1 Time reversal

1.1 Without spin

Time-dependent Schrödinger equation:

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

'Local' time-reversal transformation, T:

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

Transformed Schrödinger equation

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

On the other hand,

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

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,

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

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:

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

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

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

$$\Downarrow$$

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

$$\Downarrow$$

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

This equation is obviously satisfied if

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

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

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

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:

$$T^{-1} = C\sigma_y = \sigma_y^* C = -\sigma_y C = -T \tag{32}$$
$$\Downarrow \tag{33}$$
$$T^2 = -1 \tag{34}$$

From the relationship,

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

it follows that

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

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

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

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 Kramers degeneracy

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

$$H\psi = E\psi \tag{39}$$

where

$$T^{-1}HT = H\ . \tag{40}$$

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

$$T^{-1}HT\psi = E\psi \Longrightarrow H\left(T\psi\right) = E\left(T\psi\right)\ . \tag{41}$$

The representation of T is

$$T = \sigma_y^{(1)}\ldots\sigma_y^{(N)}C = (-1)^N C\sigma_y^{(1)}\ldots\sigma_y^{(N)} = (-1)^N T^{-1} \implies T^2 = (-1)^N\ , \tag{42}$$

$$T^{+} = T^{-1} = (-1)^N T\ , \tag{43}$$

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

$$T\mathbf{S}^{(k)} = -\mathbf{S}^{(k)}T\ . \tag{44}$$

Furthermore,

$$\begin{aligned}\langle\psi|T\psi\rangle &= \left\langle\psi|\sigma_y^{(1)}\ldots\sigma_y^{(N)}C\psi\right\rangle = (-1)^N\left\langle\psi|C\,\sigma_y^{(1)}\ldots\sigma_y^{(N)}\psi\right\rangle \underset{\text{Eq. (10)}}{=} (-1)^N\left\langle\sigma_y^{(1)}\ldots\sigma_y^{(N)}\psi|C\,\psi\right\rangle \\ &= (-1)^N\left\langle\psi|\sigma_y^{1}\ldots\sigma_y^{N}C\,\psi\right\rangle = (-1)^N\langle\psi|T\psi\rangle\end{aligned} \tag{45}$$

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

1.4 Kramers degeneracy of Bloch-states

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

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}\Delta V(\mathbf{r}) + \frac{\hbar}{4m^2c^2}(\nabla V \times \mathbf{p})\,\sigma \tag{46}$$

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

$$T^{-1}HT = H\ . \tag{47}$$

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

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

$$H(T\psi) = \varepsilon(T\psi) \tag{49}$$

and $T\psi$ is orthogonal to ψ.

What is $T\psi$? A Bloch-eigenfunction is defined as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}u_{\mathbf{k}}(\mathbf{r}) \tag{50}$$

$$H_{\mathbf{k}} = \frac{(\mathbf{p}+\hbar\mathbf{k})^2}{2m} + V(\mathbf{r}) - \frac{(\mathbf{p}+\hbar\mathbf{k})^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}\Delta V(\mathbf{r}) + \frac{\hbar}{4m^2c^2}(\nabla V \times (\mathbf{p}+\hbar\mathbf{k}))\,\sigma \tag{51}$$

$$H_{\mathbf{k}}u_{\mathbf{k}} = \varepsilon_{\mathbf{k}}u_{\mathbf{k}} \tag{52}$$

It is straightforward to show that

$$T^{-1}H_{\mathbf{k}}T = H_{-\mathbf{k}} \tag{53}$$

thus,

$$T^{-1}H_{\mathbf{k}}u_{\mathbf{k}} = \varepsilon_{\mathbf{k}}T^{-1}u_{\mathbf{k}} \tag{54}$$

$$\Downarrow$$

$$H_{-\mathbf{k}}\left(T^{-1}u_{\mathbf{k}}\right) = \varepsilon_{\mathbf{k}}\left(T^{-1}u_{\mathbf{k}}\right) \tag{55}$$

$$\Downarrow$$

$$\varepsilon_{-\mathbf{k}} = \varepsilon_{\mathbf{k}} \tag{56}$$

and the two degenerate wavefunctions are:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}\begin{pmatrix} u_{\mathbf{k}\uparrow}(\mathbf{r}) \\ u_{\mathbf{k}\downarrow}(\mathbf{r}) \end{pmatrix} \quad \text{and} \quad \psi^{(1)}_{-\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{kr}}\begin{pmatrix} iu^*_{\mathbf{k}\downarrow}(\mathbf{r}) \\ -iu^*_{\mathbf{k}\uparrow}(\mathbf{r}) \end{pmatrix} \tag{57}$$

1.5 Space inversion

Let's consider the case when also space inversion applies:

$$V(I\,\mathbf{r}) = V(-\mathbf{r}) = V(\mathbf{r}) \tag{58}$$

$$\Downarrow$$

$$I\,H_{-\mathbf{k}}\,I = H_{\mathbf{k}} \tag{59}$$

This also implies that $\varepsilon_{-\mathbf{k}} = \varepsilon_{\mathbf{k}}$ with the corresponding wavefunction for $-\mathbf{k}$,

$$\psi^{(2)}_{-\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{kr}}\begin{pmatrix} u_{\mathbf{k}\uparrow}(-\mathbf{r}) \\ u_{\mathbf{k}\downarrow}(-\mathbf{r}) \end{pmatrix}\ . \tag{60}$$

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

$$\int \psi_{-\mathbf{k}}^{(1)+}(\mathbf{r})\,\psi_{-\mathbf{k}}^{(2)}(\mathbf{r})\,d^3r = -i\int \left[u_{\mathbf{k}\downarrow}(\mathbf{r})\,u_{\mathbf{k}\uparrow}(-\mathbf{r}) - u_{\mathbf{k}\uparrow}(\mathbf{r})\,u_{\mathbf{k}\downarrow}(-\mathbf{r})\right] d^3r = 0 \tag{61}$$

Corollary: The Bloch-states of a nonmagnetic centro-symmetric crystal are at least twofold degenerate.

1.6 Sorting out 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 prechosen 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,

$$\psi_{\mathbf{k}}^{(+)} = c_1\psi_{\mathbf{k}}^{(1)} + c_2\psi_{\mathbf{k}}^{(2)} \tag{62}$$

$$\psi_{\mathbf{k}}^{(-)} = -c_2^*\psi_{\mathbf{k}}^{(1)} + c_1^*\psi_{\mathbf{k}}^{(2)} \tag{63}$$

$c_1, c_2 \in \mathbb{C},\ |c_1|^2 + |c_2|^2 = 1$, such that

$$\left\langle \psi_{\mathbf{k}}^{(+/-)} \left|\sigma_x\right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = \left\langle \psi_{\mathbf{k}}^{(+/-)} \left|\sigma_y\right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = 0 \tag{64}$$

and

$$\left\langle \psi_{\mathbf{k}}^{(+/-)} \left|\sigma_z\right| \psi_{\mathbf{k}}^{(+/-)} \right\rangle = \pm P_{\mathbf{k}} \tag{65}$$

$$0 \leq P_{\mathbf{k}} \leq 0 \tag{66}$$

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

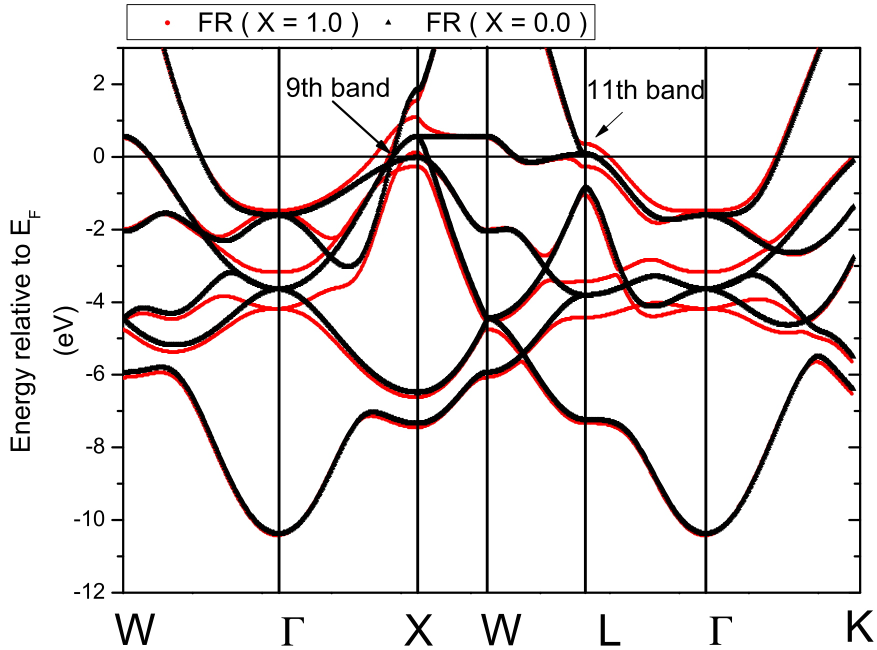

FIG. 2: Band structure of Pt from the fully relativistic (red) and the relativistic with the spin-orbit coupling scaled to zero (black) calculation.

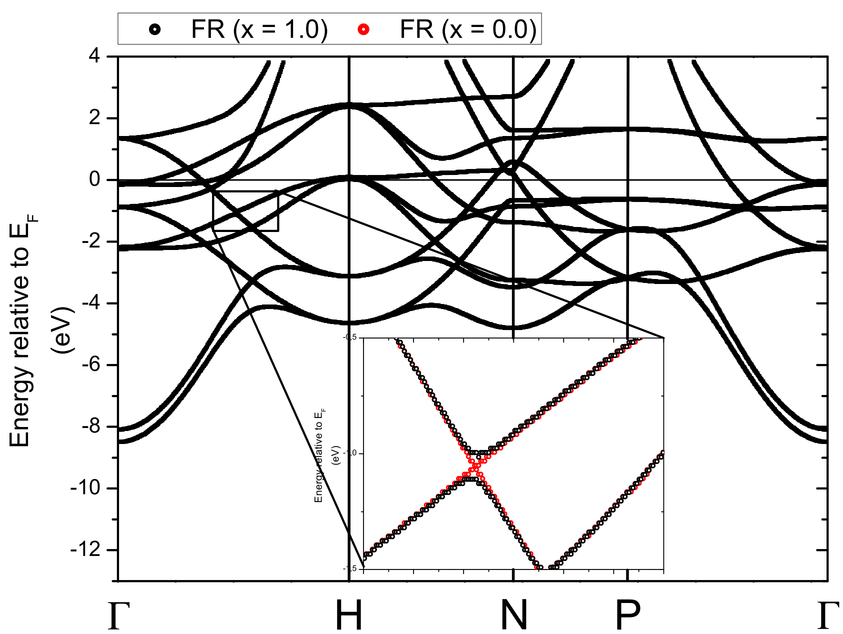

FIG. 3: Calculated fully relativistic band structure of bcc Fe. The small inset shows a comparison to the calculation with the spin-orbit coupling scaled to zero (x=0). The spin-orbit interaction leads to avoided crossings.

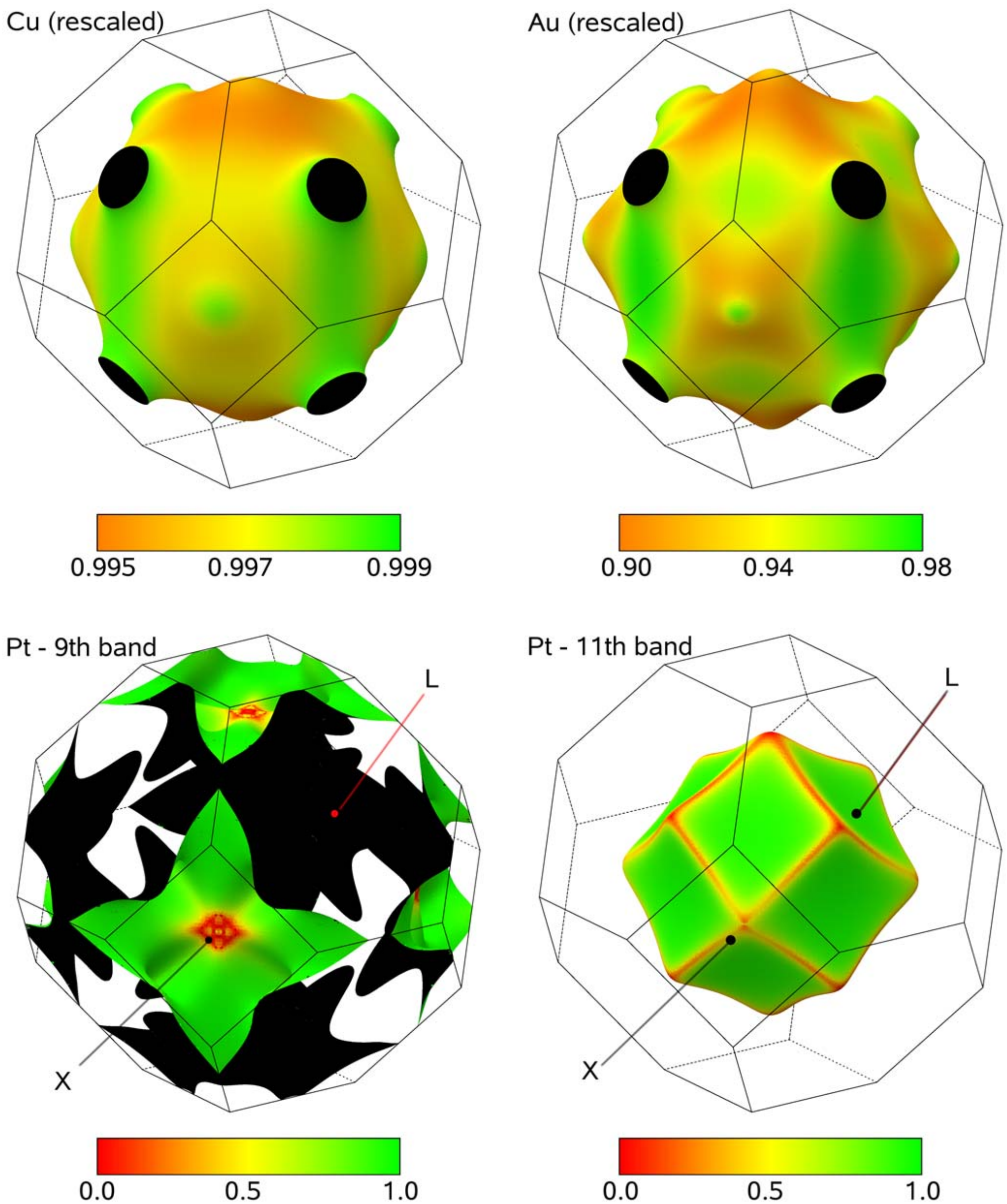

FIG. 4: Calculated relativistic Fermi surface of Cu (upper left), Au (upper right) and Pt (lower left: 9th band, lower right: 11th band), and the expectation values of $\hat{\beta}\sigma_z$ for the $\left|\Psi_k^+\right\rangle$ states are indicated as color code. Note the different scale for Cu and Au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

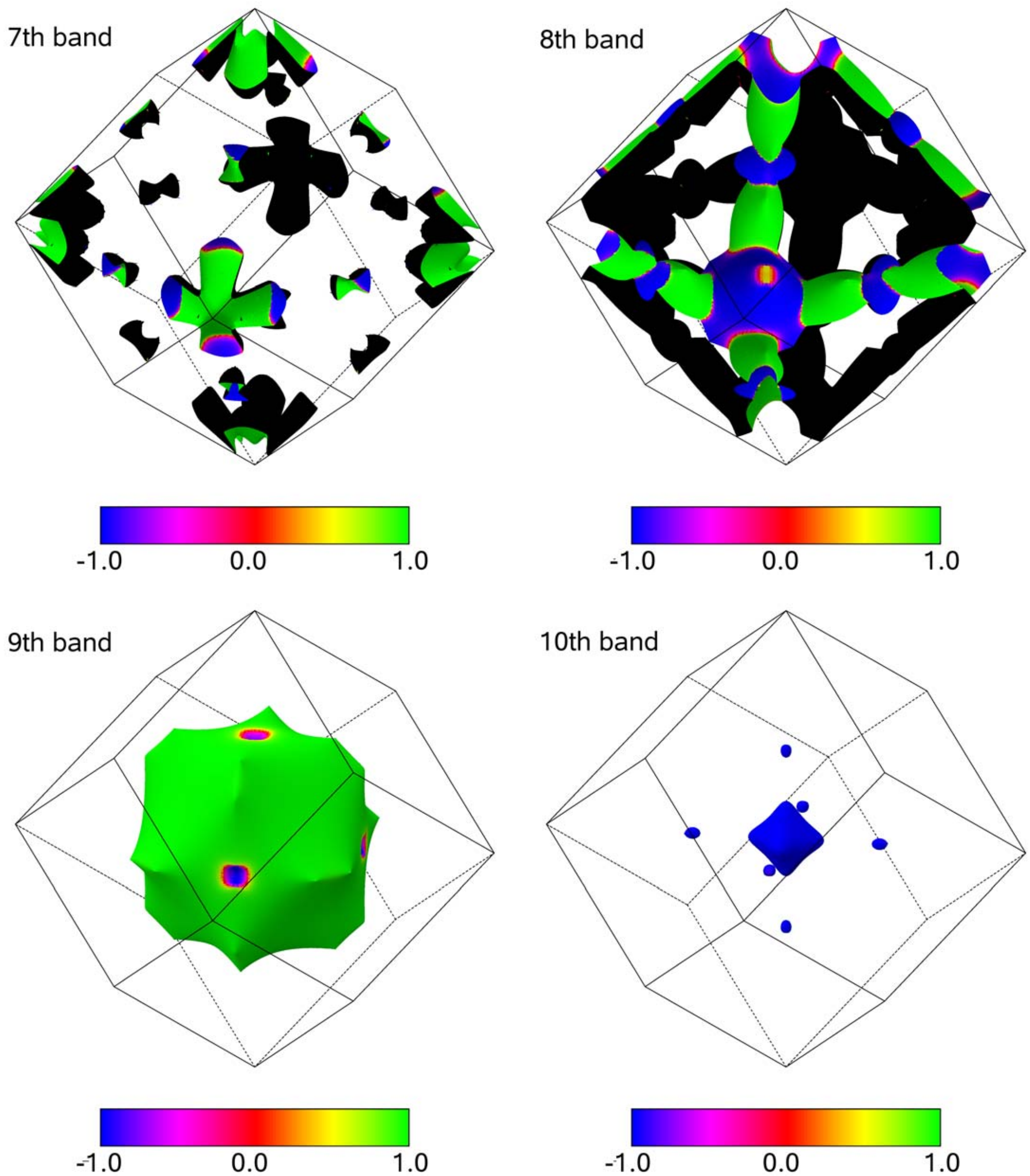

FIG. 5: Calculated relativistic Fermi surface for the bands 7-10 of bcc Fe. The expectation values of the $\hat{\beta}\sigma_z$ operator are given as color code.