

The SPINOR object of the CP-PAW code

Peter E. Blöchl

Copyright Peter E. Blöchl; Sept.2, 2013-January 27, 2015
Institute of Theoretical Physics; Clausthal University of Technology;
D-38678 Clausthal Zellerfeld; Germany;
<http://www.pt.tu-clausthal.de/atp/>

Contents

1	Todo	2
1.1	Time-inversion symmetry	2
2	SPINOR object	3
2.1	Spin orbitals	3
2.2	Pauli matrices and observables	3
2.3	Representation of a matrices in terms of Pauli matrices	4
2.3.1	Identity in a spinor representation	6
2.3.2	Hermitean conjugate in a spinor representation	6
2.3.3	Multiplication of matrices in a spinor representation	6
2.3.4	Inversion of a matrix in a spinor representation	7
2.3.5	Hermitean Matrices	8
2.4	Density matrices and spin orbitals with defined spin	9
2.5	Potentials and spin orbitals	10
2.6	Description of Subroutines	13
2.6.1	SPINOR\$CONVERT	16
A	Vector representation of Pauli matrices	17

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?

which leads to

$$\begin{aligned}
 B_{12} &= -\underbrace{A_{11}^{-1} A_{12}}_{a_{12}} B_{22} \\
 B_{21} &= -\underbrace{A_{22}^{-1} A_{21}}_{a_{21}} B_{11} \\
 B_{11} &= \left(A_{11} - A_{12} \underbrace{A_{22}^{-1} A_{21}}_{-a_{21}} \right)^{-1} \\
 B_{22} &= \left(A_{22} - A_{21} \underbrace{A_{11}^{-1} A_{12}}_{a_{12}} \right)^{-1}
 \end{aligned}$$

The operations are done in the following order

$$\begin{aligned}
 C_{11} &= A_{11}^{-1} \\
 C_{12} &= -C_{11} A_{12} = -A_{11}^{-1} A_{12} \\
 C_{22} &= A_{22} + A_{21} C_{12} = A_{22} - A_{21} A_{11}^{-1} A_{12} \\
 B_{22} &= C_{22}^{-1} = \left(A_{22} - A_{21} A_{11}^{-1} A_{12} \right)^{-1} \\
 B_{12} &= C_{12} B_{22} \\
 C_{22} &= A_{22}^{-1} \\
 C_{21} &= -C_{22} A_{21} = -A_{22}^{-1} A_{21} \\
 C_{11} &= A_{11} + A_{12} C_{21} = A_{11} - A_{12} A_{22}^{-1} A_{21} \\
 B_{11} &= C_{11}^{-1} = \left(A_{11} - A_{12} A_{22}^{-1} A_{21} \right)^{-1} \\
 B_{21} &= C_{21} B_{11}
 \end{aligned}$$

The matrix A_{11}^{-1} can be overlayed with B_{11} , A_{22}^{-1} can be overlayed with B_{22} , C_{12} can be overlayed with B_{12} , and C_{21} can be overlayed with 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

$$a(2n)^3 = 4a^3 + 6bn^3 + cn^2 \quad \rightarrow \quad a = \frac{3}{2}b + \frac{c}{4n} \quad (2.23)$$

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

2.3.5 Hermitean Matrices

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

$$\rho_{a,b,\sigma,\sigma'} = \rho_{b,a,\sigma',\sigma}^* \Leftrightarrow \rho_{a,b}^{(j)} = \left(\rho_{b,a}^{(j)} \right)^* \quad (2.24)$$

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

This is derived in the following. First we show that

$$\rho_{a,b}^{(j)} = \left(\rho_{b,a}^{(j)} \right)^* \quad (2.25)$$

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

$$\rho_{a,b,\sigma,\sigma'} = \rho_{b,a,\sigma',\sigma}^* \quad (2.26)$$

This is shown as follows

$$\begin{aligned} \rho_{a,b}^{(j)} &\stackrel{\text{Eq. 2.9}}{=} \sum_{\sigma\sigma'} \rho_{a,b,\sigma,\sigma'} \left(\sigma_{\sigma,\sigma'}^{(j)} \right)^* \stackrel{\text{Eq. 2.26}}{=} \sum_{\sigma\sigma'} \rho_{b,a,\sigma',\sigma}^* \left(\sigma_{\sigma,\sigma'}^{(j)} \right)^* \stackrel{\sigma^{(j)} = \sigma'^{(j)\dagger}}{=} \sum_{\sigma\sigma'} \rho_{b,a,\sigma',\sigma}^* \left(\sigma_{\sigma',\sigma}^{(j)} \right)^* \\ &\stackrel{\text{Eq. 2.9}}{=} \left(\rho_{b,a}^{(j)} \right)^* \end{aligned} \quad (2.27)$$

Now we derive the opposite direction:

$$\begin{aligned} \rho_{a,b,\sigma,\sigma'} &\stackrel{\text{Eq. 2.9}}{=} \frac{1}{2} \sum_{j=0}^3 \rho_{a,b,\sigma,\sigma'}^{(j)} \sigma_{\sigma,\sigma'}^{(j)} \stackrel{\text{Eq. 2.25}}{=} \frac{1}{2} \sum_{j=0}^3 \left(\rho_{b,a}^{(j)} \right)^* \sigma_{\sigma,\sigma'}^{(j)} \stackrel{\sigma^{(j)} = \sigma'^{(j)\dagger}}{=} \left(\frac{1}{2} \sum_{j=0}^3 \rho_{b,a,\sigma',\sigma}^{(j)} \sigma_{\sigma',\sigma}^{(j)} \right)^* \\ &\stackrel{\text{Eq. 2.9}}{=} \left(\rho_{b,a,\sigma',\sigma} \right)^* \end{aligned} \quad (2.28)$$

2.4 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

$$\chi_\alpha(\vec{x}) = \bar{\chi}_\alpha(\vec{r}) \xi_\alpha(\sigma) \quad (2.29)$$

Typically, the spin orbitals are eigenstates to σ_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

$$\begin{aligned} \rho(\vec{x}, \vec{x}') &= \sum_{\alpha,\beta} \chi_\alpha(\vec{x}) \rho_{\alpha,\beta} \chi_\beta^*(\vec{x}') \\ &= \sum_{\alpha,\beta} \bar{\chi}_\alpha(\vec{r}) \underbrace{\xi_\alpha(\sigma) \rho_{\alpha,\beta} \xi_\beta^*(\sigma')}_{\rho_{\alpha,\beta,\sigma,\sigma'}} \bar{\chi}_\beta^*(\vec{r}') \\ &= \sum_{\alpha,\beta} \bar{\chi}_\alpha(\vec{r}) \rho_{\alpha,\beta,\sigma,\sigma'} \bar{\chi}_\beta^*(\vec{r}') \end{aligned} \quad (2.30)$$

Here we have defined the density matrix with explicit spin dependence

$$\rho_{\alpha,\beta,\sigma,\sigma'} \stackrel{\text{def}}{=} \xi_\alpha(\sigma) \rho_{\alpha,\beta} \xi_\beta^*(\sigma') \quad (2.31)$$

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

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

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

2.5 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

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

- Another form

$$\begin{aligned} E &= F\left[\underbrace{\sum_{\alpha,\beta} \chi_\alpha(\vec{x}) \rho_{\alpha,\beta} \chi_\beta^*(\vec{x}')}_{\rho(\vec{x},\vec{x}')}\right] \\ V_{\alpha,\beta} &= \frac{\partial E}{\partial \rho_{\alpha,\beta}^*} = \left(\frac{\partial E}{\partial \rho_{\alpha,\beta}}\right)^* \stackrel{\text{Eq. 2.30}}{=} \left(\int d^4x \int d^4x' \frac{\partial E}{\partial \rho(\vec{x},\vec{x}')} \chi_\alpha(\vec{x}) \chi_\beta^*(\vec{x}')\right)^* \\ &= \int d^4x \int d^4x' \chi_\alpha^*(\vec{x}) \underbrace{\frac{\partial E}{\partial \rho^*(\vec{x},\vec{x}')} \chi_\beta(\vec{x})}_{v(\vec{x},\vec{x}')} = \int d^4x \int d^4x' \chi_\alpha^*(\vec{x}) v(\vec{x},\vec{x}') \chi_\beta(\vec{x}') \\ &= \langle \chi_\alpha | \hat{V} | \chi_\beta \rangle \end{aligned}$$

- Similarly, we obtain

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

- 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}_α 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.

$$\begin{aligned}
 \bar{V}_{\alpha,\beta}^{(j)} &\stackrel{\text{def}}{=} \frac{\partial E}{\partial \bar{\rho}_{\alpha,\beta}^{(j)*}} \\
 V_{\alpha,\beta,\sigma,\sigma'} &= \frac{\partial E}{\partial \rho_{\alpha,\beta,\sigma,\sigma'}^*} = \sum_j \frac{\partial E}{\partial \bar{\rho}_{\alpha,\beta}^{(j)*}} \frac{\partial \bar{\rho}_{\alpha,\beta}^{(j)*}}{\partial \rho_{\alpha,\beta,\sigma,\sigma'}^*} = \sum_j \bar{V}_{\alpha,\beta}^{(j)} \left(\frac{\partial \bar{\rho}_{\alpha,\beta}^{(j)}}{\partial \rho_{\alpha,\beta,\sigma,\sigma'}} \right)^* \\
 &\stackrel{\text{Eq. 2.9}}{=} \sum_j \bar{V}_{\alpha,\beta}^{(j)} \left(\sigma_{\sigma,\sigma'}^{(j)} \right)^*
 \end{aligned}$$

$$\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'} \\
&\stackrel{\text{Eq. 2.10}}{=} \sum_{a,b} \left\{ \underbrace{\frac{\delta E}{\delta \rho_{a,b,\uparrow,\uparrow}}}_{V_{b,a,\uparrow,\uparrow}} \underbrace{\frac{1}{2} \left(\delta \rho_{a,b}^{(t)} + \delta \rho_{a,b}^{(z)} \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_{a,b}^{(x)} + i \delta \rho_{a,b}^{(y)} \right)}_{\delta \rho_{a,b,\downarrow,\uparrow}} \right. \\
&\quad \left. + \underbrace{\frac{\delta E}{\delta \rho_{a,b,\uparrow,\downarrow}}}_{V_{b,a,\downarrow,\uparrow}} \underbrace{\frac{1}{2} \left(\delta \rho_{a,b}^{(x)} - i \delta \rho_{a,b}^{(y)} \right)}_{\delta \rho_{a,b,\uparrow,\downarrow}} + \underbrace{\frac{\delta E}{\delta \rho_{a,b,\downarrow,\downarrow}}}_{V_{b,a,\downarrow,\downarrow}} \underbrace{\frac{1}{2} \left(\delta \rho_{a,b}^{(t)} - \delta \rho_{a,b}^{(z)} \right)}_{\delta \rho_{a,b,\downarrow,\downarrow}} \right\} \\
&= \sum_{a,b} \left\{ \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}_{b,a}^{(t)}} \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}_{b,a}^{(x)}} \delta \rho_{a,b}^{(x)} \right. \\
&\quad \left. + \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}_{b,a}^{(y)}} \delta \rho_{a,b}^{(y)} + \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}_{b,a}^{(z)}} \delta \rho^{(z)} \right\} \\
&= \sum_{j=0}^3 \sum_{a,b} \bar{V}_{b,a}^{(j)} \delta \rho_{a,b}^{(j)} \tag{2.32}
\end{aligned}$$

Thus

$$\begin{aligned}
\bar{V}_{b,a}^{(t)} &= \frac{1}{2} (V_{b,a,\uparrow,\uparrow} + V_{b,a,\downarrow,\downarrow}) \\
\bar{V}_{b,a}^{(x)} &= \frac{1}{2} (V_{b,a,\uparrow,\downarrow} + V_{b,a,\downarrow,\uparrow}) \\
\bar{V}_{b,a}^{(y)} &= \frac{i}{2} (V_{b,a,\uparrow,\downarrow} - V_{b,a,\downarrow,\uparrow}) \\
\bar{V}_{b,a}^{(z)} &= \frac{1}{2} (V_{b,a,\uparrow,\uparrow} - V_{b,a,\downarrow,\downarrow}) \tag{2.33}
\end{aligned}$$

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

$$\rho^{(t)} = \rho_{\uparrow,\uparrow} + \rho_{\downarrow,\downarrow}$$

$$\rho^{(x)} = \rho_{\uparrow,\downarrow} + \rho_{\downarrow,\uparrow}$$

$$\rho^{(y)} = i(\rho_{\uparrow,\downarrow} - \rho_{\downarrow,\uparrow})$$

$$\rho^{(z)} = \rho_{\uparrow,\uparrow} - \rho_{\downarrow,\downarrow}$$

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

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

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

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

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

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

$$v^{(x)} = \frac{1}{2}(v_{\uparrow,\downarrow} + v_{\downarrow,\uparrow})$$

$$v^{(y)} = \frac{i}{2}(v_{\uparrow,\downarrow} - v_{\downarrow,\uparrow})$$

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

$$v_{\uparrow,\uparrow} = v^{(t)} + v^{(z)}$$

$$v_{\uparrow,\downarrow} = v^{(x)} - i v^{(y)}$$

$$v_{\downarrow,\uparrow} = v^{(x)} + i v^{(y)}$$

$$v_{\downarrow,\downarrow} = v^{(t)} - v^{(z)}$$

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

2.6 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 basis 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

$$\begin{aligned}
 \langle A \rangle &= \sum_n f_n \langle \psi_n | \hat{A} | \psi_n \rangle \\
 &= \sum_{\alpha, \beta, \sigma, \sigma'} \underbrace{\left(\sum_n \langle \beta, \sigma' | \psi_n \rangle f_n \langle \psi_n | \alpha, \sigma \rangle \right)}_{\rho_{\beta, \alpha, \sigma', \sigma}} A_{\alpha, \beta, \sigma, \sigma'} \\
 &= \sum_{\alpha, \beta, \sigma, \sigma'} \rho_{\beta, \alpha, \sigma', \sigma} A_{\alpha, \beta, \sigma, \sigma'}
 \end{aligned} \tag{2.34}$$

This defines the matrix elements of the density matrix as

$$\rho_{\alpha, \beta, \sigma, \sigma'} = \langle \beta, \sigma' | \psi_n \rangle f_n \langle \psi_n | \alpha, \sigma \rangle \tag{2.35}$$

(t,x,y,z) representation

Let us transform the matrix elements

$$\begin{aligned}
 A_{\alpha, \beta}^{(j)} &= \sum_{\sigma, \sigma'} A_{\alpha, \beta, \sigma, \sigma'} \sigma_{\sigma', \sigma}^{(j)} \\
 \rho_{\alpha, \beta}^{(j)} &= \sum_{\sigma, \sigma'} \rho_{\alpha, \beta, \sigma, \sigma'} \sigma_{\sigma', \sigma}^{(j)}
 \end{aligned} \tag{2.36}$$

The back transformation is correspondingly

$$\begin{aligned}
 A_{\alpha, \beta, \sigma, \sigma'} &= \frac{1}{2} \sum_{j=0}^3 A_{\alpha, \beta}^{(j)} \sigma_{\sigma, \sigma'}^{(j)} \\
 \rho_{\alpha, \beta, \sigma, \sigma'} &= \frac{1}{2} \sum_{j=0}^3 \rho_{\alpha, \beta}^{(j)} \sigma_{\sigma, \sigma'}^{(j)}
 \end{aligned} \tag{2.37}$$

Proof:

$$\begin{aligned}
 \frac{1}{2} \sum_{j=0}^3 \rho_{\alpha, \beta}^{(j)} \sigma_{\sigma, \sigma'}^{(j)} &= \frac{1}{2} \sum_{j=0}^3 \underbrace{\left(\sum_{\sigma'', \sigma'''} \rho_{\alpha, \beta, \sigma'', \sigma'''} \sigma_{\sigma''', \sigma''}^{(j)} \right)}_{\rho_{\alpha, \beta}^{(j)}} \sigma_{\sigma, \sigma'}^{(j)} \\
 &= \sum_{\sigma'', \sigma'''} \rho_{\alpha, \beta, \sigma'', \sigma'''} \underbrace{\left(\frac{1}{2} \sum_{j=0}^3 \sigma_{\sigma''', \sigma''}^{(j)} (\sigma_{\sigma', \sigma}^{(j)})^* \right)}_{\delta_{\sigma''', \sigma'} \delta_{\sigma'', \sigma}} \\
 &= \rho_{\alpha, \beta, \sigma, \sigma'}
 \end{aligned} \tag{2.38}$$

Expectation value by trace

Now we need the expression for the expectation value

$$\begin{aligned}
 \langle A \rangle &= \text{Tr}(\hat{\rho} \hat{A}) = \sum_{\alpha, \beta, \sigma, \sigma'} \rho_{\alpha, \beta, \sigma, \sigma'} A_{\beta, \alpha, \sigma', \sigma} = \sum_{\alpha, \beta, \sigma, \sigma'} \underbrace{\frac{1}{2} \sum_{j=0}^3 \bar{\rho}_{\alpha, \beta}^{(j)} \sigma_{\sigma, \sigma'}^{(j)}}_{\rho_{\alpha, \beta, \sigma, \sigma'}} A_{\beta, \alpha, \sigma', \sigma} \\
 &= \frac{1}{2} \sum_{j=0}^3 \sum_{\alpha, \beta} \bar{\rho}_{\alpha, \beta}^{(j)} \underbrace{\left(\sum_{\sigma, \sigma'} A_{\beta, \alpha, \sigma', \sigma} \sigma_{\sigma, \sigma'}^{(j)} \right)}_{A_{\beta, \alpha}^{(j)}} = \frac{1}{2} \sum_{j=0}^3 \sum_{\alpha, \beta} \bar{\rho}_{\alpha, \beta}^{(j)} A_{\beta, \alpha}^{(j)}
 \end{aligned}$$

Physical

Total density

$$\rho_t = \rho^{(0)} = \rho_{\uparrow, \uparrow} + \rho_{\downarrow, \downarrow} \quad (2.39)$$

$$\rho_x = \rho^{(1)} = \rho_{\uparrow, \downarrow} + \rho_{\downarrow, \uparrow} \quad (2.40)$$

$$\rho_y = \rho^{(2)} = -i(\rho_{\uparrow, \downarrow} - \rho_{\downarrow, \uparrow}) \quad (2.41)$$

$$\rho_z = \rho^{(3)} = \rho_{\uparrow, \uparrow} - \rho_{\downarrow, \downarrow} \quad (2.42)$$

An expectation value is

$$\begin{aligned}
 A_{\uparrow, \uparrow} &= \frac{1}{2} (A^{(t)} + A^{(z)}) \\
 A_{\uparrow, \downarrow} &= \frac{1}{2} (A^{(x)} - iA^{(y)}) \\
 A_{\downarrow, \uparrow} &= \frac{1}{2} (A^{(x)} + iA^{(y)}) \\
 A_{\downarrow, \downarrow} &= \frac{1}{2} (A^{(t)} - A^{(z)})
 \end{aligned} \quad (2.43)$$

$$\begin{aligned}
 dE &= \sum_{\alpha, \beta, \sigma, \sigma'} \frac{dE}{d\rho_{\beta, \alpha, \sigma', \sigma}} d\rho_{\beta, \alpha, \sigma', \sigma} \\
 &= \sum_{\alpha, \beta, \sigma, \sigma'} \sum_{j=0}^3 \frac{dE}{d\rho_{\beta, \alpha}^{(j)}} \frac{d\rho_{\beta, \alpha}^{(j)}}{d\rho_{\beta, \alpha, \sigma', \sigma}} d\rho_{\beta, \alpha, \sigma', \sigma} \\
 &= \sum_{j=0}^3 \sum_{\alpha, \beta} \frac{dE}{d\rho_{\beta, \alpha}^{(j)}} \left(\sum_{\sigma, \sigma'} \sigma_{\sigma, \sigma'}^{(j)} d\rho_{\beta, \alpha, \sigma', \sigma} \right) \\
 &= \sum_{j=0}^3 \sum_{\alpha, \beta} \left(\frac{dE}{d\rho_{\beta, \alpha}^{(j)}} \right) d\rho_{\beta, \alpha}^{(j)}
 \end{aligned} \quad (2.44)$$

There is an ambiguity because of the trace formula

$$A = \frac{1}{2} \sum_{j=0}^3 \rho^{(j)} A^{(j)} \quad (2.45)$$

$$dE = \sum_{j=0}^3 \frac{dE}{d\rho^{(j)}} d\rho^{(j)} \quad (2.46)$$

$$v^{(j)} = 2 \frac{dE}{d\rho^{(j)}} \quad (2.47)$$

Using the transformation equation for expectation values

$$v_{\sigma,\sigma'} = \frac{1}{2} \sum_{j=0}^3 v^{(j)} \sigma_{\sigma,\sigma'}^{(j)} = \sum_{j=0}^3 \frac{dE}{d\rho^{(j)}} \sigma_{\sigma,\sigma'}^{(j)} \quad (2.48)$$

$$\begin{aligned} v_{\uparrow,\uparrow} &= \frac{1}{2}(v_t + v_z) \\ v_{\uparrow,\downarrow} &= \frac{1}{2}(v_x - i v_y) \\ v_{\downarrow,\uparrow} &= \frac{1}{2}(v_x + i v_y) \\ v_{\downarrow,\downarrow} &= \frac{1}{2}(v_t - v_z) \end{aligned} \quad (2.49)$$

2.6.1 SPINOR\$CONVERT

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

$$\begin{aligned} A_{\alpha,\beta}^{(j)} &= \frac{1}{2} \sum_{\sigma,\sigma'} A_{\alpha,\beta,\sigma,\sigma'} \sigma_{\sigma',\sigma}^{(j)} \\ \rho_{\alpha,\beta}^{(j)} &= \sum_{\sigma,\sigma'} \rho_{\alpha,\beta,\sigma,\sigma'} \sigma_{\sigma',\sigma}^{(j)} \end{aligned} \quad (2.50)$$

- 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.

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

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

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

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

$$\boldsymbol{\sigma}^{(0)} \triangleq \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad \boldsymbol{\sigma}^{(1)} \triangleq \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \quad \boldsymbol{\sigma}^{(2)} \triangleq \begin{pmatrix} 0 \\ -i \\ i \\ 0 \end{pmatrix} \quad \boldsymbol{\sigma}^{(3)} \triangleq \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix}$$

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

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

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

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

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

$$\begin{aligned} \sum_{\sigma, \sigma', \bar{\sigma}, \bar{\sigma}'} A_{\sigma, \sigma'} \sigma_{\sigma, \sigma'}^{(j)} \left(\sigma_{\bar{\sigma}, \bar{\sigma}'}^{(j')} \right)^* B_{\bar{\sigma}, \bar{\sigma}'} &= \left[\vec{A} \cdot \vec{\sigma}^{(j)} \right] \left[\left(\vec{\sigma}^{(j')} \right)^* \cdot \vec{B} \right] = \vec{A} \left[\left(\vec{\sigma}^{(j)} \right)^* \otimes \vec{\sigma}^{(j')} \right] \vec{B} \\ \Rightarrow \quad \sigma_{\sigma, \sigma'}^{(j)} \left(\sigma_{\bar{\sigma}, \bar{\sigma}'}^{(j')} \right)^* &= \left[\left(\vec{\sigma}^{(j)} \right)^* \otimes \vec{\sigma}^{(j')} \right]_{\sigma, \sigma'; \bar{\sigma}, \bar{\sigma}'} \end{aligned} \quad (\text{A.5})$$

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

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

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

$$\frac{1}{2} \sum_j \sigma_{\sigma, \sigma'}^{(j)} \left(\sigma_{\bar{\sigma}, \bar{\sigma}'}^{(j)} \right)^* = \delta_{\sigma, \bar{\sigma}} \delta_{\sigma', \bar{\sigma}'} \quad (\text{A.7})$$

Product table of Pauli matrices

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

$$\begin{aligned} \sigma^{(i)} \sigma^{(j)} &= \begin{pmatrix} \sigma^{(0)} & \sigma^{(x)} & \sigma^{(y)} & \sigma^{(z)} \\ \sigma^{(x)} & \sigma^{(0)} & i\sigma^{(z)} & -i\sigma^{(y)} \\ \sigma^{(y)} & -i\sigma^{(z)} & \sigma^{(0)} & i\sigma^{(x)} \\ \sigma^{(z)} & i\sigma^{(y)} & -i\sigma^{(x)} & \sigma^{(0)} \end{pmatrix} \\ &= \sum_k \left(\delta_{ij} \delta_{k,0} + \delta_{i,0} \delta_{j,k} + \delta_{i,k} \delta_{j,0} - 2\delta_{i,0} \delta_{j,0} \delta_{k,0} \right. \\ &\quad \left. + i(1 - \delta_{i,0})(1 - \delta_{j,0})(1 - \delta_{k,0}) \epsilon_{i,j,k} \right) \sigma^{(k)} \end{aligned} \quad (\text{A.8})$$

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

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

$$\left(\frac{(\sigma^{(0)})^2}{\sigma^{(0)} \cdot \vec{\sigma}} \middle| \frac{\sigma^{(0)} \vec{\sigma}}{\sigma^{(i)} \sigma^{(j)}} \right) = \left(\frac{\sigma^{(0)}}{\vec{\sigma}} \middle| \frac{\vec{\sigma}}{\delta_{ij} \sigma^{(0)} + i \sum_{k=1,3} \epsilon_{i,j,k} \sigma^{(k)}} \right) \quad (\text{A.10})$$

Thus we obtain

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

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>.