1 Time reversal

1.1 Without spin

Time-dependent Schrödinger equation:

$$i\hbar\partial_t\psi\left(\mathbf{r},t\right)=\left[-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}\right)\right]\psi\left(\mathbf{r},t\right) \tag{1}$$

'Local' time-reversal transformation, T:

$$t_1<t_2<\ldots<t_n\Rightarrow Tt_1>Tt_2>\ldots>Tt_n \tag{2}$$
$$T\left(t_2-t_1\right)=-\left(t_2-t_1\right) \tag{3}$$
$$T=T^{-1} \tag{4}$$

Transformed Schrödinger equation

$$\frac{d\left(f\circ T\right)\left(t\right)}{dt}=\frac{f\left(Tt+Tdt\right)-f\left(Tt\right)}{dt}=\frac{f\left(Tt-dt\right)-f\left(Tt\right)}{dt}=-\frac{df\left(Tt\right)}{dt} \tag{5}$$
$$\Downarrow$$
$$-i\hbar\partial_t\psi'\left(\mathbf{r},Tt\right)=\left[-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}\right)\right]\psi'\left(\mathbf{r},Tt\right) \tag{6}$$

On the other hand,

$$-i\hbar\partial_t\psi^*\left(\mathbf{r},t\right)=\left[-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}\right)\right]\psi^*\left(\mathbf{r},t\right) \tag{7}$$
$$\Downarrow$$
$$\underline{\psi'\left(\mathbf{r},Tt\right)=\psi^*\left(\mathbf{r},t\right)=C\,\psi\left(\mathbf{r},t\right)} \tag{8}$$

Properties:

$$C^2=1\ ,C^{-1}=C \tag{9}$$

C is anti-hermitian,

$$\langle\psi|C\varphi\rangle=\langle\varphi|C\psi\rangle=\langle C\psi|\varphi\rangle^* \tag{10}$$

and anti-linear,

$$C\left(c_1\varphi_1+c_2\varphi_2\right)=c_1^*C\varphi_1+c_2^*C\varphi_2\ . \tag{11}$$

However, the transformation C preserves the norm of the wavefunctions,

$$\langle C\psi|C\psi\rangle=\langle\psi|\psi\rangle\ \ . \tag{12}$$

Relationship to operators:

$$C\left(\mathbf{r}\psi\right)=\mathbf{r}\left(C\psi\right)\Longrightarrow C\mathbf{r}=\mathbf{r}C \tag{13}$$
$$C\left(\mathbf{p}\psi\right)=C\left(\frac{\hbar}{i}\nabla\psi\right)=-\frac{\hbar}{i}\nabla C\psi=-\mathbf{p}\left(C\psi\right)\Longrightarrow C\mathbf{p}=-\mathbf{p}C \tag{14}$$
$$C\mathbf{L}=C\left(\mathbf{r}\times\mathbf{p}\right)=\mathbf{r}\times C\mathbf{p}=-\left(\mathbf{r}\times\mathbf{p}\right)C=-\mathbf{L}C \tag{15}$$

1.2 With spin

Hamilton operator

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\mathbf{B} \tag{16}$$

Pauli-Schrödinger equation

$$i\hbar\partial_t\psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) + \frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\mathbf{B}\right]\psi(\mathbf{r},t) \tag{17}$$

Time-reversed magnetic field: $\mathbf{B}'= -\mathbf{B}$

Time-reversed Pauli-Schrödinger equation

$$-i\hbar\partial_t\psi'(\mathbf{r},Tt) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) + \frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\mathbf{B}'\right]\psi'(\mathbf{r},Tt) \tag{18}$$

$$= \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) - \frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\mathbf{B}\right]\psi'(\mathbf{r},Tt) \tag{19}$$

On the other hand:

$$-i\hbar\partial_t\psi^*(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) + \frac{\mu_B}{\hbar}(\mathbf{L}^*+2\mathbf{S}^*)\mathbf{B}\right]\psi^*(\mathbf{r},t) \tag{20}$$

$$= \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) - \frac{\mu_B}{\hbar}(\mathbf{L}-2\mathbf{S}^*)\mathbf{B}\right]\psi^*(\mathbf{r},t) \tag{21}$$

It is then tempting to suppose that $\exists\,\mathsf{L}\in\mathcal{L}(\mathbb{C}^2)$

$$\psi'(\mathbf{r},Tt) = \mathsf{L}C\,\psi(\mathbf{r},t) = \mathsf{L}\,\psi^*(\mathbf{r},t) \tag{22}$$

$$\Downarrow$$

$$-i\hbar\,\mathsf{L}\partial_t\psi^*(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) - \frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S})\mathbf{B}\right]\mathsf{L}\psi^*(\mathbf{r},t) \tag{23}$$

$$\Downarrow$$

$$-i\hbar\partial_t\psi^*(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) - \frac{\mu_B}{\hbar}\left(\mathbf{L}+2\mathsf{L}^{-1}\mathbf{S}\mathsf{L}\right)\mathbf{B}\right]\psi^*(\mathbf{r},t) \tag{24}$$

This equation is obviously satisfied if

$$\mathsf{L}^{-1}\mathbf{S}\mathsf{L}= -\mathbf{S}^* = -C\,\mathbf{S}\,C \Longrightarrow \mathbf{S}\,\mathsf{L}C = -\mathsf{L}C\,\mathbf{S} \tag{25}$$

Let's introduce the simplified notation: $T \mathrel{\hat=} \mathsf{L}C$

$$T\mathbf{S} = -\mathbf{S}T\,. \tag{26}$$

It is easy to prove that

$$\underline{T = \sigma_y\,C} \tag{27}$$

is a satisfactory choice (in many text-books $T = i\sigma_y C$ is chosen).

Proof of Eq. (26):

$$\sigma_x^* = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \sigma_x \quad \sigma_y^* = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = -\sigma_y \quad \sigma_z^* = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \sigma_z \tag{28}$$

$$\Downarrow$$

$$T^{-1}\sigma_x T = (-\sigma_y C)\,\sigma_x\,(\sigma_y C) = \sigma_y\sigma_x\sigma_y = -\sigma_x \tag{29}$$

$$T^{-1}\sigma_y T = (-\sigma_y C)\,\sigma_y\,(\sigma_y C) = -\sigma_y \tag{30}$$

$$T^{-1}\sigma_z T = (-\sigma_y C)\,\sigma_z\,(\sigma_y C) = \sigma_y\sigma_z\sigma_y = -\sigma_z \tag{31}$$

Properties:

$$\underline{T^{-1} = C\sigma_y = \sigma_y^* C = -\sigma_y C = -T} \tag{32}$$

$$\Downarrow \tag{33}$$

$$\underline{T^2 = -1} \tag{34}$$

From the relationship,

$$\begin{aligned}\langle\psi|T\varphi\rangle = \langle\psi|\sigma_y C\varphi\rangle = \langle\sigma_y\psi|C\varphi\rangle = \left(\sigma_y^{rs}\right)^* \langle\psi_s|C\varphi_r\rangle = \left\langle\varphi_r|C\sigma_y^{rs}\psi_s\right\rangle \\ = \langle\varphi|C\sigma_y\psi\rangle = -\langle\varphi|T\psi\rangle = -\langle T\psi|\varphi\rangle^* \ ,\end{aligned} \tag{35}$$

it follows that

$$\underline{\langle\psi|T\psi\rangle = -\langle\psi|T\psi\rangle = 0}\ , \tag{36}$$

i.e. ψ and $T\psi$ are orthogonal and, also, T is norm-conserving,

$$\langle T\psi|T\psi\rangle = -\left\langle\psi|T^2\psi\right\rangle = \langle\psi|\psi\rangle \ . \tag{37}$$

Note also that

$$\langle\psi|\varphi\rangle = \left\langle\psi|TT^{-1}\varphi\right\rangle = -\left\langle T\psi|T^{-1}\varphi\right\rangle^* = \langle T\psi|T\varphi\rangle^* \ .$$

The operator of spin-orbit coupling, $\frac{\hbar}{4m^2c^2}\left(\nabla V \times \mathbf{p}\right)\sigma$, commutes with T:

$$T^{-1}\left(\nabla V \times \mathbf{p}\right)\sigma T = \left(T^{-1}\left(\nabla V \times \mathbf{p}\right)T\right)\left(T^{-1}\sigma T\right) = \left(\nabla V \times (-\mathbf{p})\right)(-\sigma) = \left(\nabla V \times \mathbf{p}\right)\sigma \ . \tag{38}$$

1.3 Quenching of the orbital moment

The angular momentum operator changes sign upon time reversal:

$$T^{-1}\mathbf{L}T = C\sigma_y\mathbf{L}\sigma_y C = C\mathbf{L}C = -\mathbf{L} \Longrightarrow T\mathbf{L}T = \mathbf{L} \tag{39}$$

In the spinless case, i.e. in case of scalar wavefunctions and *non-degenerate eigenstates*:

$$C\psi = \psi^* = e^{i\alpha}\psi \tag{40}$$

$$\langle\psi|\mathbf{L}\psi\rangle = \left\langle C\psi|C\mathbf{L}C^2\psi\right\rangle^* = -\langle C\psi|\mathbf{L}C\psi\rangle^* = -\langle\psi|\mathbf{L}\psi\rangle^* = -\langle\psi|\mathbf{L}\psi\rangle = 0\,. \tag{41}$$

In case of degenerate eigenstates, if ψ is an eigenstate of the Hamiltonian then $T\psi$ (or $C\psi$) is also an eigenstate with the same energy, thus, it belongs to the same eigen-subspace. Then

$$\langle C\psi|\mathbf{L}C\psi\rangle = \langle \psi|C\mathbf{L}C\psi\rangle^* = -\langle \psi|\mathbf{L}\psi\rangle^* = -\langle \psi|\mathbf{L}\psi\rangle \tag{42}$$

where we used that $\langle \psi|\mathbf{L}\psi\rangle \in \mathbb{R}$. Thus by choosing the eigenfunctions

$$\psi_\pm = \frac{\sqrt{2}}{2}(\psi \pm C\psi) \tag{43}$$

$$\langle \psi_\pm|\mathbf{L}\psi_\pm\rangle = \frac{1}{2}\langle(\psi \pm C\psi)|\mathbf{L}(\psi \pm C\psi)\rangle = \pm\frac{1}{2}\left(\langle \psi|\mathbf{L}C\psi\rangle + \langle C\psi|\mathbf{L}\psi\rangle\right)$$

$$\langle C\psi|\mathbf{L}\psi\rangle = \langle C\mathbf{L}\psi|\psi\rangle = \langle C\mathbf{L}CC\psi|\psi\rangle = -\langle \mathbf{L}C\psi|\psi\rangle = -\langle C\psi|\mathbf{L}\psi\rangle$$

$$\Downarrow$$

$$\langle \psi_\pm|\mathbf{L}\psi_\pm\rangle = 0 \tag{44}$$

i.e. *the expectation value of* $\mathbf{L}$ *over any eigen-subspace of the Hamiltonian is zero.*

In case of a system spin-polarized along the z direction with no spin-orbit coupling and the Landau paramagnetic term neglected, the eigenstates are pure spinors:

$$\psi_+ = \begin{pmatrix} u_+ \\ 0 \end{pmatrix} \quad \psi_- = \begin{pmatrix} 0 \\ u_- \end{pmatrix} \tag{45}$$

where

$$H_\pm u_\pm = \varepsilon_\pm u_\pm \tag{46}$$

with

$$H_\pm = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \pm \mu_B B_z(\mathbf{r}) \ . \tag{47}$$

The theorem proven for scalar wavefunctions then applies separately for both the spin channels, i.e the orbital moment vanishes again.

1.4 Kramers degeneracy

Let us consider an eigenfunction, $\psi(\mathbf{r}_1 s_1, \ldots, \mathbf{r}_N s_N)$ of the N-electron Hamiltonian,

$$H\psi = E\psi \tag{48}$$

where

$$T^{-1}HT = H \ . \tag{49}$$

The time-reversed wavefunction, $T\psi$, is then also eigenfunction of H with the same eigenvalue,

$$T^{-1}HT\psi = E\psi \Longrightarrow H(T\psi) = E(T\psi) \ . \tag{50}$$

The representation of T which satisfies

$$T\mathbf{S}^{(k)} = -\mathbf{S}^{(k)}T \ . \tag{51}$$

for any $k = 1, \ldots, N$, is

$$T = \sigma_y^{(1)} \ldots \sigma_y^{(N)} C = (-1)^N C \sigma_y^{(1)} \ldots \sigma_y^{(N)} = (-1)^N T^{-1} \implies T^2 = (-1)^N \ . \tag{52}$$

that means

$$\underline{T^{-1} = (-1)^N T} \ . \tag{53}$$

Furthermore,

$$\begin{aligned} \underline{\langle \psi | T \psi \rangle} &= \langle \psi | \sigma_y^{(1)} \ldots \sigma_y^{(N)} C \psi \rangle = \langle \sigma_y^{(1)} \ldots \sigma_y^{(N)} \psi | C \, \psi \rangle \underset{\text{Eq. (10)}}{=} \langle \psi | C \sigma_y^{(1)} \ldots \sigma_y^{(N)} \, \psi \rangle \\ &= (-1)^N \langle \psi | \sigma_y^1 \ldots \sigma_y^N C \, \psi \rangle = \underline{(-1)^N \langle \psi | T \psi \rangle} \end{aligned} \tag{54}$$

Corollary: For *odd number of electrons* ψ and $T\psi$ are orthogonal, therefore, the eigenstates of the system are at least twofold degenerate.

1.5 Kramers degeneracy of Bloch-states

We consider the Hamiltonian derived from the Dirac equation up to first order of $1/c^2$:

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2} \Delta V(\mathbf{r}) + \frac{\hbar}{4m^2c^2} (\nabla V(\mathbf{r}) \times \mathbf{p}) \, \sigma \tag{55}$$

This one-electron Hamiltonian is invariant w.r.t. time-reversal,

$$T^{-1} H T = H \ . \tag{56}$$

From the previous section it follows that the eigenstates are at least two-fold degenerate:

$$H\psi = \varepsilon \psi \tag{57}$$

$$H(T\psi) = \varepsilon (T\psi) \tag{58}$$

and $T\psi$ is orthogonal to ψ.

Let's see what is $T\psi$? A Bloch-state eigenfunction is defined as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}} u_{\mathbf{k}}(\mathbf{r}) \tag{59}$$

$$H_{\mathbf{k}} u_{\mathbf{k}} = \varepsilon_{\mathbf{k}} u_{\mathbf{k}} \tag{60}$$

Hamiltonian for non-spinpolarized periodic solid:

$$H_{\mathbf{k}} = \frac{(\mathbf{p} + \hbar\mathbf{k})^2}{2m} + V(\mathbf{r}) - \frac{(\mathbf{p} + \hbar\mathbf{k})^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2} \Delta V(\mathbf{r}) + \frac{\hbar}{4m^2c^2} (\nabla V(\mathbf{r}) \times (\mathbf{p} + \hbar\mathbf{k})) \, \sigma \tag{61}$$

It is straightforward to show that

$$\underline{T^{-1} H_{\mathbf{k}} T = H_{-\mathbf{k}}} \tag{62}$$

thus,

$$T^{-1} H_{\mathbf{k}} u_{\mathbf{k}} = \varepsilon_{\mathbf{k}} T^{-1} u_{\mathbf{k}} \tag{63}$$

$$\Downarrow$$

$$H_{-\mathbf{k}}\left(T^{-1}u_{\mathbf{k}}\right)=\varepsilon_{\mathbf{k}}\left(T^{-1}u_{\mathbf{k}}\right) \tag{64}$$

$$\Downarrow$$

$$\underline{\varepsilon_{-\mathbf{k}}=\varepsilon_{\mathbf{k}}} \tag{65}$$

and the two degenerate wavefunctions are:

$$\psi_{\mathbf{k}}\left(\mathbf{r}\right)=e^{i\mathbf{kr}}\begin{pmatrix} u_{\mathbf{k}\uparrow}\left(\mathbf{r}\right) \\ u_{\mathbf{k}\downarrow}\left(\mathbf{r}\right)\end{pmatrix} \quad \text{and} \quad \psi_{-\mathbf{k}}^{(1)}\left(\mathbf{r}\right)=e^{-i\mathbf{kr}}\begin{pmatrix} iu_{\mathbf{k}\downarrow}^{*}\left(\mathbf{r}\right) \\ -iu_{\mathbf{k}\uparrow}^{*}\left(\mathbf{r}\right)\end{pmatrix} \tag{66}$$

1.6 Space inversion

Let's consider the case when also *space inversion* (i) applies:

$$V\left(i\,\mathbf{r}\right)=V\left(-\mathbf{r}\right)=V\left(\mathbf{r}\right) \tag{67}$$

$$\nabla V\left(i\,\mathbf{r}\right)=-\nabla V\left(\mathbf{r}\right) \tag{68}$$

$$\Delta V\left(i\,\mathbf{r}\right)=\Delta V\left(\mathbf{r}\right) \tag{69}$$

$$i\,\mathbf{p}\,f\left(i\,\mathbf{r}\right)=-\mathbf{p}\,f\left(-\mathbf{r}\right) \tag{70}$$

$$\Downarrow$$

$$H_{\mathbf{k}}\left(i\,\mathbf{r}\right)u_{\mathbf{k}}\left(i\,\mathbf{r}\right)=H_{-\mathbf{k}}\left(\mathbf{r}\right)u_{\mathbf{k}}\left(-\mathbf{r}\right) \tag{71}$$

$$\Downarrow$$

$$H_{-\mathbf{k}}\left(\mathbf{r}\right)u_{\mathbf{k}}\left(-\mathbf{r}\right)=\varepsilon_{\mathbf{k}}u_{\mathbf{k}}\left(-\mathbf{r}\right) \tag{72}$$

This also implies that

$$\varepsilon_{-\mathbf{k}}=\varepsilon_{\mathbf{k}} \tag{73}$$

and

$$u_{-\mathbf{k}}\left(\mathbf{r}\right)=u_{\mathbf{k}}\left(-\mathbf{r}\right)\ .$$

The corresponding Bloch-eigenfunction for $-\mathbf{k}$**,**

$$\psi_{-\mathbf{k}}^{(2)}\left(\mathbf{r}\right)=e^{-i\mathbf{kr}}\begin{pmatrix} u_{\mathbf{k}\uparrow}\left(-\mathbf{r}\right) \\ u_{\mathbf{k}\downarrow}\left(-\mathbf{r}\right)\end{pmatrix}\ . \tag{74}$$

In case of both time-reversal and inversion symmetry, the two eigenfunctions for $-\mathbf{k}$ with the same energy $\varepsilon_{-\mathbf{k}}\left(=\varepsilon_{\mathbf{k}}\right)$ are orthogonal:

$$\int\psi_{-\mathbf{k}}^{(1)+}\left(\mathbf{r}\right)\psi_{-\mathbf{k}}^{(2)}\left(\mathbf{r}\right)d^{3}r=-i\int\left[u_{\mathbf{k}\downarrow}\left(\mathbf{r}\right)u_{\mathbf{k}\uparrow}\left(-\mathbf{r}\right)-u_{\mathbf{k}\uparrow}\left(\mathbf{r}\right)u_{\mathbf{k}\downarrow}\left(-\mathbf{r}\right)\right]d^{3}r=0 \tag{75}$$

Corollary: The Bloch-states (related to a given **k)** of a nonmagnetic centro-symmetric crystal are at least twofold degenerate.

1.7 Sorting out the eigenstates by spin-expectation value

In general, the eigenfunctions $\psi_{\mathbf{k}}^{(\mu)}$ $(\mu = 1, 2)$ are not eigenfunctions of the spin-operator S_z for any chosen quantization axis z. This is only the case in the absence of spin-orbit coupling. Nevertheless, it is possible to construct the orthonormal linear combinations,

$$\psi_{\mathbf{k}}^{(+)} = c_1 \psi_{\mathbf{k}}^{(1)} + c_2 \psi_{\mathbf{k}}^{(2)} \tag{76}$$

$$\psi_{\mathbf{k}}^{(-)} = -c_2^* \psi_{\mathbf{k}}^{(1)} + c_1^* \psi_{\mathbf{k}}^{(2)} \tag{77}$$

such that $|c_1|^2 + |c_2|^2 = 1$

$$\left\langle \psi_{\mathbf{k}}^{(+/-)} \left| \sigma_x \right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = \left\langle \psi_{\mathbf{k}}^{(+/-)} \left| \sigma_y \right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = 0 \tag{78}$$

and

$$\left\langle \psi_{\mathbf{k}}^{(+/-)} \left| \sigma_z \right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = \pm P_{\mathbf{k}} \tag{79}$$

$$0 \leq P_{\mathbf{k}} \leq 1 \tag{80}$$

Thus we can sort out the two degenerate states by the 'spin-character', $P_{\mathbf{k}}$.

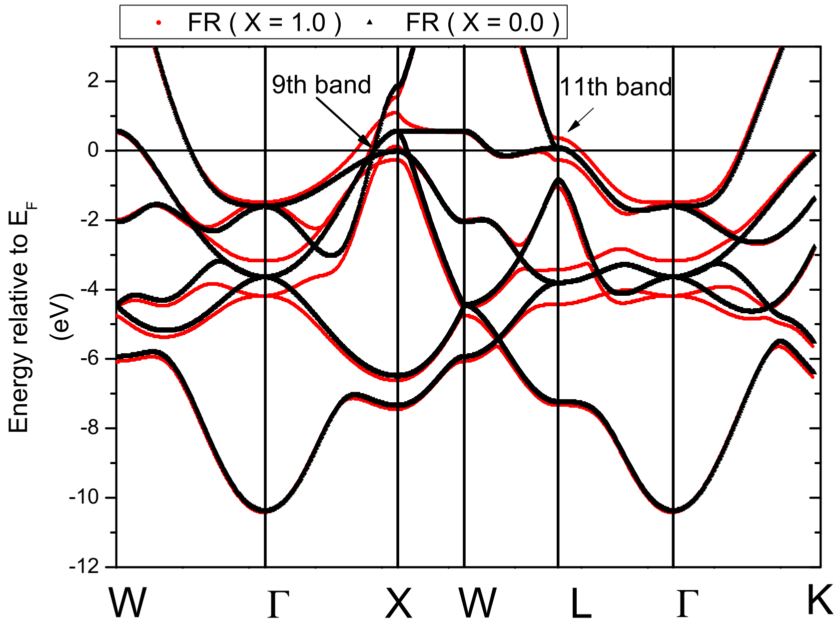

FIG. 2: Band structure of Pt from the fully relativistic (red) and the relativistic with the spin-orbit coupling scaled to zero (black) calculation.

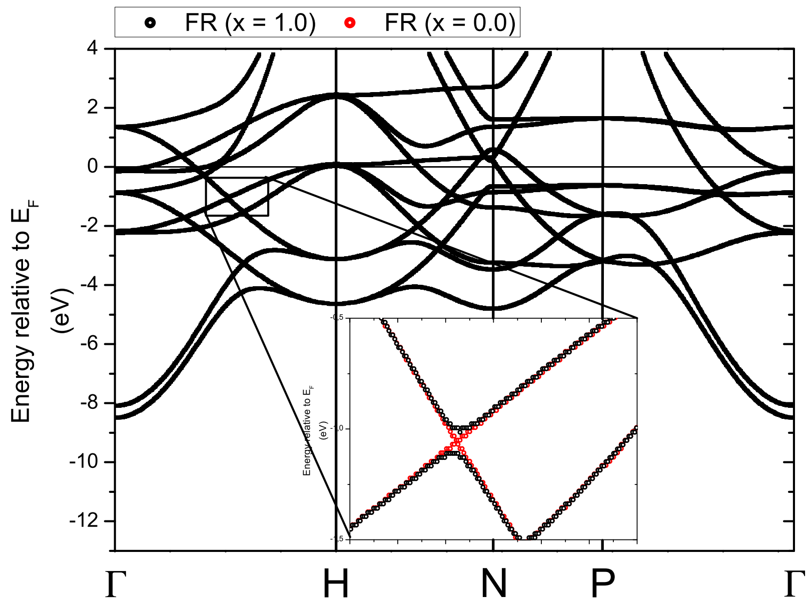

FIG. 3: Calculated fully relativistic band structure of bcc Fe. The small inset shows a comparison to the calculation with the spin-orbit coupling scaled to zero (x=0). The spin-orbit interaction leads to avoided crossings.

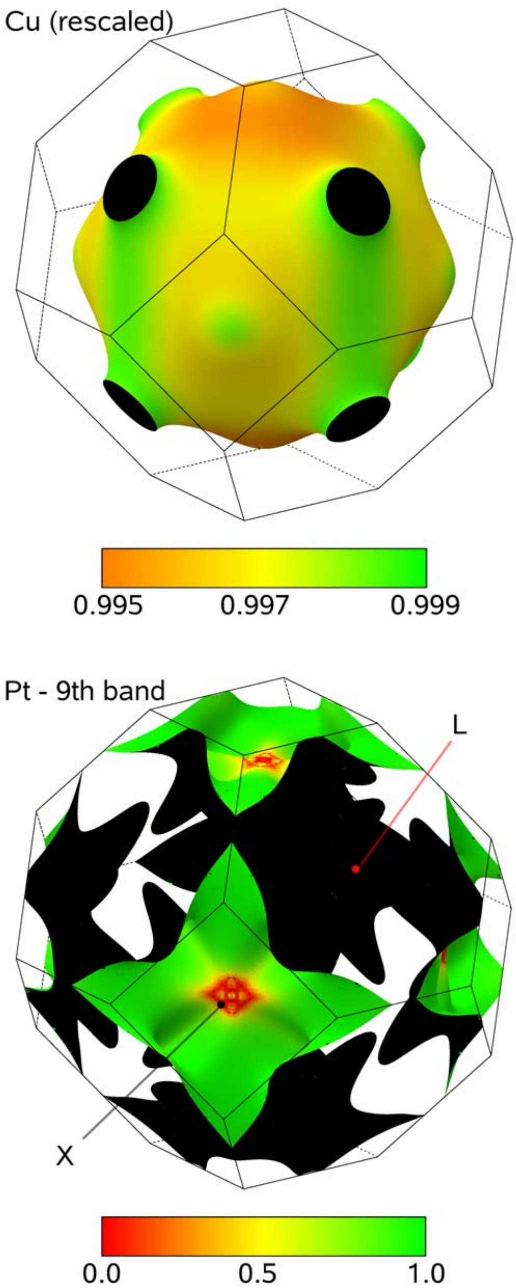

FIG. 4: Calculated relativistic Fermi surface of Cu (upper left), Au (upper right) and Pt (lower left: 9th band, lower right: 11th band), and the expectation values of $\hat{\beta}\sigma_z$ for the $\left|\Psi_k^+\right\rangle$ states are indicated as color code. Note the different scale for Cu and Au in comparison to Pt.

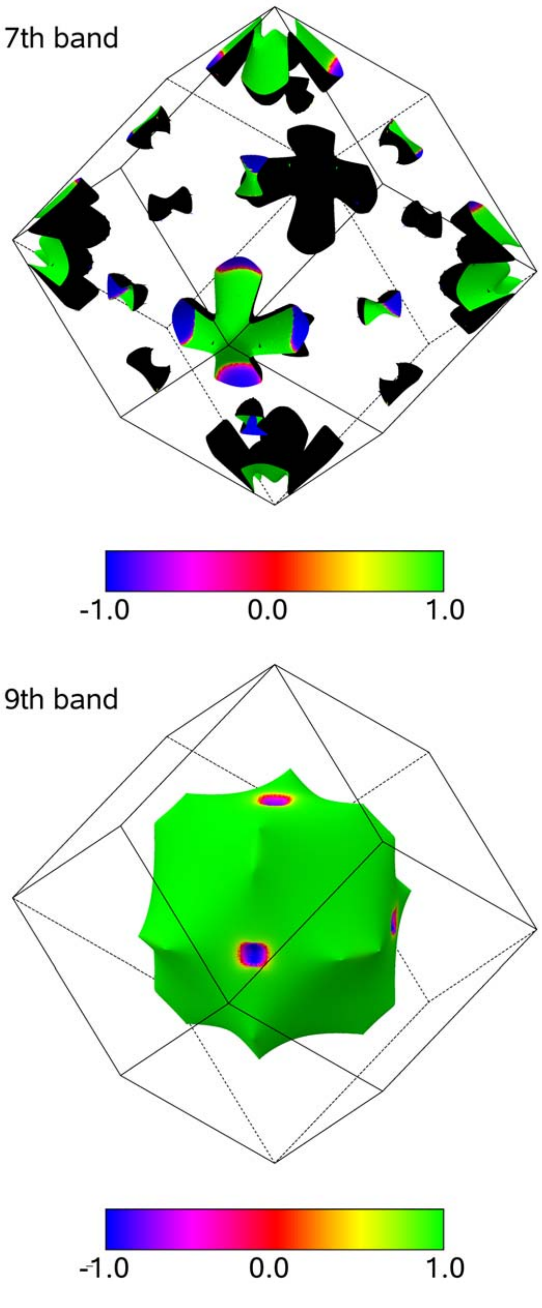

FIG. 5: Calculated relativistic Fermi surface for the bands 7-10 of bcc Fe. The expectation values of the $\hat{\beta}\sigma_z$ operator are given as color code.