}\Big) \\ &= \sum_{j=0}^{3}\sum_{\alpha,\beta} \Big(\frac{dE}{d\rho^{(j)}_{\beta,\alpha}}\Big) d\rho^{(j)}_{\beta,\alpha} \end{aligned} \tag{2.52}$$

There is an ambiguity becauae of the trace formula

$$A = \frac{1}{2}\sum_{j=0}^{3} \rho^{(j)} A^{(j)} \tag{2.53}$$

$$dE = \sum_{j=0}^{3} \frac{dE}{d\rho^{(j)}} d\rho^{(j)} \tag{2.54}$$

$$v^{(j)} = 2\frac{dE}{d\rho^{(j)}} \tag{2.55}$$

Using the transformation equation for expectation values

$$v_{\sigma,\sigma'} = \frac{1}{2}\sum_{j=0}^{3} v^{(j)}\sigma^{(j)}_{\sigma,\sigma'} = \sum_{j=0}^{3} \frac{dE}{d\rho^{(j)}}\sigma^{(j)}_{\sigma,\sigma'} \tag{2.56}$$

$$\begin{aligned}
v_{\uparrow,\uparrow} &= \frac{1}{2}(v_t + v_z) \\
v_{\uparrow,\downarrow} &= \frac{1}{2}(v_x - iv_y) \\
v_{\downarrow,\uparrow} &= \frac{1}{2}(v_x + iv_y) \\
v_{\downarrow,\downarrow} &= \frac{1}{2}(v_t - v_z)
\end{aligned} \tag{2.57}$$

2.8.1 SPINOR$CONVERT

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

$$\begin{aligned}
A^{(j)}_{\alpha,\beta} &= \frac{1}{2}\sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma} \\
\rho^{(j)}_{\alpha,\beta} &= \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'}\sigma^{(j)}_{\sigma',\sigma}
\end{aligned} \tag{2.58}$$

- `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 $j = 0$.

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

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

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

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

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

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

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.