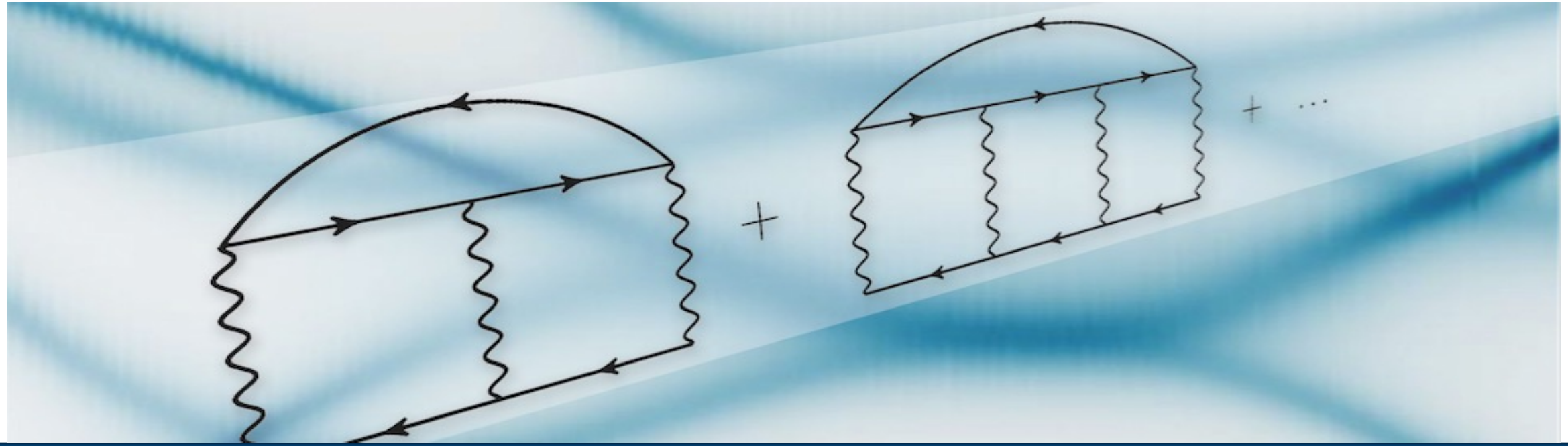
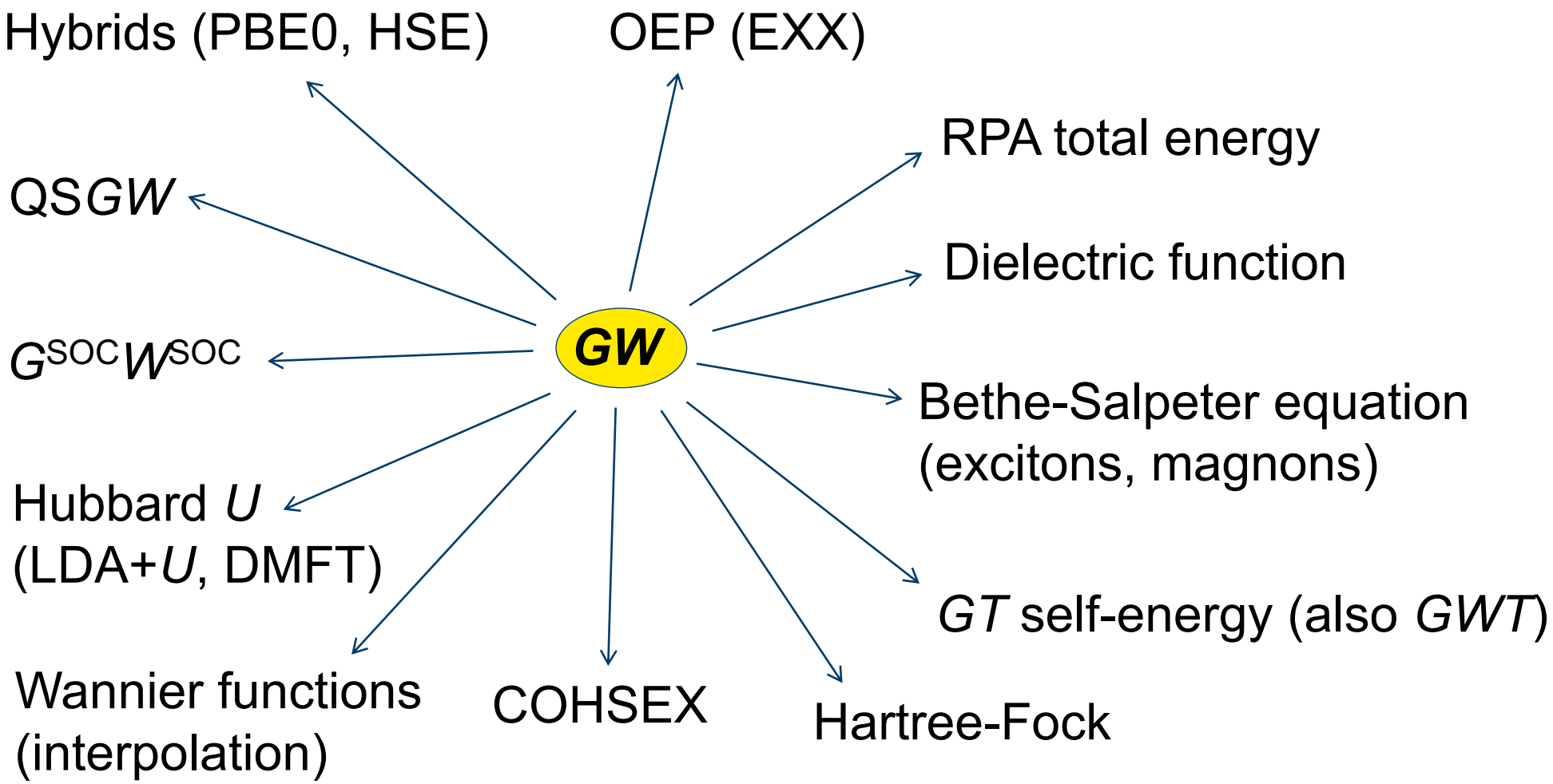


ELECTRON-PLASMON AND ELECTRON-MAGNON SCATTERING IN ELEMENTARY FERROMAGNETS FROM FIRST PRINCIPLES: *GWT* SELF-ENERGY

CHRISTOPH FRIEDRICH

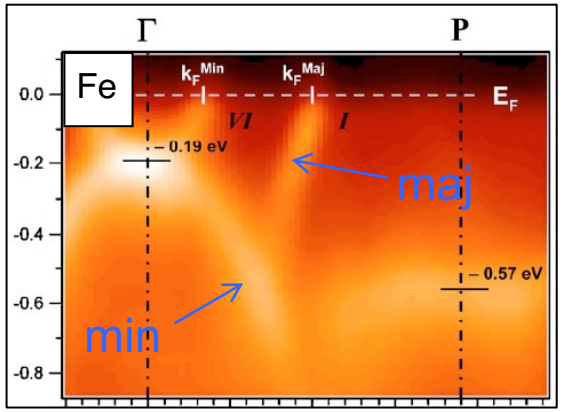
PETER GRÜNBERG INSTITUTE AND INSTITUTE FOR ADVANCED SIMULATION
FORSCHUNGSZENTRUM JÜLICH AND JARA, 52425 JÜLICH, GERMANY

SPEX

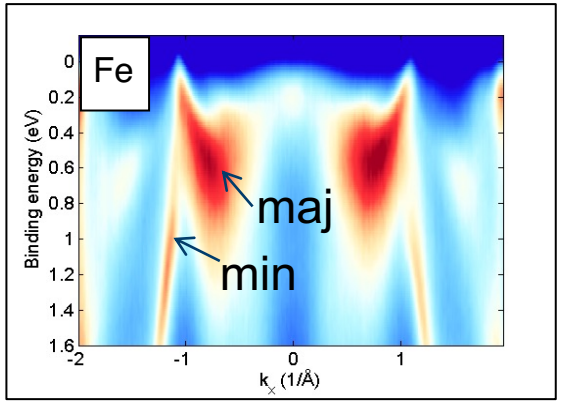

Hybrids (PBE0, HSE)
OEP (EXX)
RPA total energy
QS*GW*
Dielectric function
$G^{SOC}W^{SOC}$
GW
Bethe-Salpeter equation
(excitons, magnons)
Hubbard *U*
(LDA+*U*, DMFT)
GT self-energy (also *GWT*)
Wannier functions
(interpolation)
COHSEX
Hartree-Fock

ARPES MEASUREMENTS

Spin asymmetry in spectra

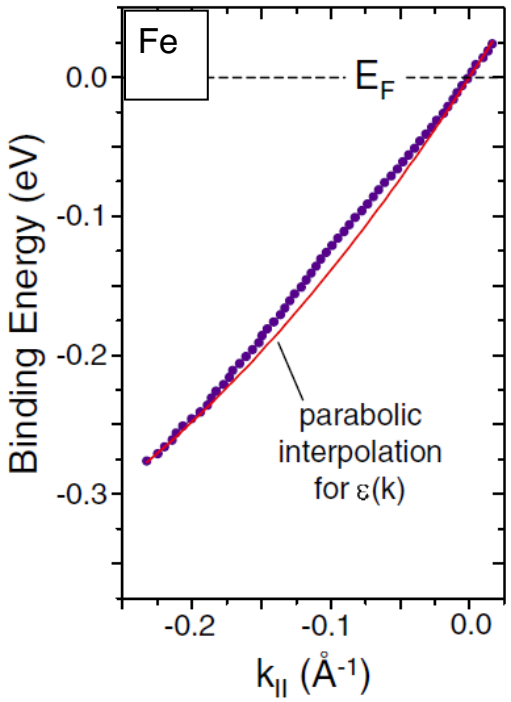


Schäfer *et al.*, PRL **72**, 155115 (2005)

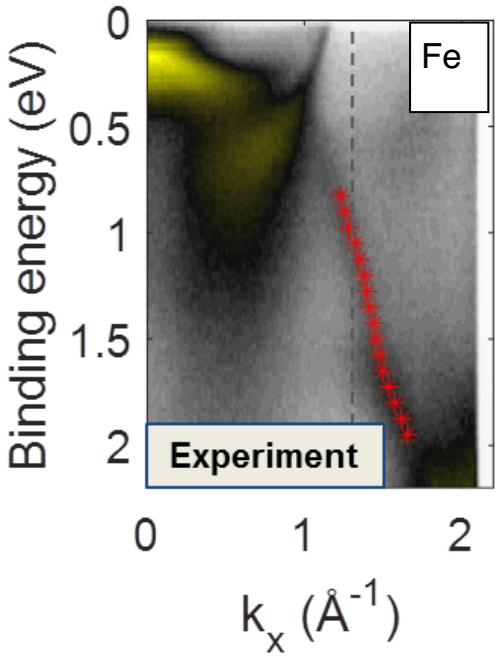


E. Mlynczak, L. Plucinski, unpublished

Anomalies in band dispersion of iron

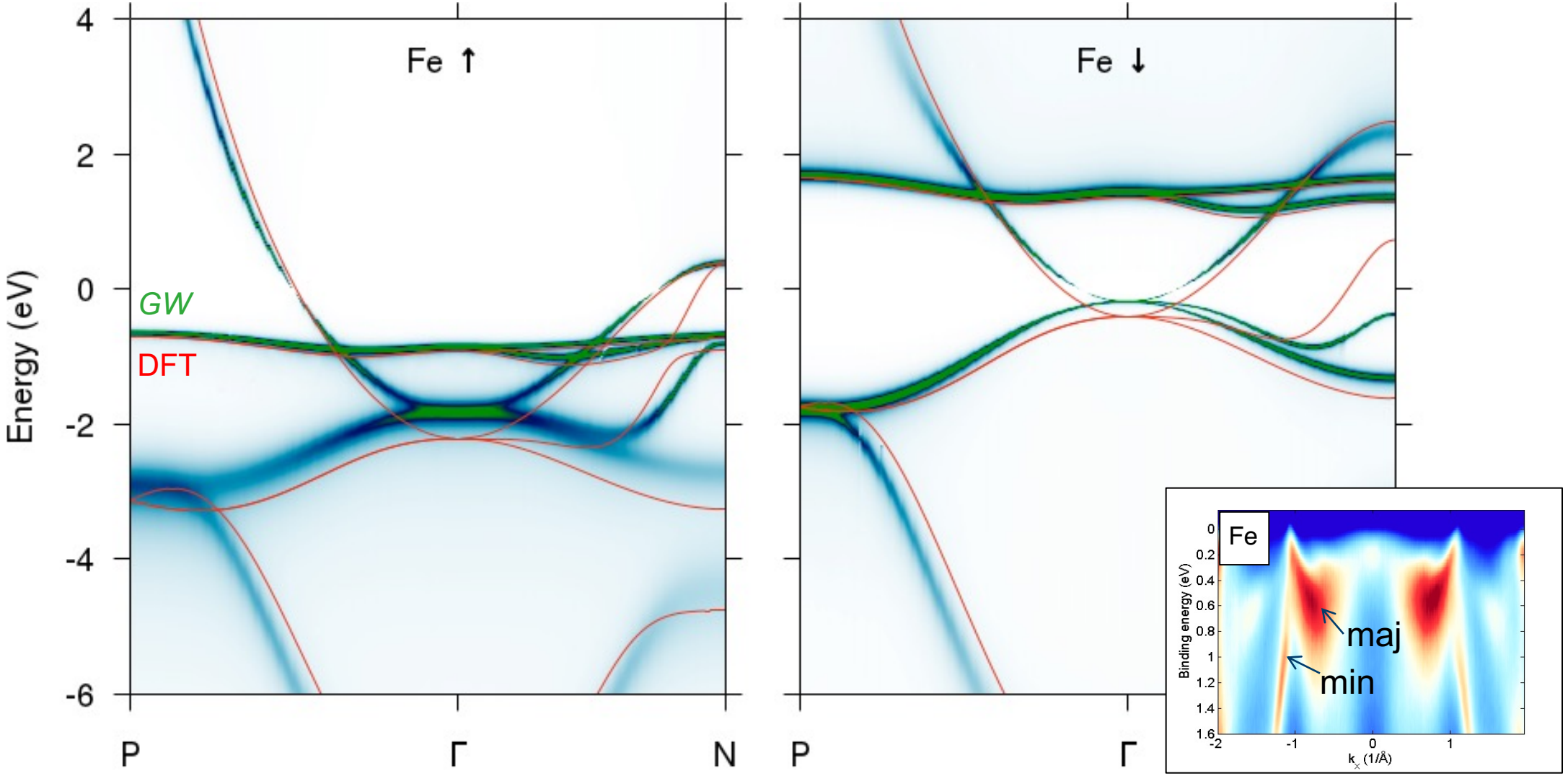


Schäfer *et al.*, PRL **92**, 097205 (2004)



E. Mlynczak *et al.*, Nature Communications 10, 505 (2019)

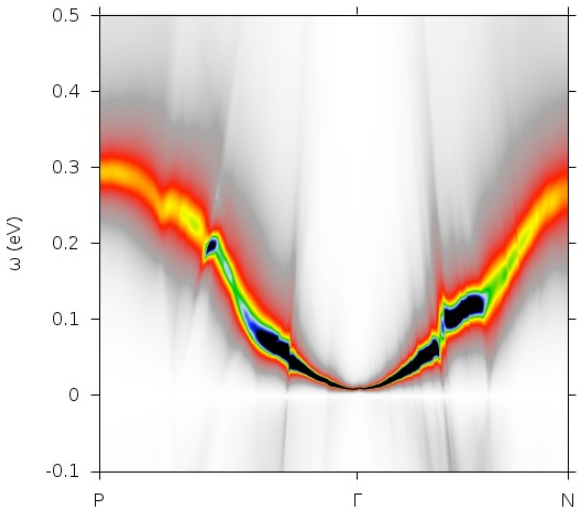
IRON *GW* CALCULATION

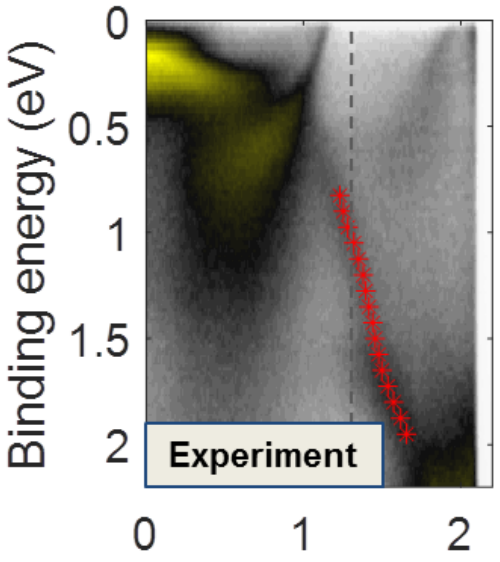


E. Mlynczak, L. Plucinski, unpublished

OVERVIEW

- Many-body spin excitations
  - Magnetic response function / *T* matrix
  - Bethe-Salpeter equation
  - Implementation (Wannier functions)
  - Examples
  - Goldstone violation
- Electron-magnon scattering
  - Iteration of Hedin equations (*GWT* self-energy)
  - Results for iron
    - comparison to DMFT and experiment
    - lifetime broadening, renormalizations, band anomalies
    - violation of causality (*GT*)
    - magnetic moments, *d*-band width, exchange splittings
- Conclusions





MAGNETIC RESPONSE FUNCTION

JÜLICH Forschungszentrum

Response of the magnetization (electronic) density with respect to changes of the external magnetic (electric) field:

Spin-orbit coupling neglected

$$R(\mathbf{r}t,\mathbf{r}'t') = \begin{pmatrix} \frac{\delta\sigma_x(\mathbf{r},t)}{\delta B_x(\mathbf{r}',t')} & \frac{\delta\sigma_x(\mathbf{r},t)}{\delta B_y(\mathbf{r}',t')} & 0 & 0 \\ \frac{\delta\sigma_y(\mathbf{r},t)}{\delta B_x(\mathbf{r}',t')} & \frac{\delta\sigma_y(\mathbf{r},t)}{\delta B_y(\mathbf{r}',t')} & 0 & 0 \\ 0 & 0 & \frac{\delta\sigma_z(\mathbf{r},t)}{\delta B_z(\mathbf{r}',t')} & \frac{\delta\sigma_z(\mathbf{r},t)}{\delta V(\mathbf{r}',t')} \\ 0 & 0 & \frac{\delta\rho(\mathbf{r},t)}{\delta B_z(\mathbf{r}',t')} & \frac{\delta\rho(\mathbf{r},t)}{\delta V(\mathbf{r}',t')} \end{pmatrix}$$

$$B_x, B_y \rightarrow B^+ = B_x + iB_y$$
$$B^- = B_x - iB_y$$

Circularly polarized *B* field

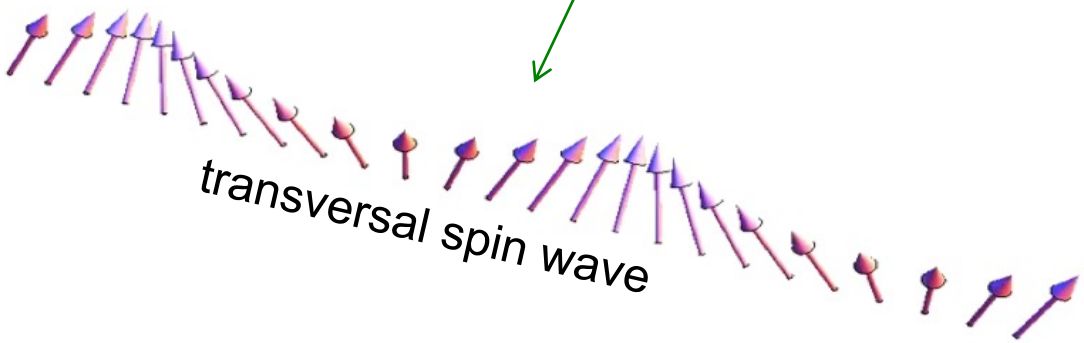
MAGNETIC RESPONSE FUNCTION

JÜLICH Forschungszentrum

Response of the magnetization (electronic) density with respect to changes of the external magnetic (electric) field:

Spin-orbit coupling neglected

$$R(\mathbf{r}t,\mathbf{r}'t') = \begin{pmatrix} \frac{\delta\sigma^+(\mathbf{r},t)}{\delta B^+(\mathbf{r}',t')} & 0 & 0 & 0 \\ 0 & \frac{\delta\sigma^-(\mathbf{r},t)}{\delta B^-(\mathbf{r}',t')} & 0 & 0 \\ 0 & 0 & \frac{\delta\sigma_z(\mathbf{r},t)}{\delta B_z(\mathbf{r}',t')} & \frac{\delta\sigma_z(\mathbf{r},t)}{\delta V(\mathbf{r}',t')} \\ 0 & 0 & \frac{\delta\rho(\mathbf{r},t)}{\delta B_z(\mathbf{r}',t')} & \frac{\delta\rho(\mathbf{r},t)}{\delta V(\mathbf{r}',t')} \end{pmatrix}$$



$$R^{+-}(\mathbf{r}t,\mathbf{r}'t') = \frac{\delta\sigma^+(\mathbf{r},t)}{\delta B^+(\mathbf{r}',t')}$$
$$= \langle\Psi_0|\mathcal{T}[\sigma^+(\mathbf{r},t)\sigma^-(\mathbf{r}',t')]|\Psi_0\rangle$$

MAGNETIC RESPONSE FUNCTION

$$R^{+-}(1,2) = \frac{\delta\sigma^{+}(1)}{\delta B^{+}(2)} \qquad \sigma^{+}(1) = -i\sum_{\alpha,\beta}\sigma^{+}_{\beta\alpha}G_{\alpha\beta}(1,1^{+})$$

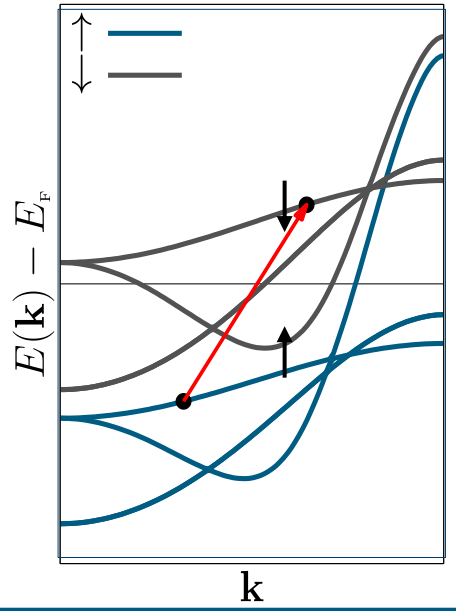
$$R = -i\frac{\delta G}{\delta B} = -i\frac{\delta}{\delta B}\left[G_0^{-1}-\Sigma\right]^{-1} = iGG\frac{\delta}{\delta B}\left[G_0^{-1}-\Sigma\right] = -iGG + GG\frac{\delta\Sigma}{\delta G}R$$

Dyson equation

Chain rule

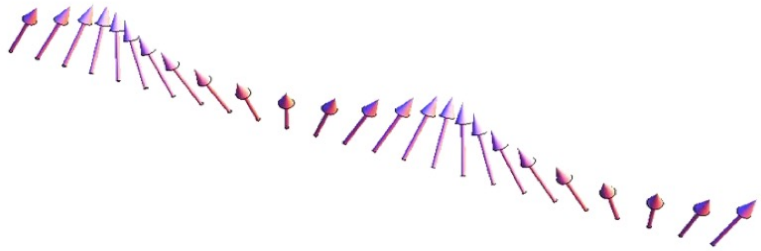
Stoner excitation

- Single particle
- Spin-flip
- Large energy scale (~eV)



Spin-wave excitation

- Collective excitation
- Small energy scale (~meV)



F. Aryasetiawan, K. Karlsson, PRB **60**, 7419 (1999)

BETHE-SALPETER EQUATION

Self-energy

$$\Sigma(12) = iG(12)W(1^+2)$$

$$\frac{\delta\Sigma}{\delta G} = iW + \cancel{iG\frac{\delta W}{\delta G}}$$

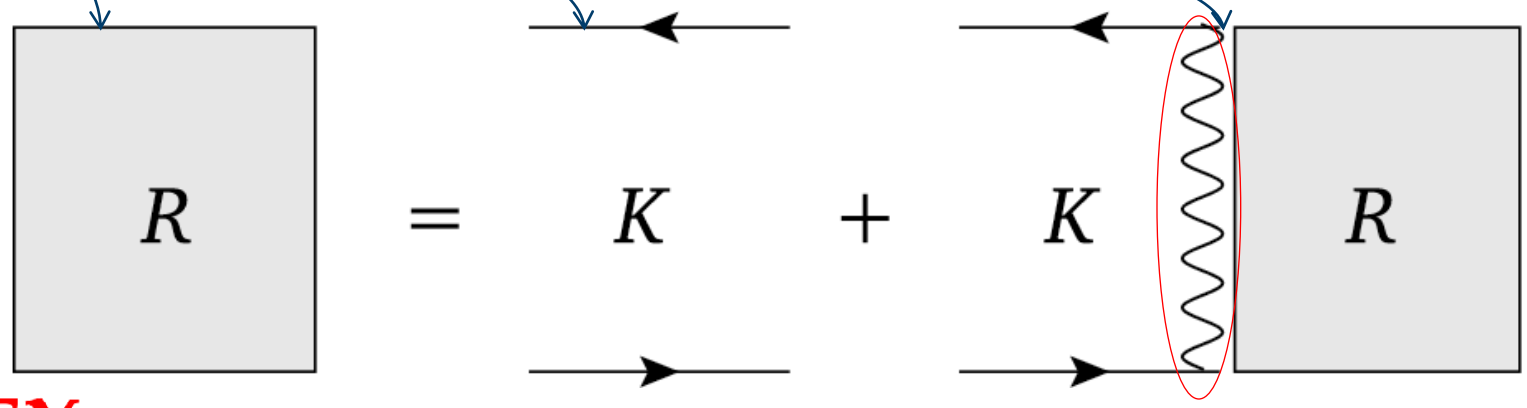
no SOC

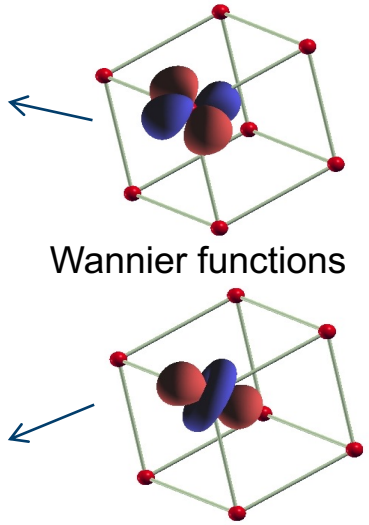
Bethe-Salpeter equation for spin excitations

$$R = K + KWR$$

Static approximation:

$$W(\omega) \to W(\omega = 0)$$





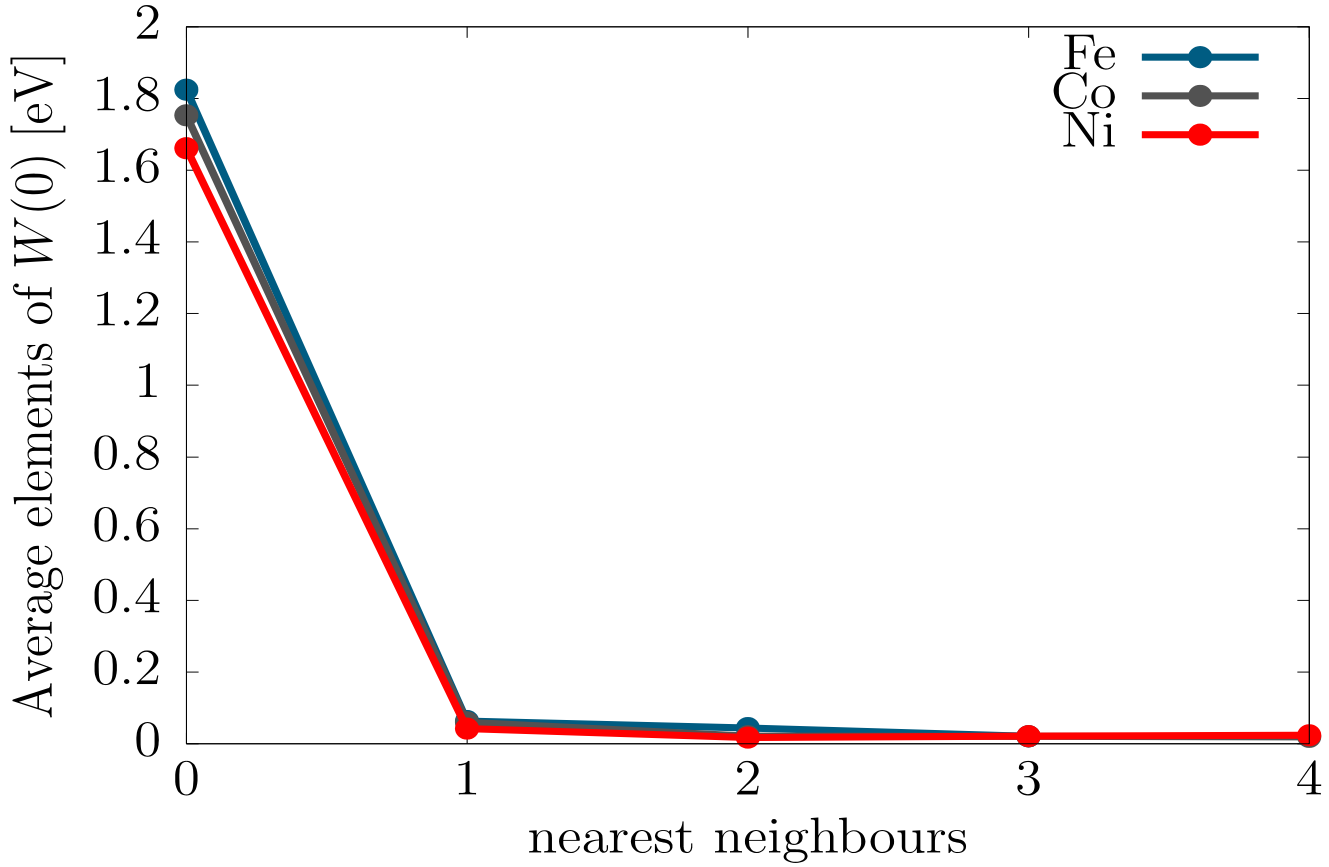
Wannier functions

onsite approximation

SPEX

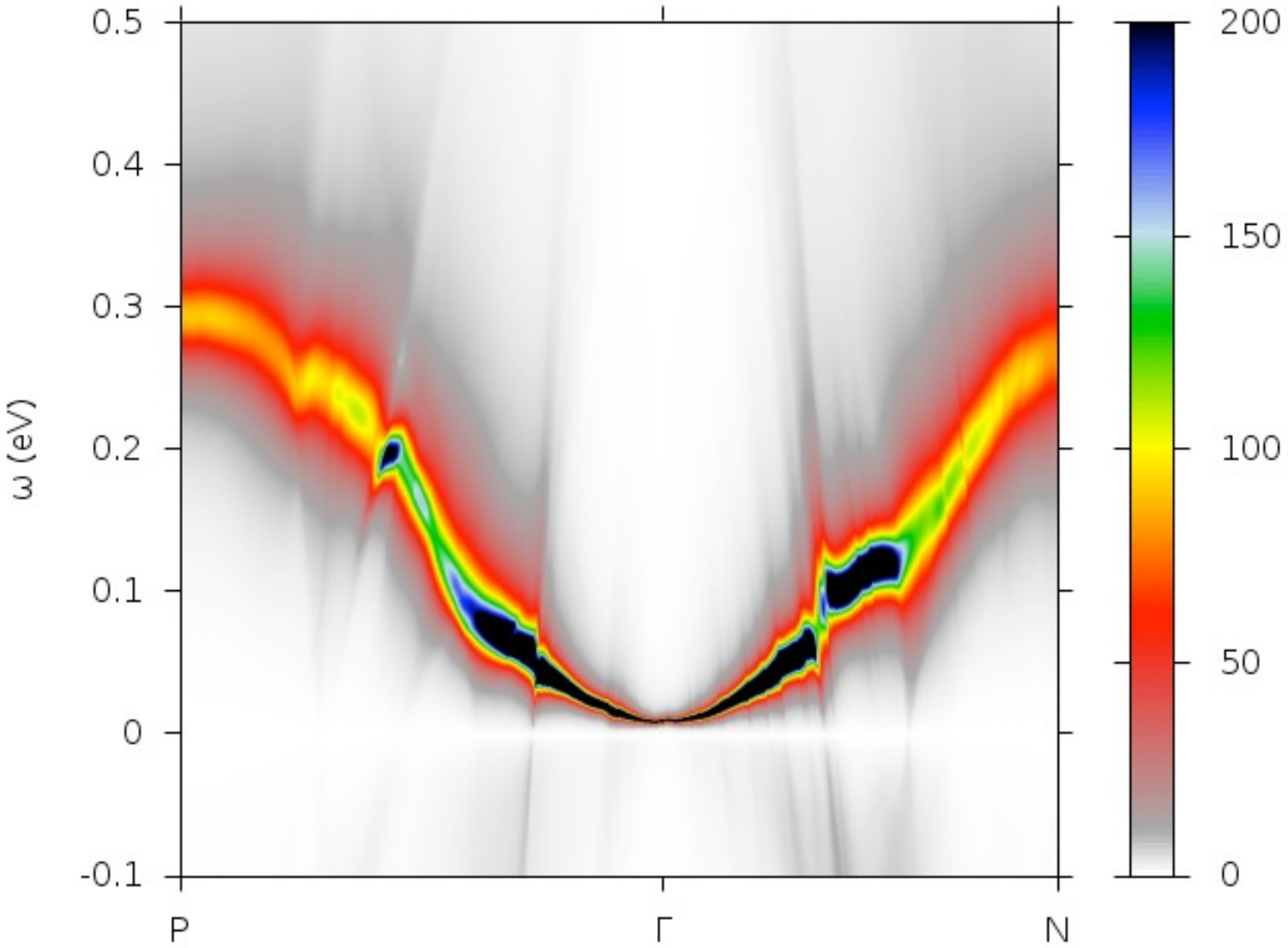
E. Sasioglu *et al.*, PRB **81**, 054434 (2010)

SPATIAL DEPENDENCE *W*

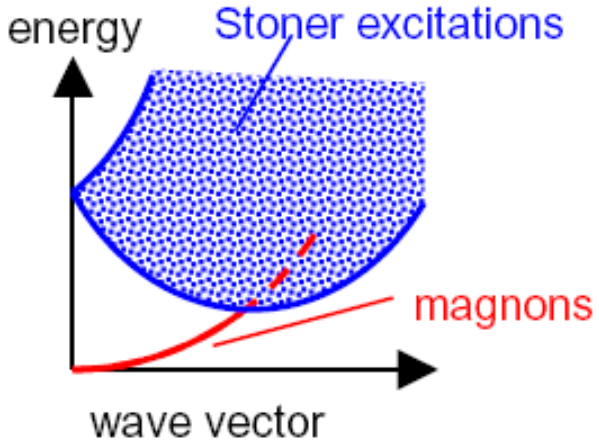


Largest contribution from the onsite interaction (~98%)

EXAMPLE: BCC IRON

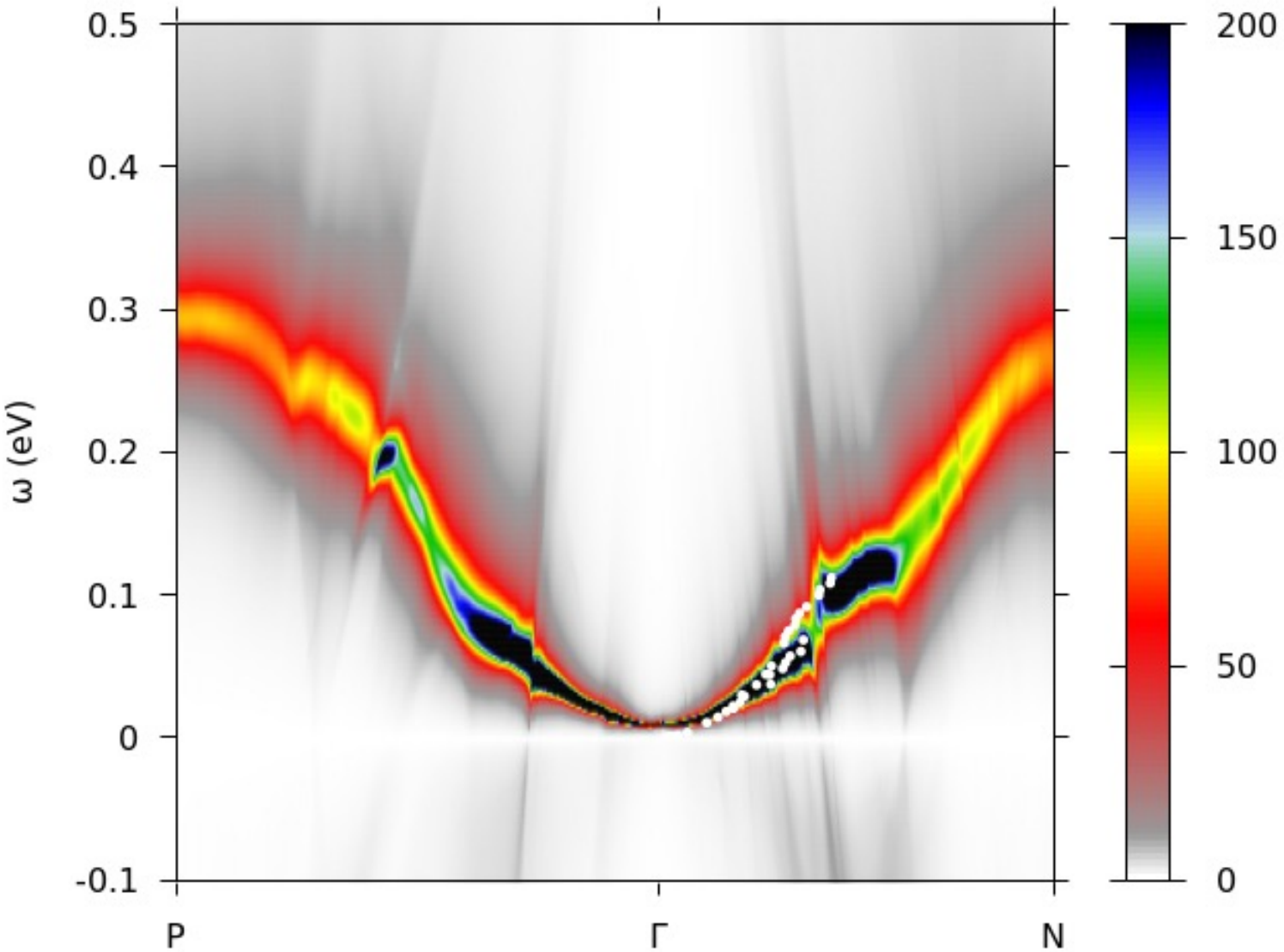


$$\mathrm{Im}\, R^{+-}(\mathbf{q}, \omega)$$

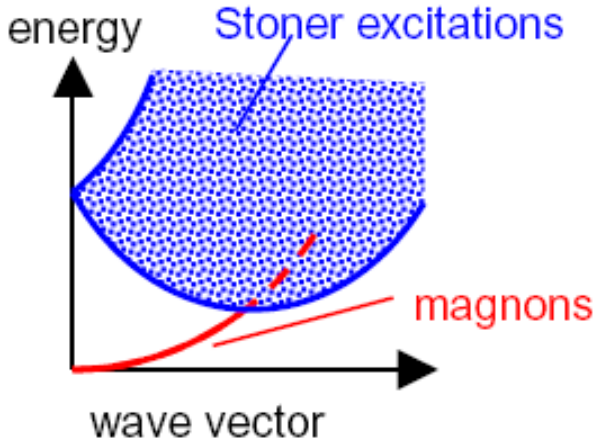


C. Friedrich, M.C.T.D. Müller, S. Blügel, "Handbook of Materials Modelling", Andreoni, Yip (eds), Springer (2019)

EXAMPLE: BCC IRON



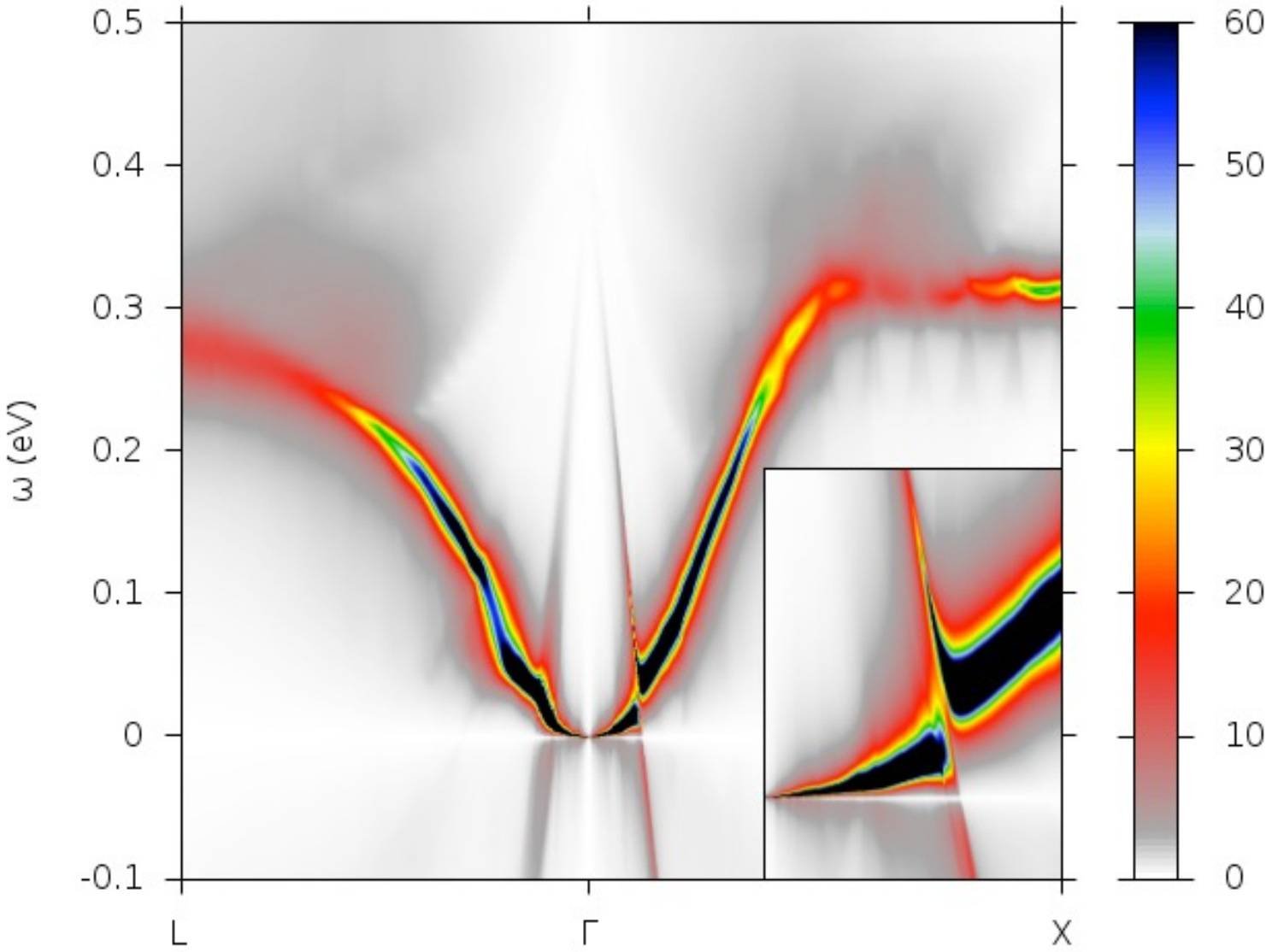
$$\mathrm{Im}\, R^{+-}(\mathbf{q}, \omega)$$

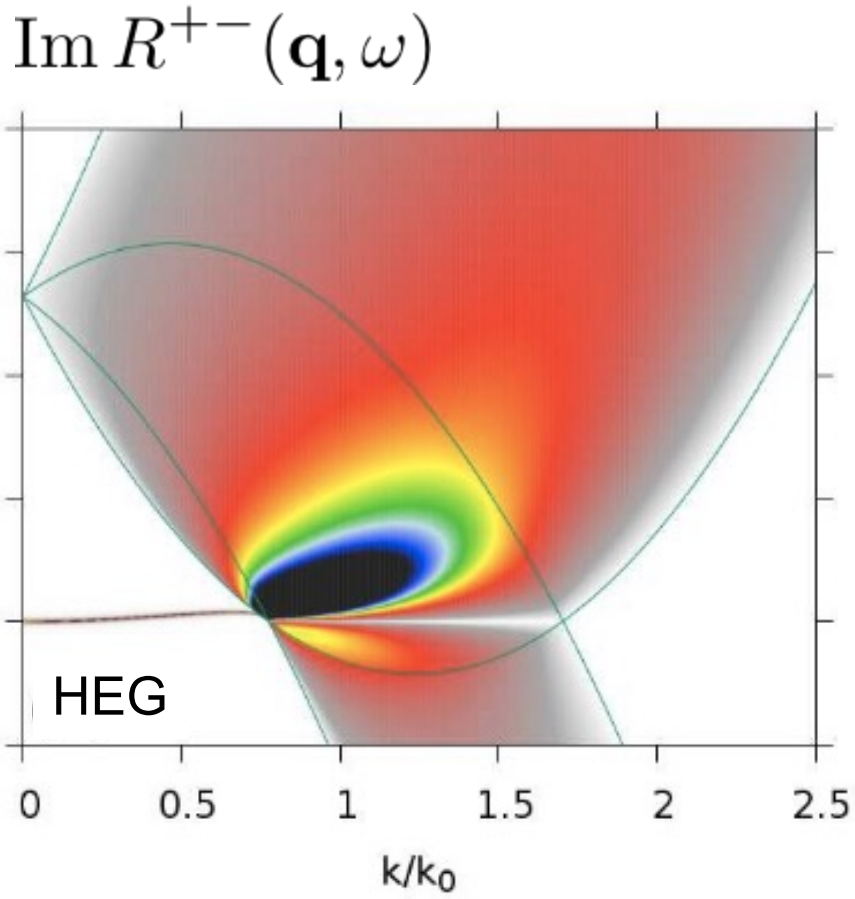


C. Friedrich, M.C.T.D. Müller, S. Blügel, "Handbook of Materials Modelling", Andreoni, Yip (eds), Springer (2019)

Experiments (white circles) Collins etal. PR 179, 417; Mook etal. PRB 7, 336

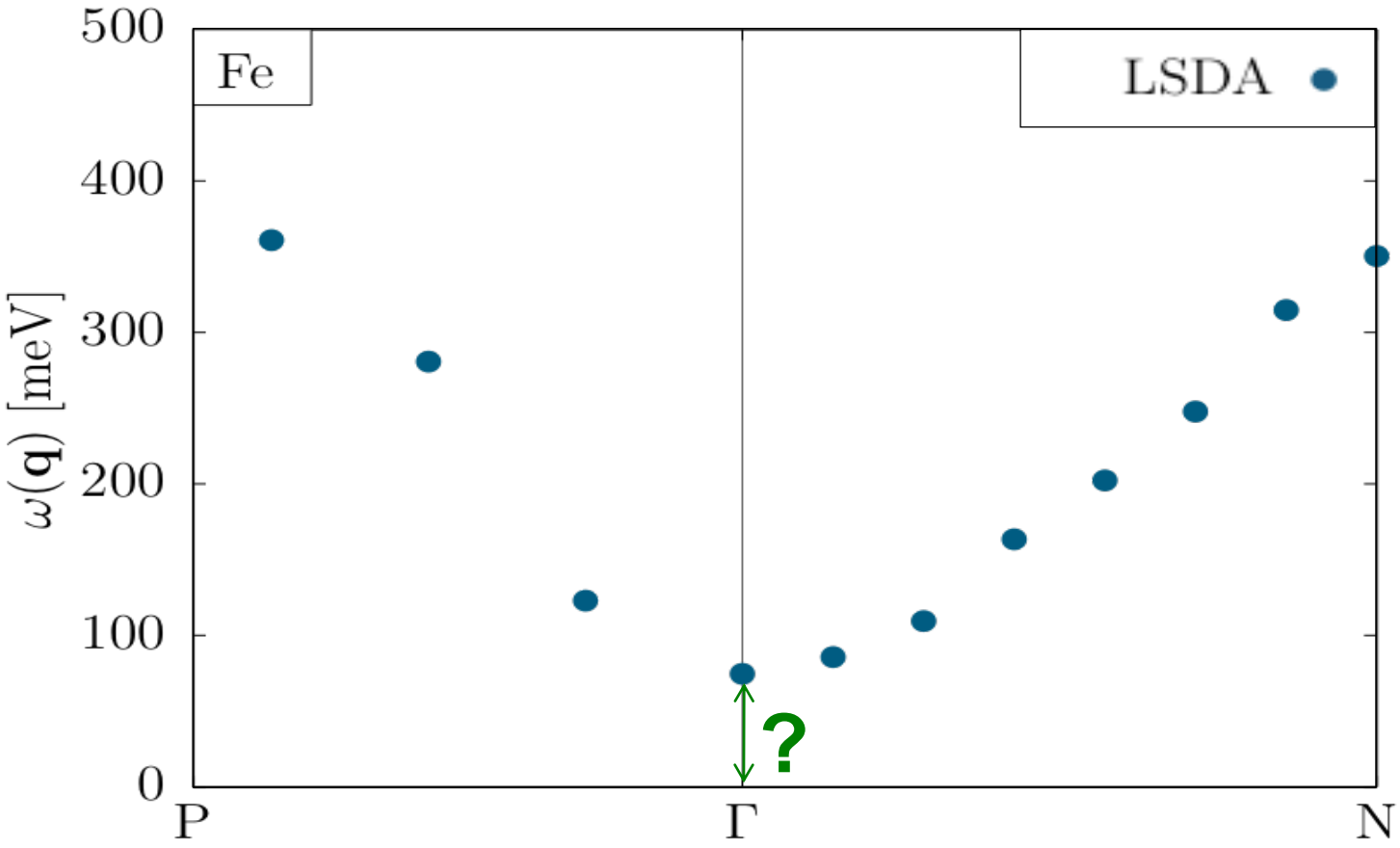
EXAMPLE: FCC NICKEL





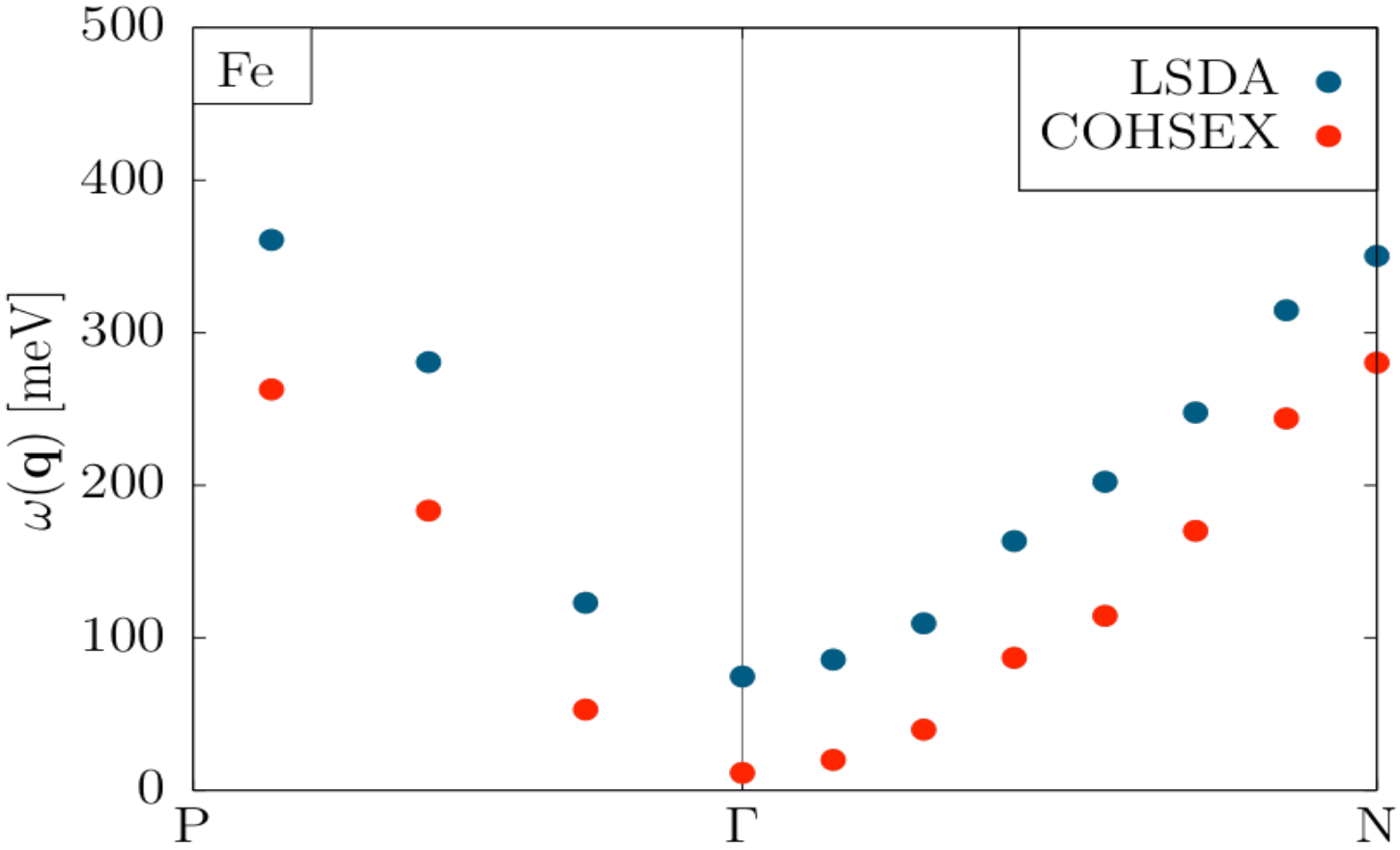
C. Friedrich, M.C.T.D. Müller, S. Blügel, "Handbook of Materials Modelling", Andreoni, Yip (eds), Springer (2019)

VIOLATION OF GOLDSTONE CONDITION



In the absence of spin-orbit coupling, the magnetization of a ferromagnet can be rotated without a cost of energy. ➔ $\lim_{q \to 0} \omega(\mathbf{q}) = 0$

VIOLATION OF GOLDSTONE CONDITION



M. Müller, C. Friedrich, S. Blügel, Phys. Rev. B **94**, 064433 (2016)

C. Friedrich, M.C.T.D. Müller, S. Blügel, "Handbook of Materials Modelling", Andreoni, Yip (eds), Springer (2019)

In the absence of spin-orbit coupling, the magnetization of a ferromagnet can be rotated without a cost of energy. ➔ $\lim_{q \to 0} \omega(\mathbf{q}) = 0$

GOLDSTONE CONDITION

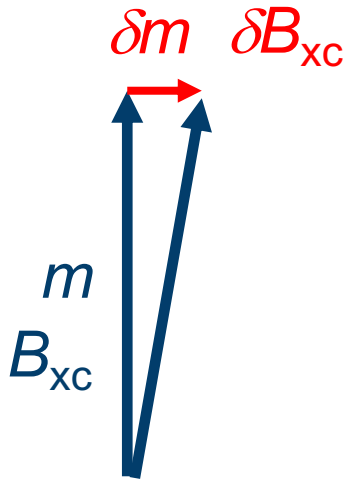
$$R = (1 - KW)^{-1} K = \frac{\delta m}{\delta B}$$

$$K^{-1}(1 - KW)\delta m = 0$$

$$K^{-1}(1 - KW)m = 0$$

$$\boxed{KWm = m}$$

Goldstone condition



$$K = \frac{\delta m}{\delta B_{\mathrm{xc}}}$$

$$K^{-1}\delta m = \delta B_{\mathrm{xc}}$$

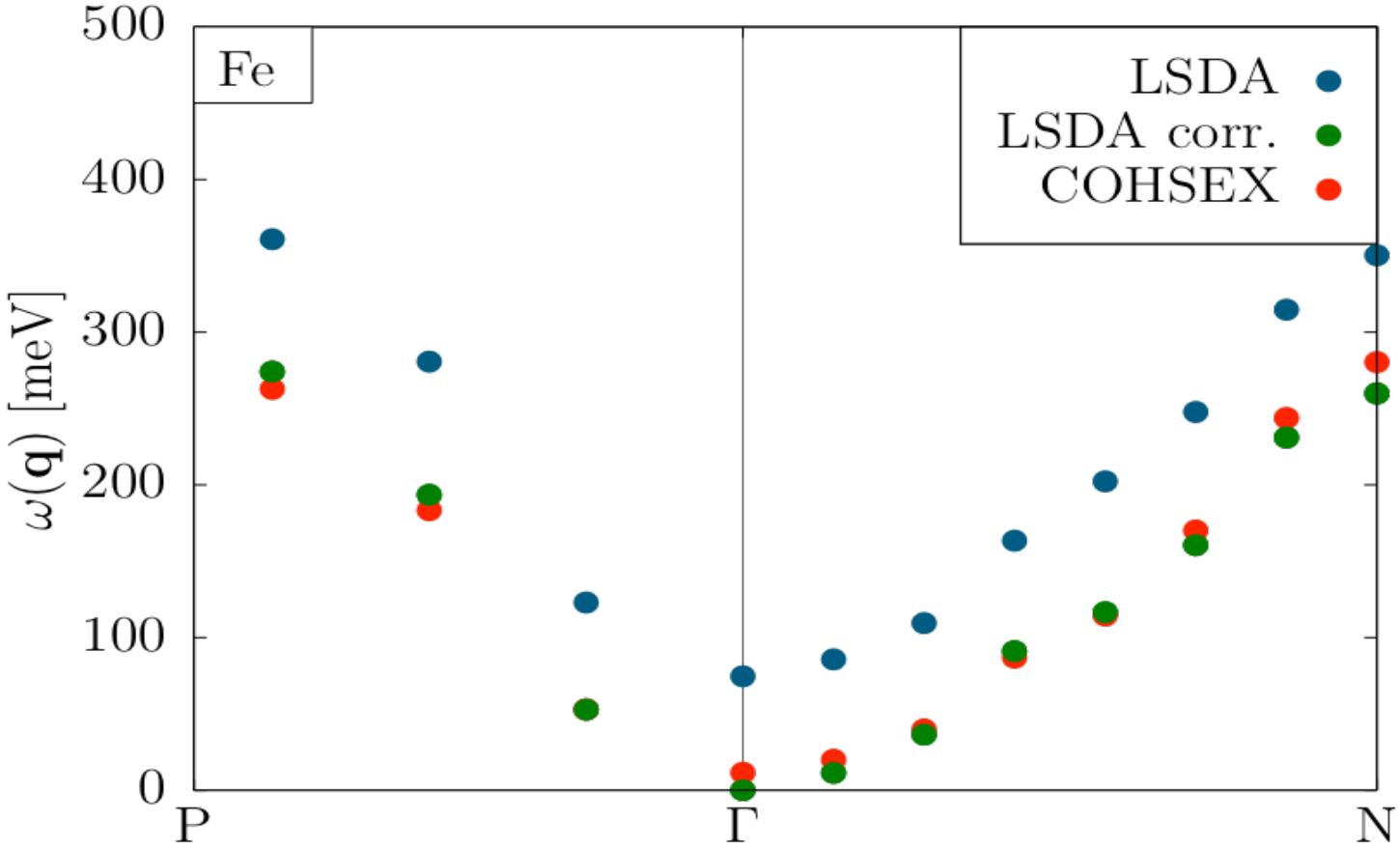
$$K^{-1}m = B_{\mathrm{xc}} = Wm$$

$$\boxed{\Delta_{\mathrm{x}} = Wm}$$

→ adjust exchange splitting Δ_x

$$\frac{\delta B_{\mathrm{xc}}}{B_{\mathrm{xc}}} = \frac{\delta m}{m}$$

VIOLATION OF GOLDSTONE CONDITION



M. Müller, C. Friedrich, S. Blügel, Phys. Rev. B **94**, 064433 (2016)

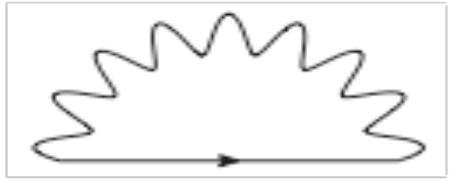
C. Friedrich, M.C.T.D. Müller, S. Blügel, "Handbook of Materials Modelling", Andreoni, Yip (eds), Springer (2019)

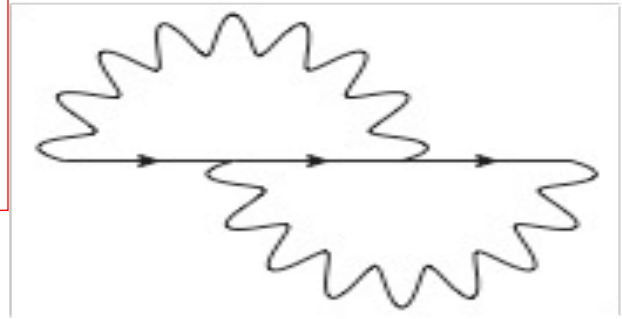
In the absence of spin-orbit coupling, the magnetization of a ferromagnet can be rotated without a cost of energy. ➔ $\lim_{q \to 0} \omega(\mathbf{q}) = 0$

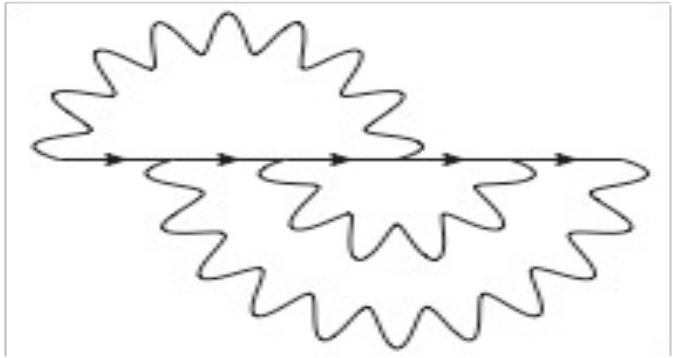
SELF-ENERGY (HEDIN EQUATIONS)

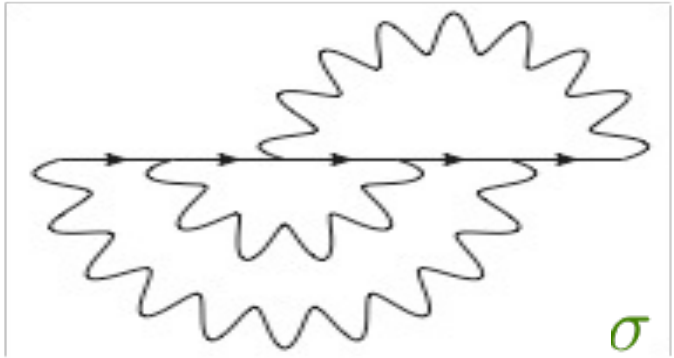
Diagrams up to third order in *W*:

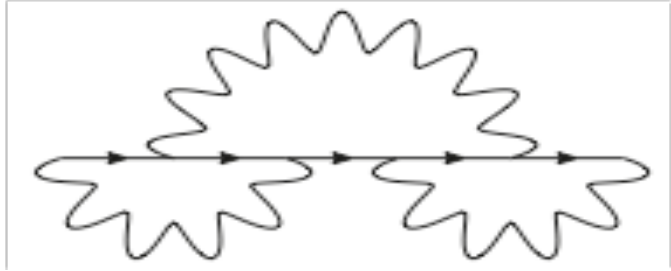
GW self-energy



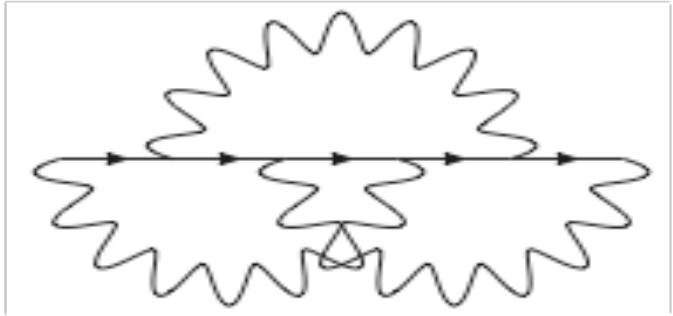


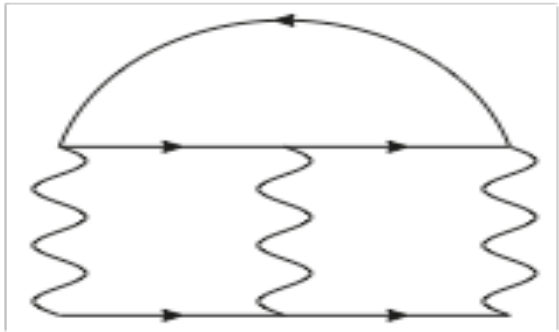




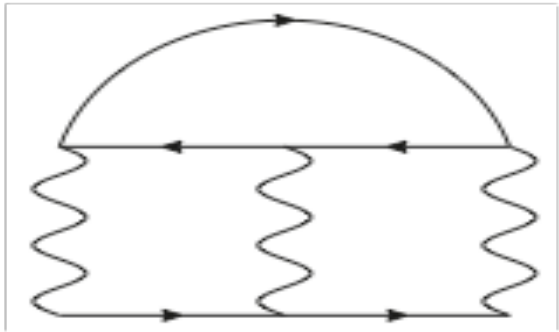


$\sigma \neq \sigma'$

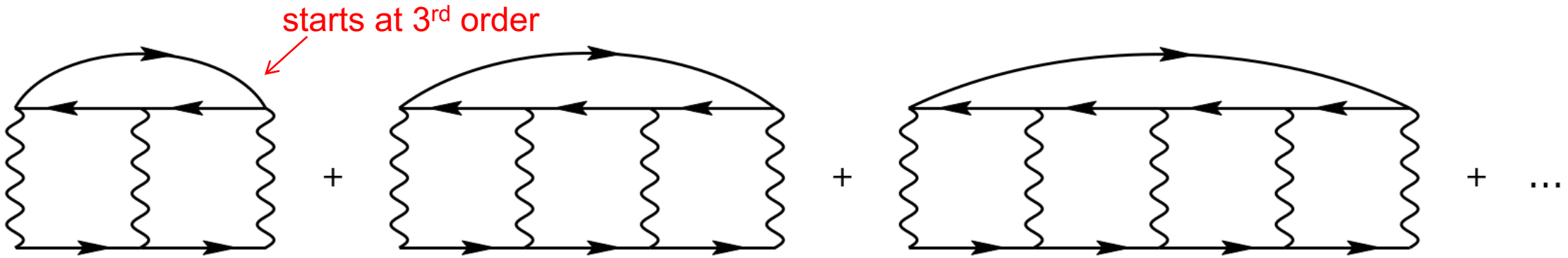




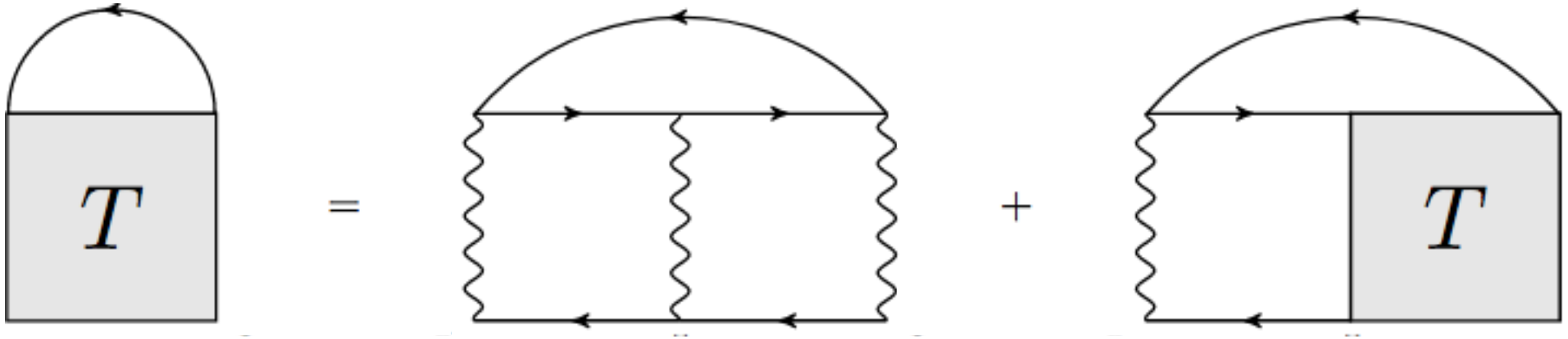
GT self-energy



GT SELF-ENERGY



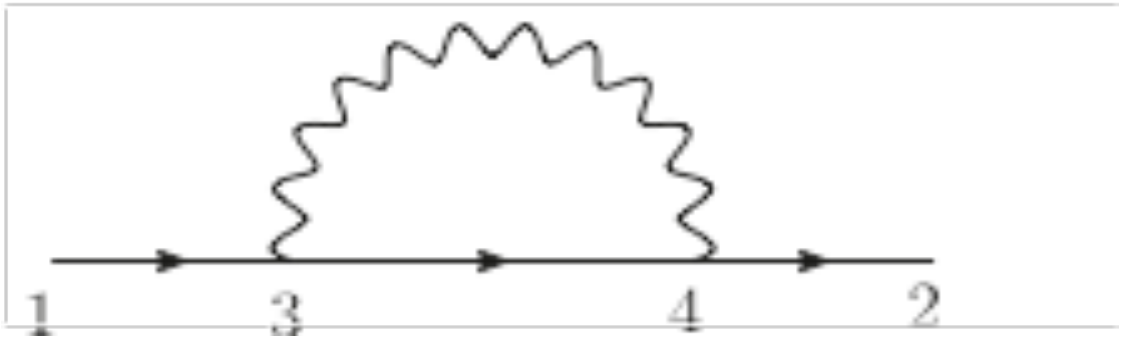
Bethe-Salpeter equation:



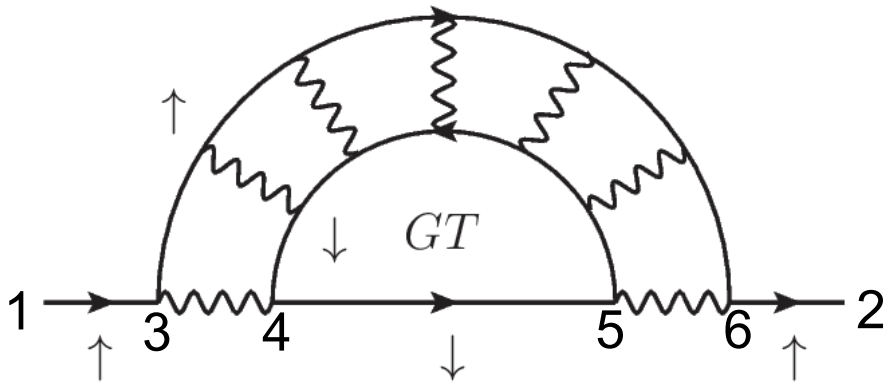
Springer, Aryasetiawan, Karlsson, Phys. Rev. Lett. **80**, 2389–2392 (1998): 6 eV satellite in Ni
Zhukov, Chulkov, Echenique, Phys. Rev. Lett. **93**, 096401 (2004): Lifetime effects in Ni and Fe
Romaniello, Bechstedt, Reining, Phys. Rev. B **85**, 155131 (2012): Diagrammatic expansion
Loos, Romaniello, J. Chem. Phys. **156**, 164101 (2022): pp channel (molecules)

INTERPRETATION

GW self-energy:

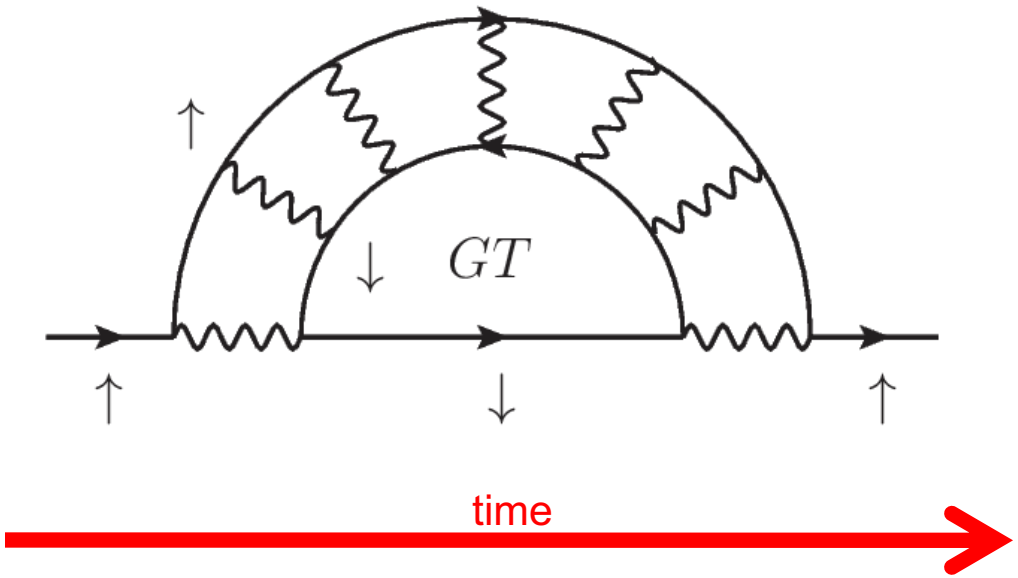


GT self-energy:

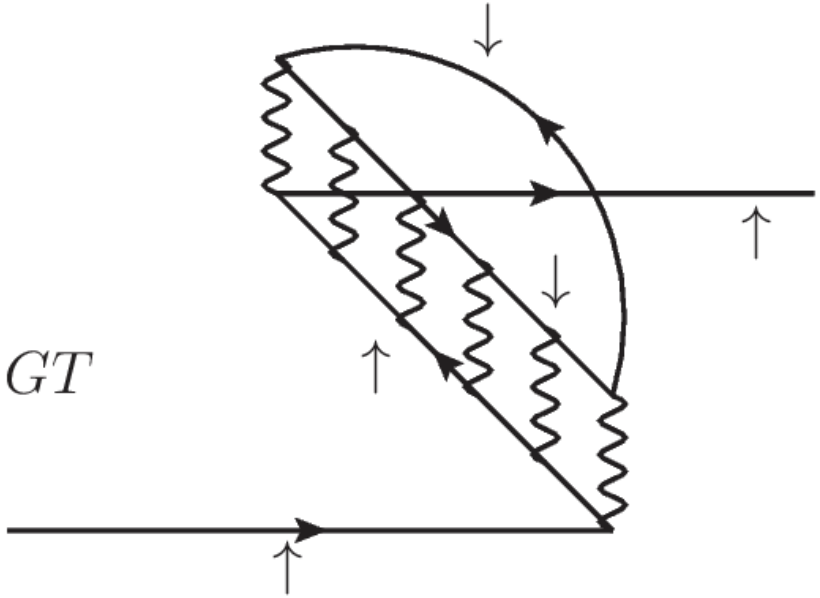


INTERPRETATION

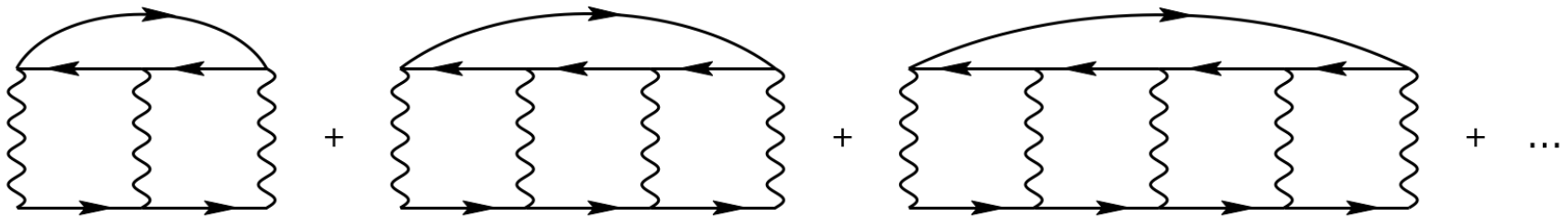
magnon is emitted
before absorbed

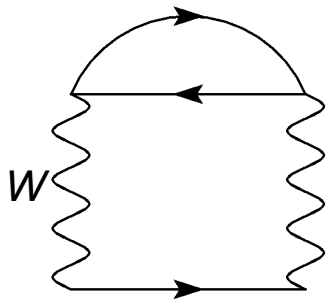


magnon is absorbed
before emitted?
electron travels back in time?

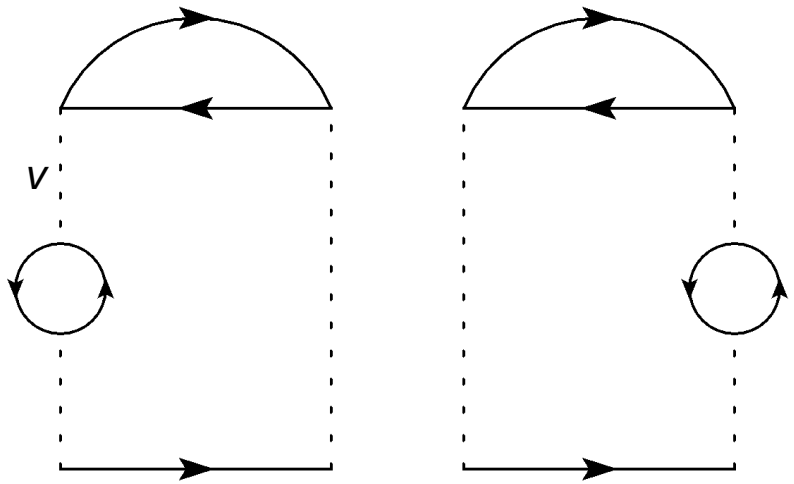


SELF-ENERGY





why not this diagram?



1. already contained in *GW* (sort of)
2. unphysical double counting in diagram

IMPLEMENTATION

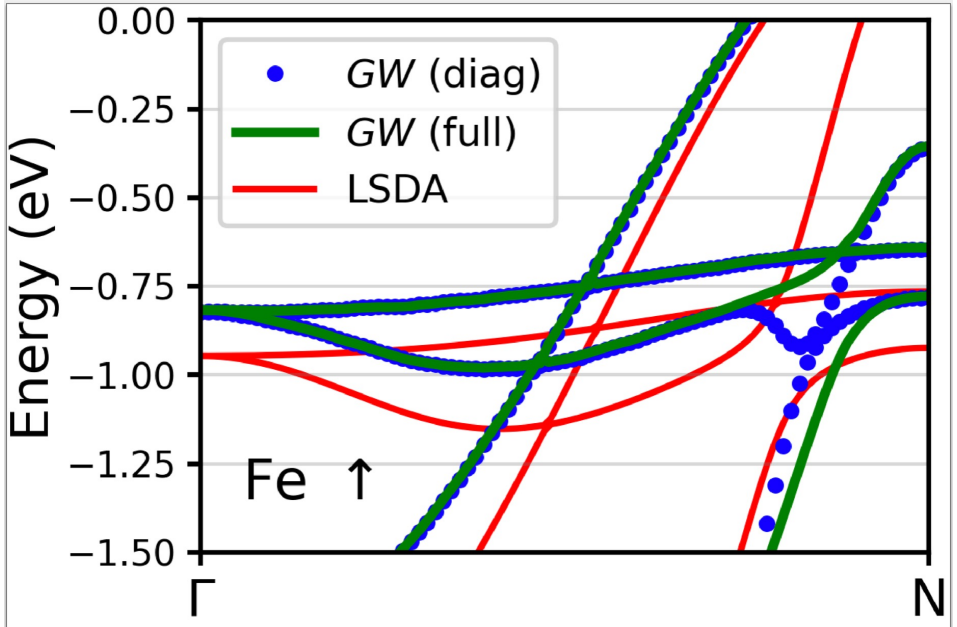
Dyson equation

$$G^\sigma(\mathbf{k},\omega) = G_0^\sigma(\mathbf{k},\omega) + G_0^\sigma(\mathbf{k},\omega)[\Sigma^\sigma(\mathbf{k},\omega) - v_{\mathrm{xc}}^\sigma(\mathbf{k})]G^\sigma(\mathbf{k},\omega)$$

Spectral function

$$A^\sigma(\mathbf{k},\omega) = \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}G(\mathbf{k},\omega)\right\}$$

$$= \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}[\omega I - H^\sigma(\mathbf{k}) - \Sigma^\sigma(\mathbf{k},\omega) + v_{\mathrm{xc}}^\sigma(\mathbf{k})]^{-1}\right\}$$



IMPLEMENTATION

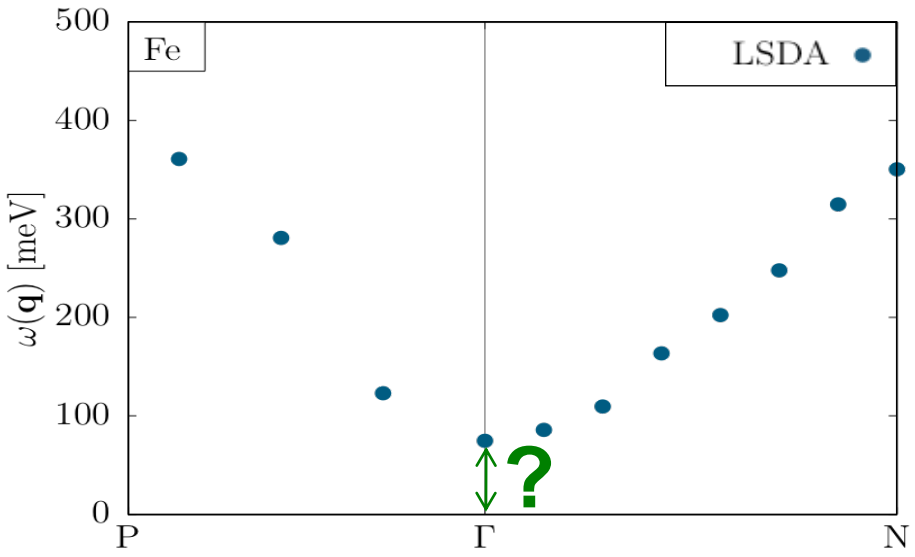
Dyson equation

$$G^\sigma(\mathbf{k},\omega) = G_0^\sigma(\mathbf{k},\omega) + G_0^\sigma(\mathbf{k},\omega)[\Sigma^\sigma(\mathbf{k},\omega) - v_{\mathrm{xc}}^\sigma(\mathbf{k})]G^\sigma(\mathbf{k},\omega)$$

Spectral function

$$A^\sigma(\mathbf{k},\omega) = \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}G(\mathbf{k},\omega)\right\}$$

$$= \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}[\omega I - H^\sigma(\mathbf{k}) - \Sigma^\sigma(\mathbf{k},\omega) + v_{\mathrm{xc}}^\sigma(\mathbf{k})]^{-1}\right\}$$



M. Müller, C. Friedrich, S. Blügel, Phys. Rev. B **94**, 064433 (2016)

C. Friedrich, M.C.T.D. Müller, S. Blügel,
"Handbook of Materials Modelling",
Andreoni, Yip (eds), Springer (2019)

IMPLEMENTATION

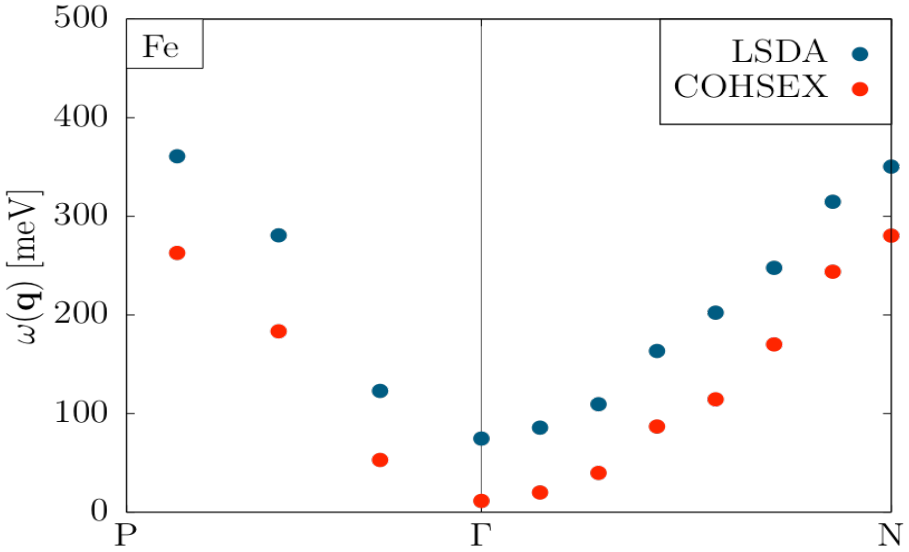
Dyson equation

$$G^\sigma(\mathbf{k},\omega) = G_0^\sigma(\mathbf{k},\omega) + G_0^\sigma(\mathbf{k},\omega)[\Sigma^\sigma(\mathbf{k},\omega) - v_{\mathrm{xc}}^\sigma(\mathbf{k})]G^\sigma(\mathbf{k},\omega)$$

Spectral function

$$A^\sigma(\mathbf{k},\omega) = \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}G(\mathbf{k},\omega)\right\}$$

$$= \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}[\omega I - H^\sigma(\mathbf{k}) - \Sigma^\sigma(\mathbf{k},\omega) + v_{\mathrm{xc}}^\sigma(\mathbf{k})]^{-1}\right\}$$



M. Müller, C. Friedrich, S. Blügel, Phys. Rev. B **94**, 064433 (2016)

C. Friedrich, M.C.T.D. Müller, S. Blügel,
"Handbook of Materials Modelling",
Andreoni, Yip (eds), Springer (2019)

IMPLEMENTATION

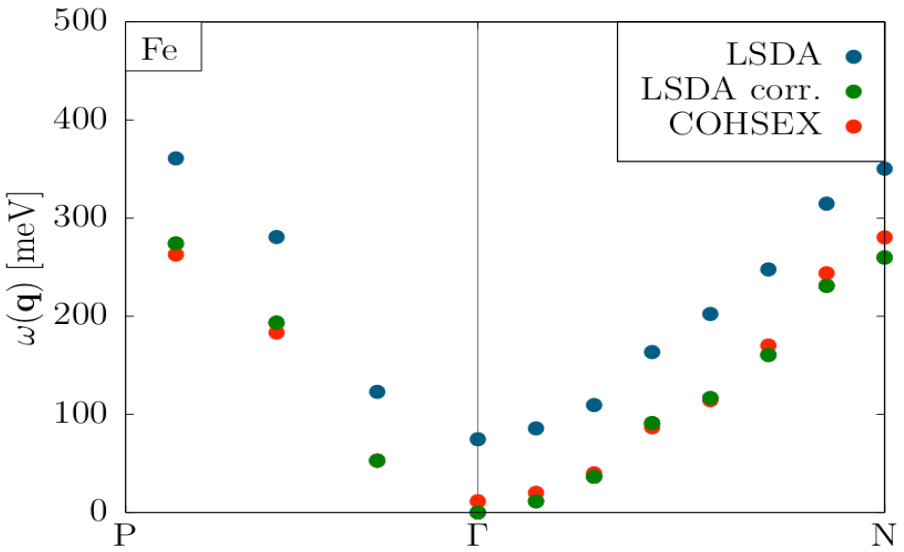
Dyson equation

$$G^\sigma(\mathbf{k},\omega) = G_0^\sigma(\mathbf{k},\omega) + G_0^\sigma(\mathbf{k},\omega)[\Sigma^\sigma(\mathbf{k},\omega) - v_{\mathrm{xc}}^\sigma(\mathbf{k})]G^\sigma(\mathbf{k},\omega)$$

Spectral function

$$A^\sigma(\mathbf{k},\omega) = \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}G(\mathbf{k},\omega)\right\}$$

$$= \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}[\omega I - H^\sigma(\mathbf{k}) - \Sigma^\sigma(\mathbf{k},\omega) + v_{\mathrm{xc}}^\sigma(\mathbf{k})]^{-1}\right\}$$



M. Müller, C. Friedrich, S. Blügel, Phys. Rev. B **94**, 064433 (2016)

C. Friedrich, M.C.T.D. Müller, S. Blügel,
"Handbook of Materials Modelling",
Andreoni, Yip (eds), Springer (2019)

IMPLEMENTATION

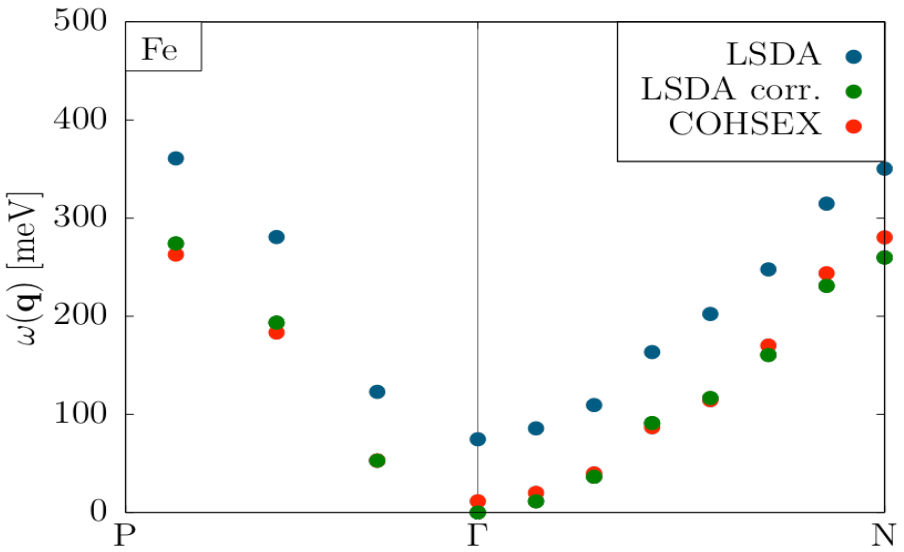
Dyson equation

$$G^\sigma(\mathbf{k},\omega) = G_0^\sigma(\mathbf{k},\omega) + G_0^\sigma(\mathbf{k},\omega)[\Sigma^\sigma(\mathbf{k},\omega) - v_{\mathrm{xc}}^\sigma(\mathbf{k})]G^\sigma(\mathbf{k},\omega)$$

Spectral function

$$A^\sigma(\mathbf{k},\omega) = \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}G(\mathbf{k},\omega)\right\}$$

$$= \frac{1}{\pi}\mathrm{sgn}(\epsilon_F - \omega)\mathrm{Im}\left\{\mathrm{tr}[\omega I - H^\sigma(\mathbf{k}) - \Sigma^\sigma(\mathbf{k},\omega) + v_{\mathrm{xc}}^\sigma(\mathbf{k})]^{-1}\right\}$$



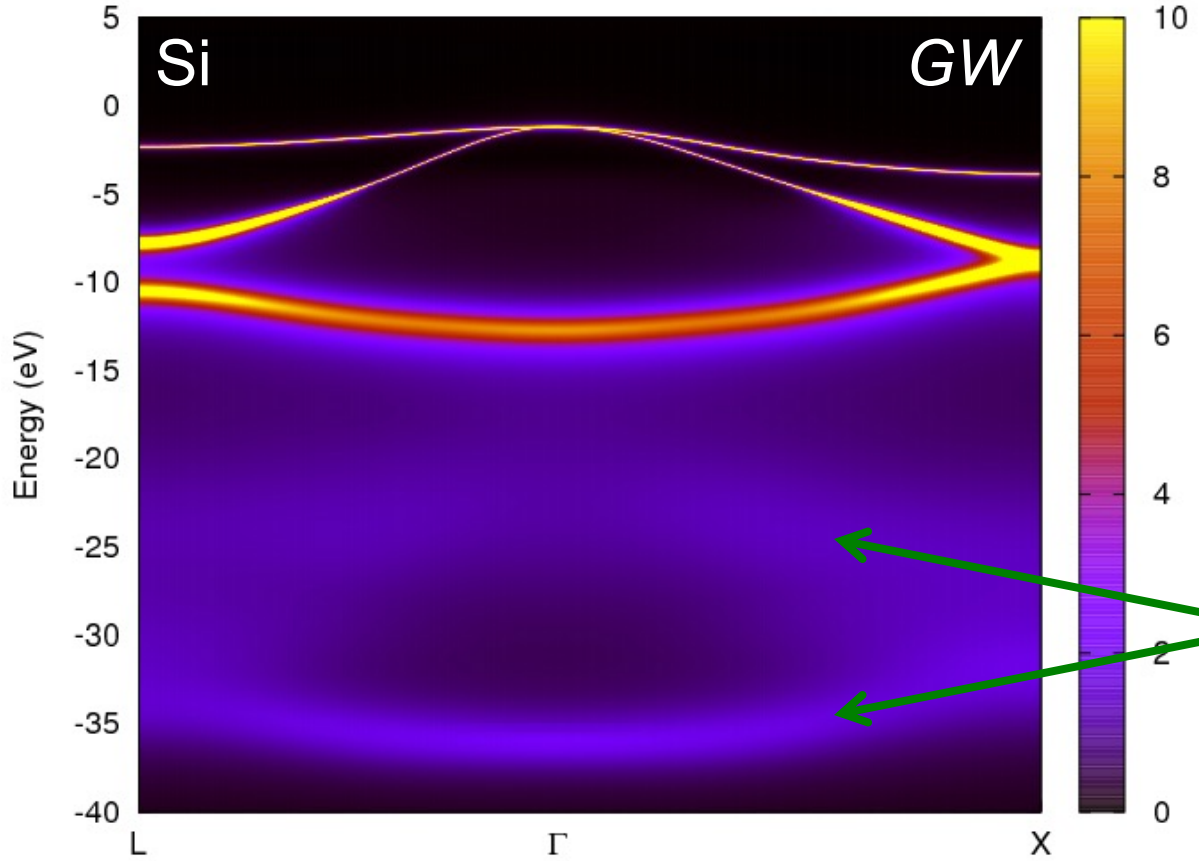
$$\omega \pm \frac{\Delta_{\mathrm{x}}}{2}$$

- to enforce Goldstone condition
- self-consistency condition
- $\Delta_{\mathrm{x}} = 0.23\,\mathrm{eV}$

$$\omega - \Delta_v$$

- self-consistency condition
- $\Delta_v = 0.96\,\mathrm{eV}$

SATELLITES



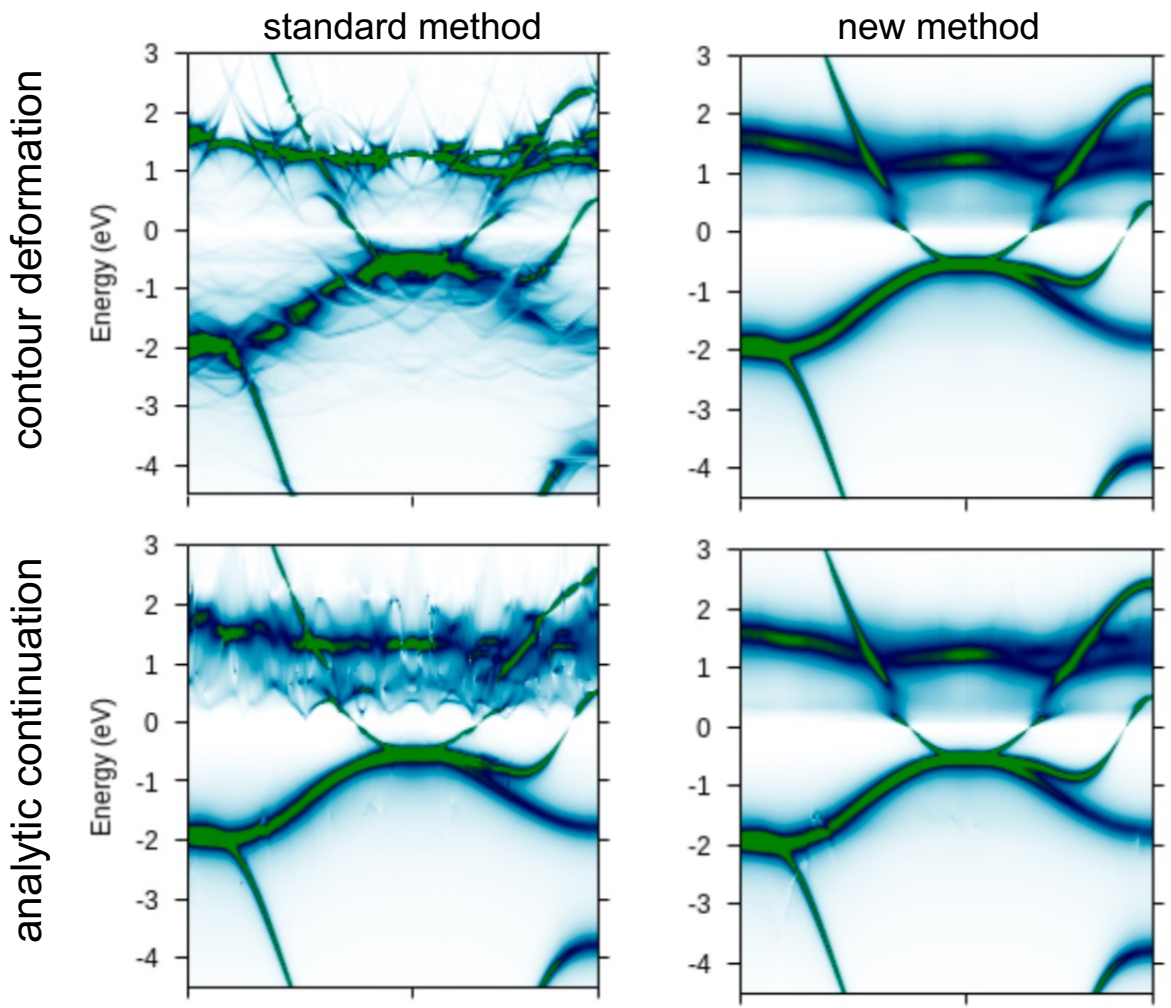
Spectral function

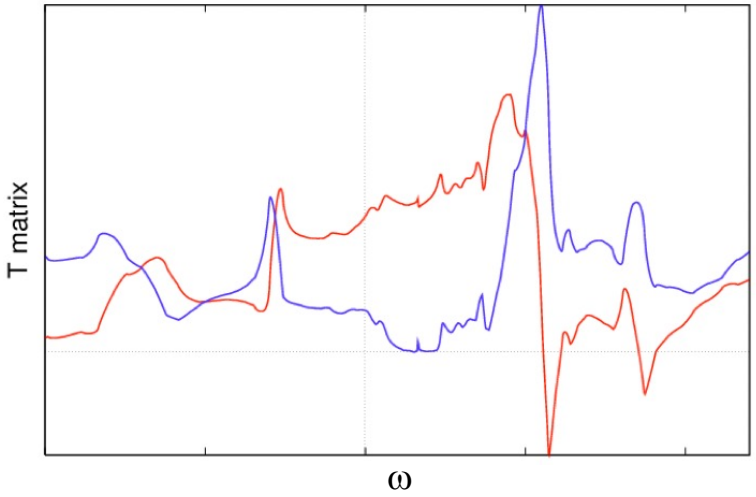
Plasmon satellites
$\omega_0 \approx 23$ eV

Magnon satellites?
$\omega_0 \sim 0\text{-}0.3$ eV

TETRAHEDRON METHOD FOR HIGHLY NONLINEAR FUNCTIONS

$$\Sigma(\omega) = \int_{\epsilon_{\mathbf{k}} < \epsilon_F} T_{\mathbf{k}}(\omega - \epsilon_{\mathbf{k}})\, d^3k$$

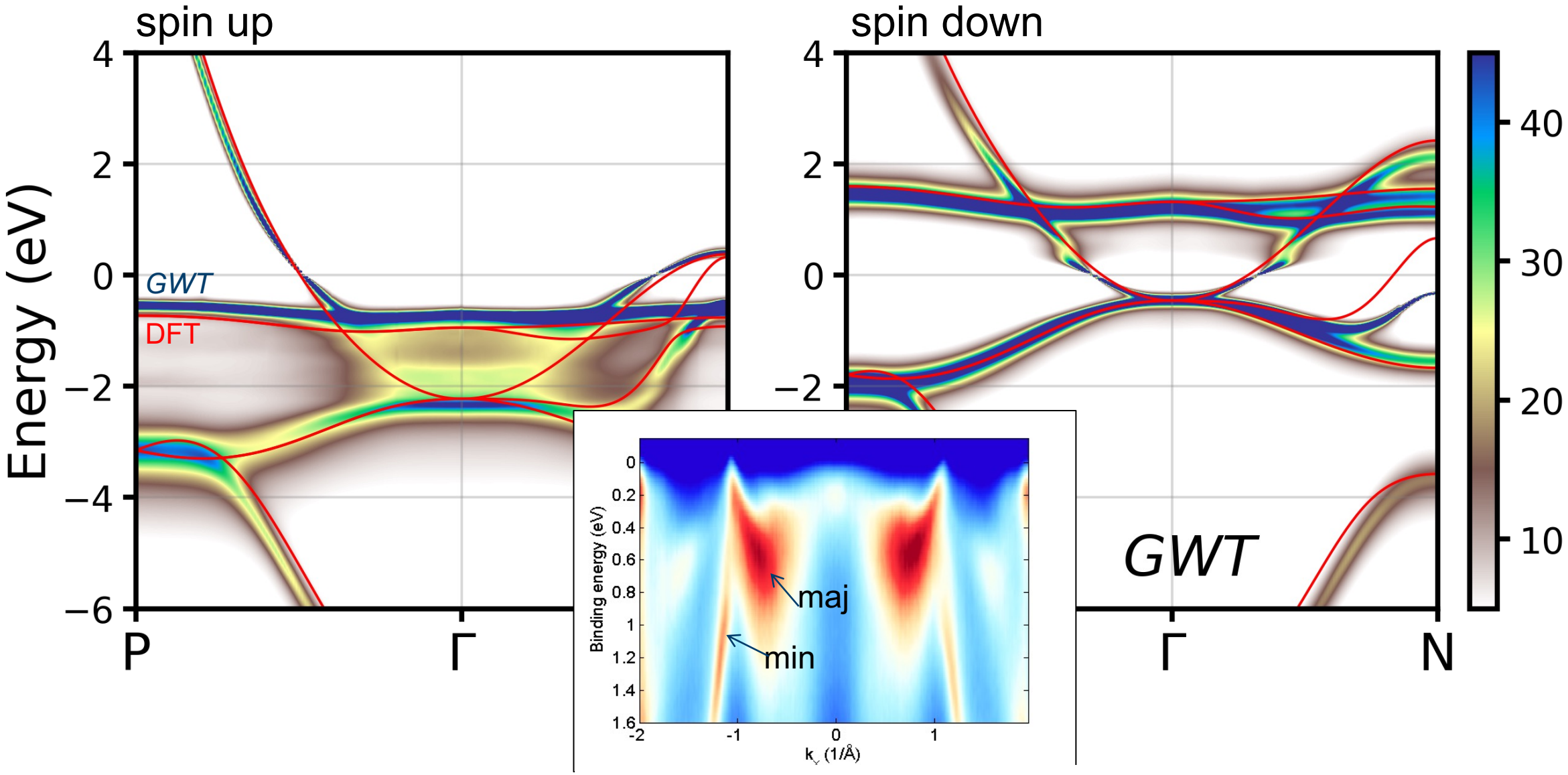




Fe, spin down (P-Γ-N), 5x5x5

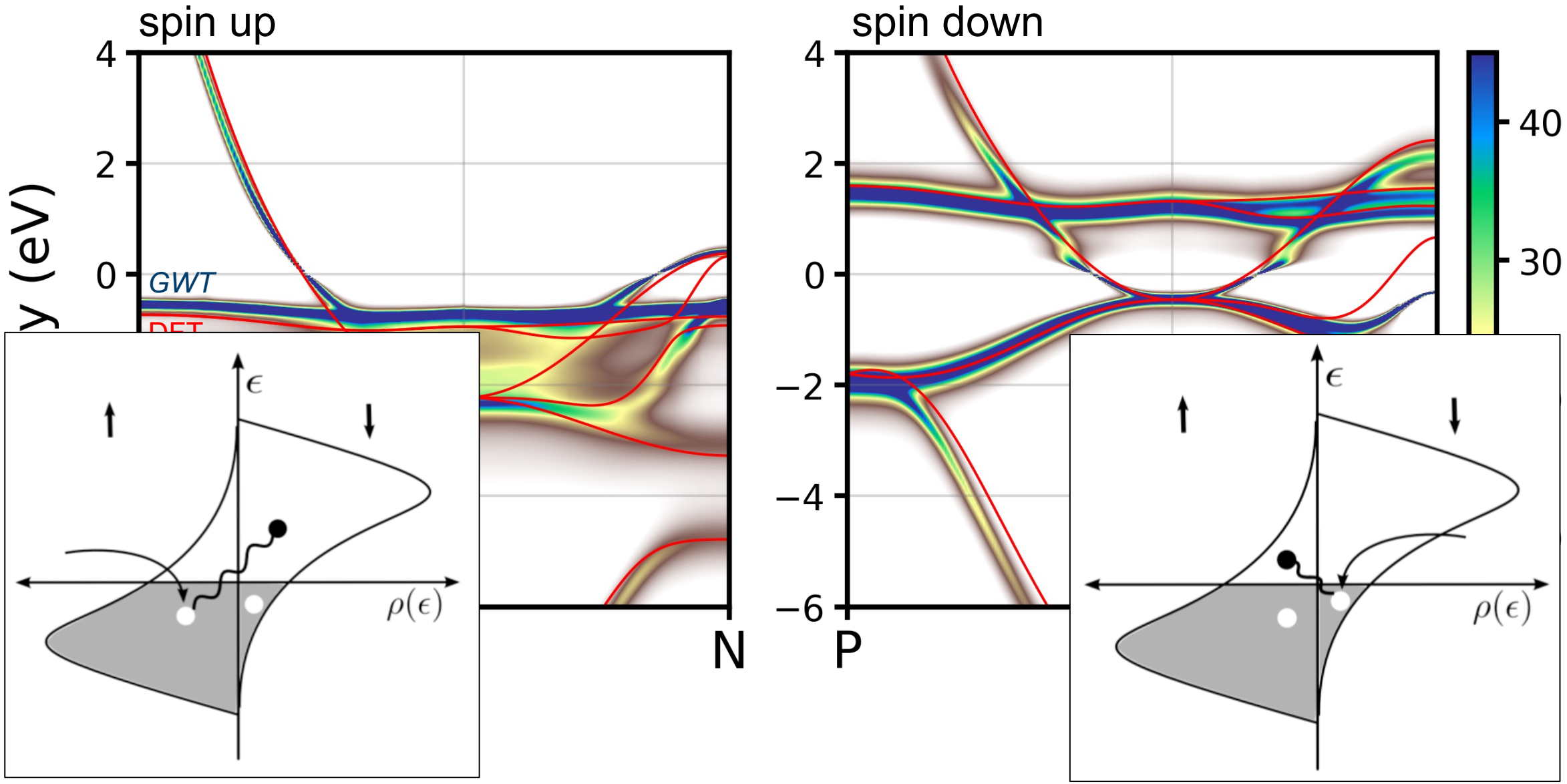
Friedrich, PRB 100, 075142 (2019)

IRON BAND STRUCTURE (*GWT*)

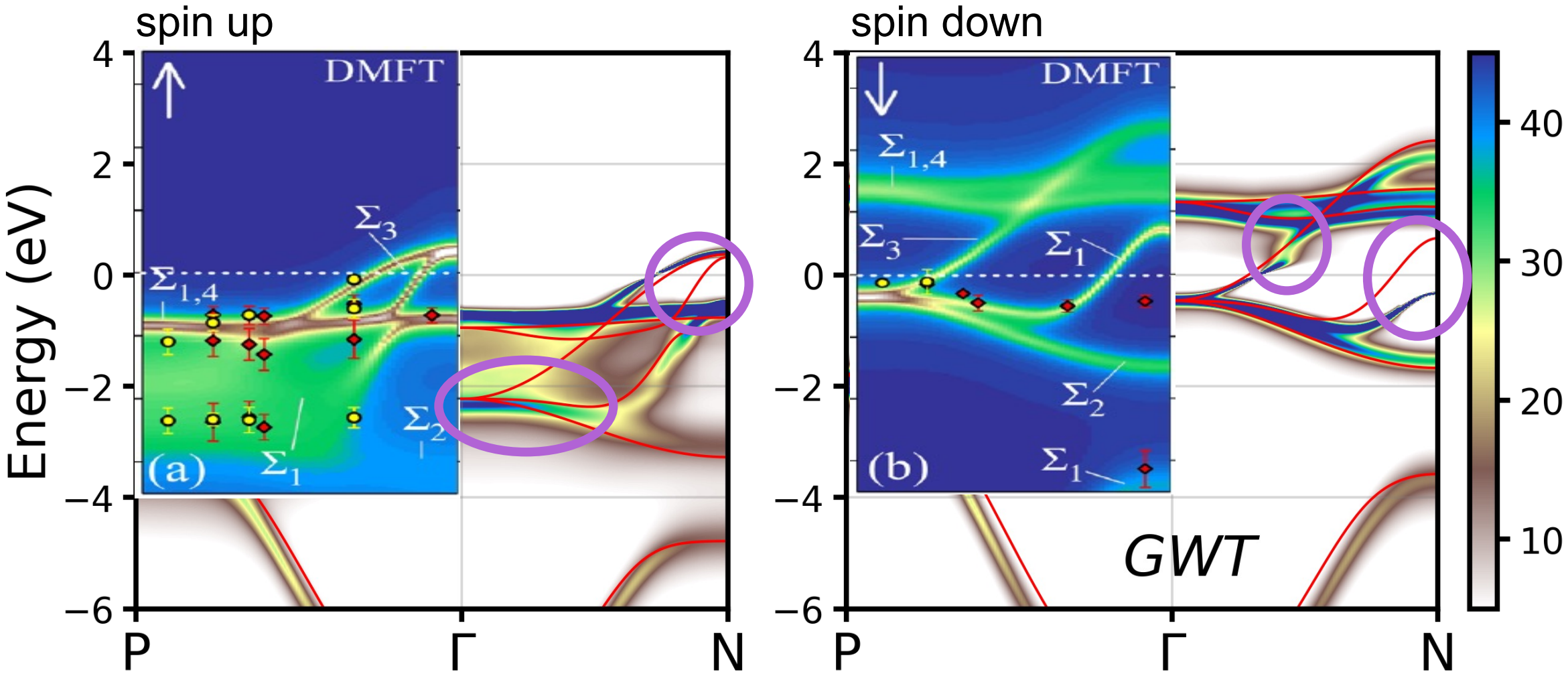


E. Mlynczak, L. Plucinski, unpublished

IRON BAND STRUCTURE (*GWT*)

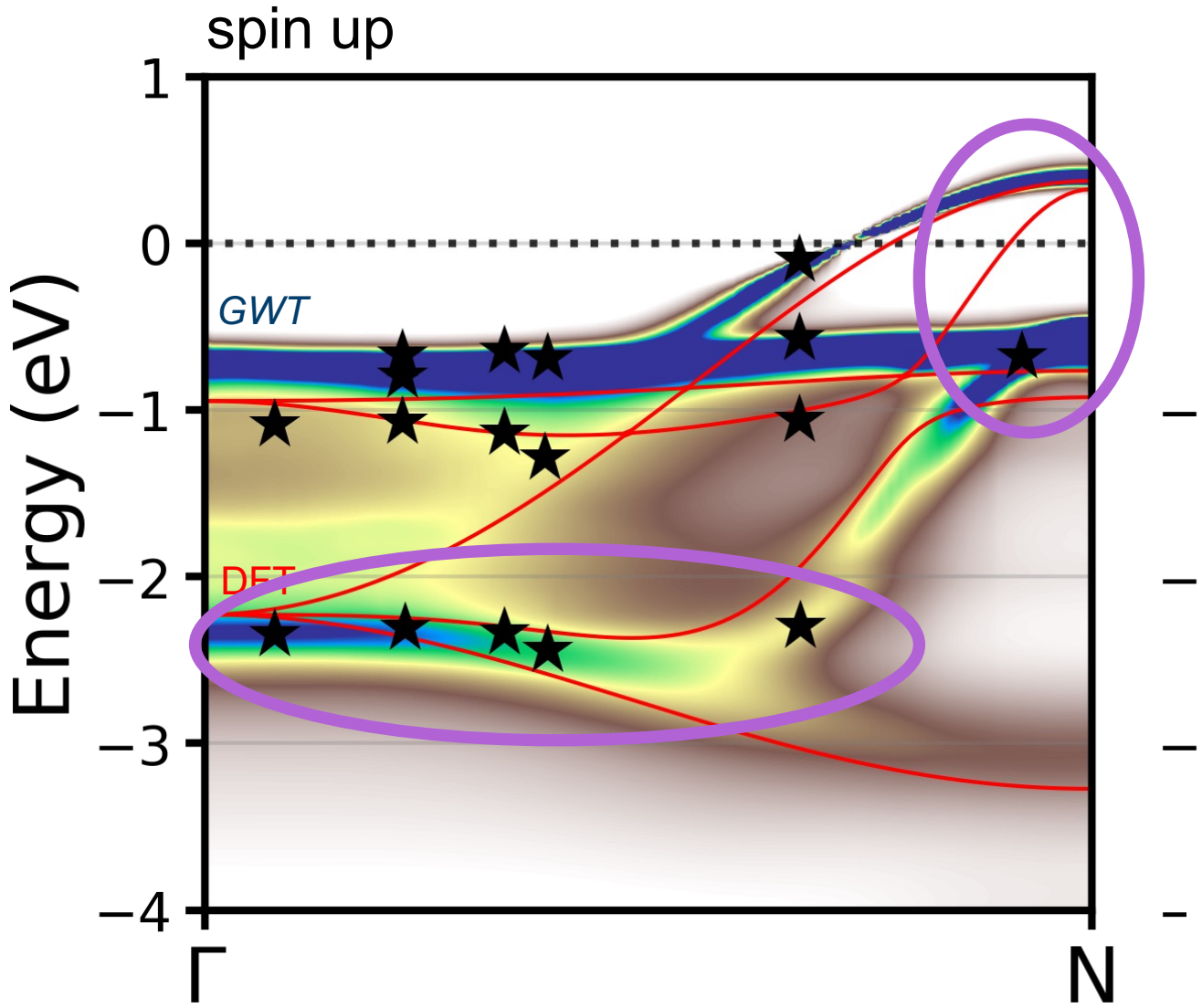


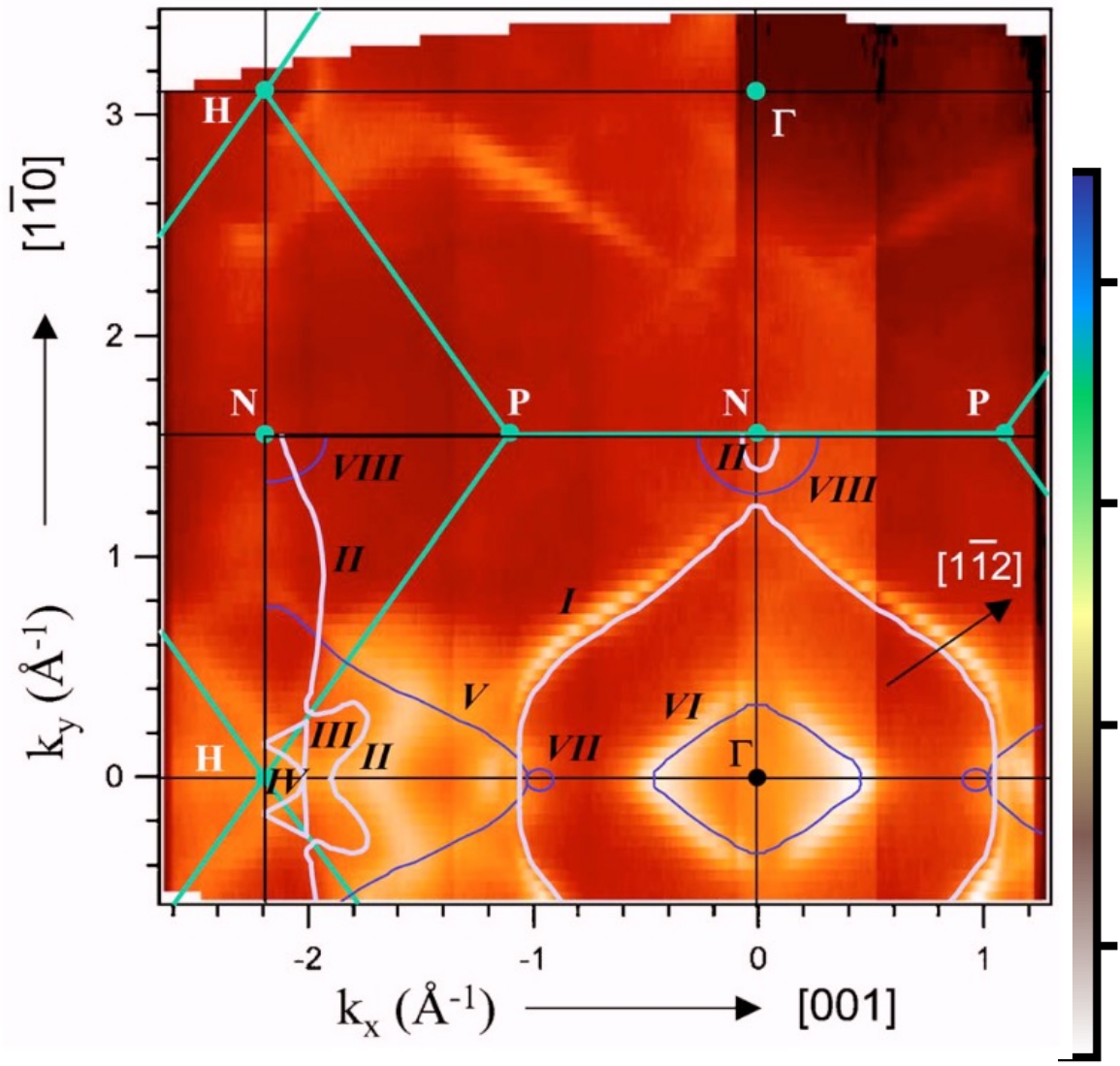
IRON BAND STRUCTURE (*GWT*)



DMFT: J. Sánchez-Barriga et al., PRL **103**, 267203 (2009)

IRON BAND STRUCTURE (*GWT*)

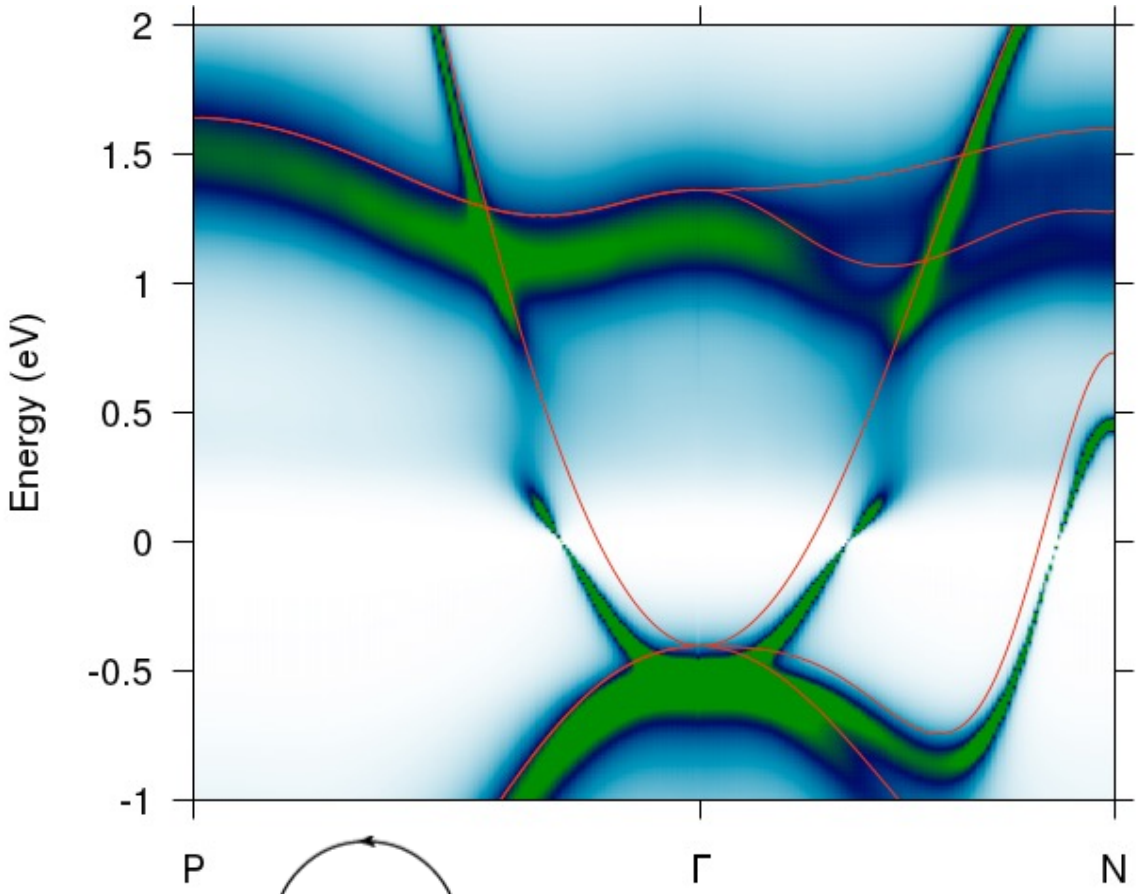


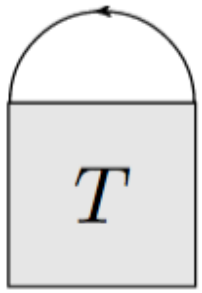


Schäfer et al., PRB 72, 155115 (2005)
Mlynczak et al., PRB 105, 115135 (2022)

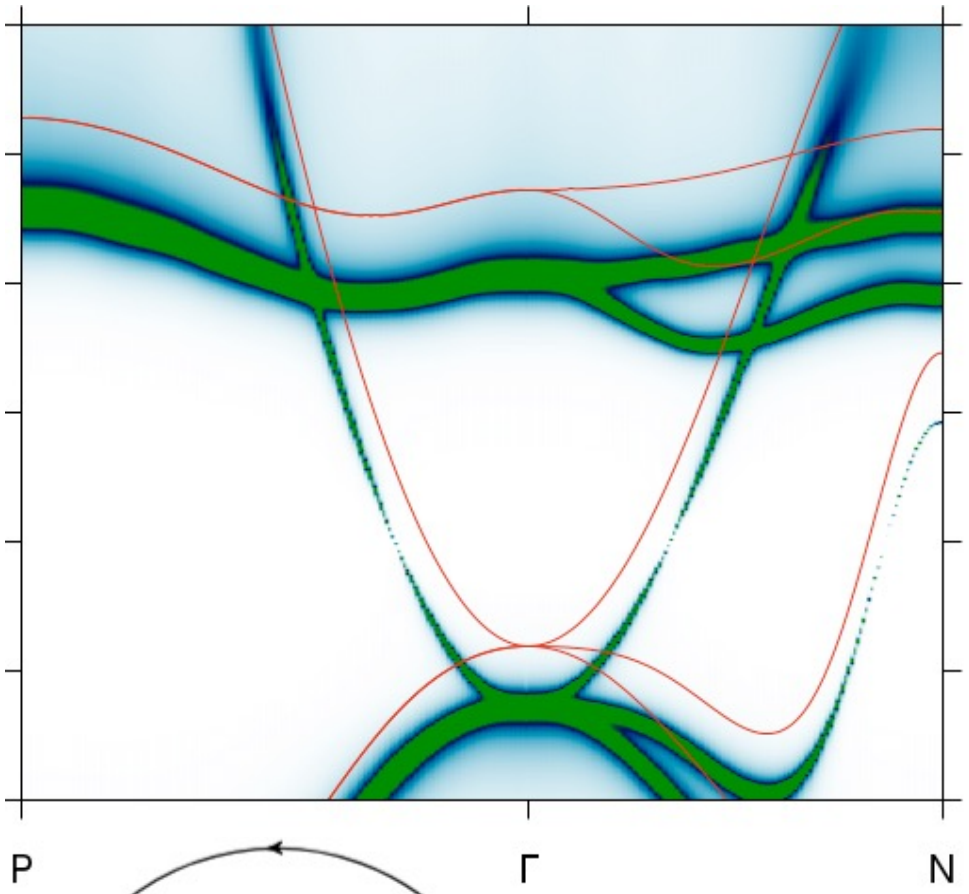
exp: J. Sánchez-Barriga et al., PRL **103**, 267203 (2009)

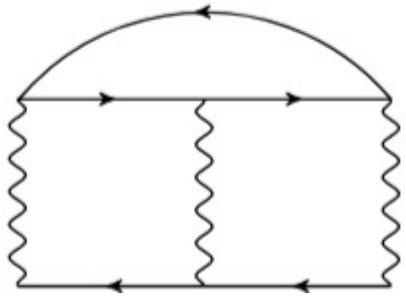
ANOMALY SPIN DOWN (IRON)





full *GT* self-energy

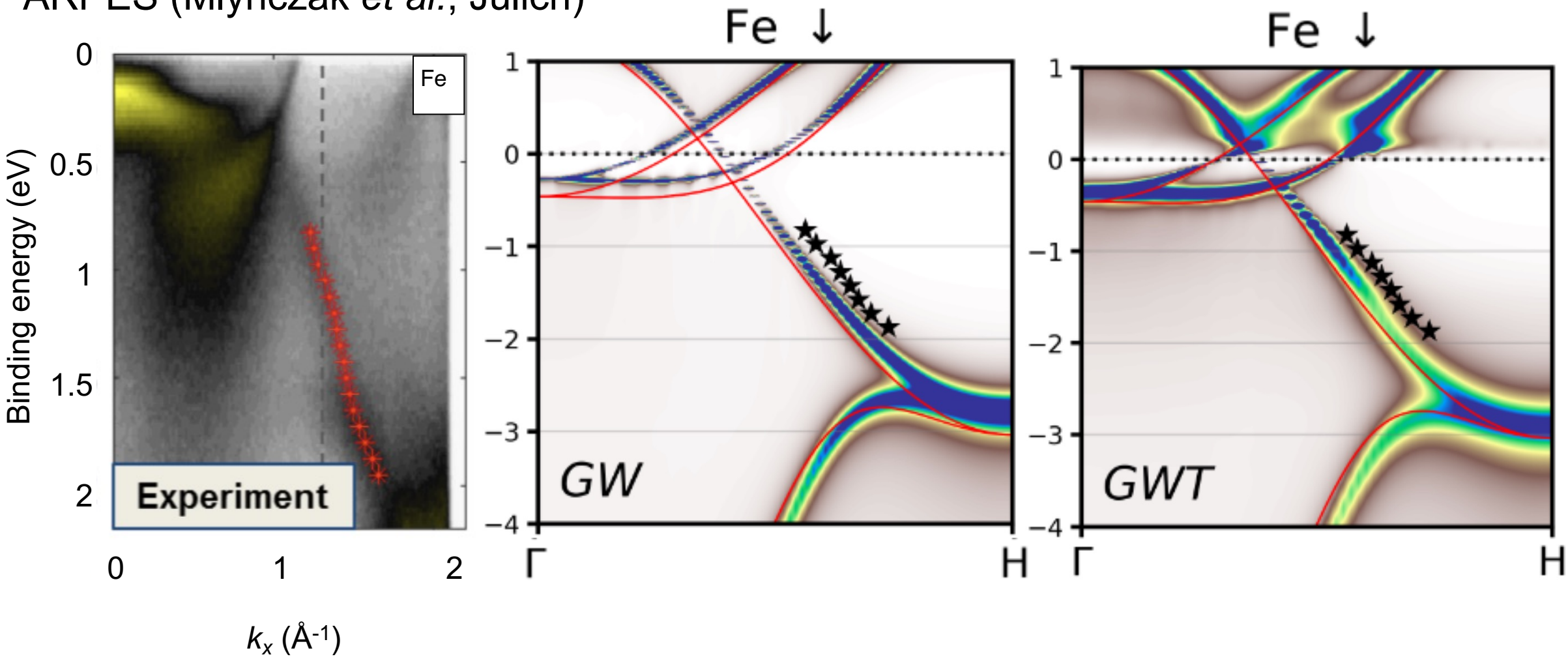




only 3rd order diagram

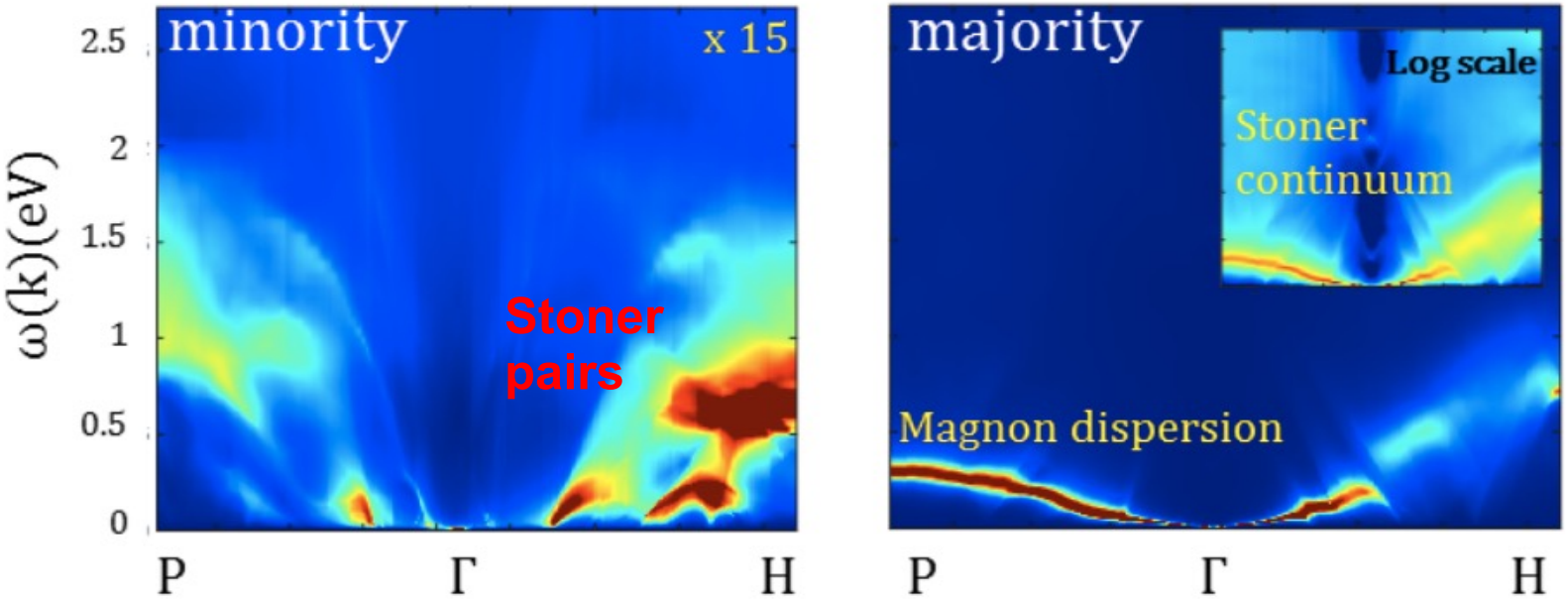
HIGH-ENERGY BAND ANOMALY (IRON)

ARPES (Mlynczak *et al.*, Jülich)

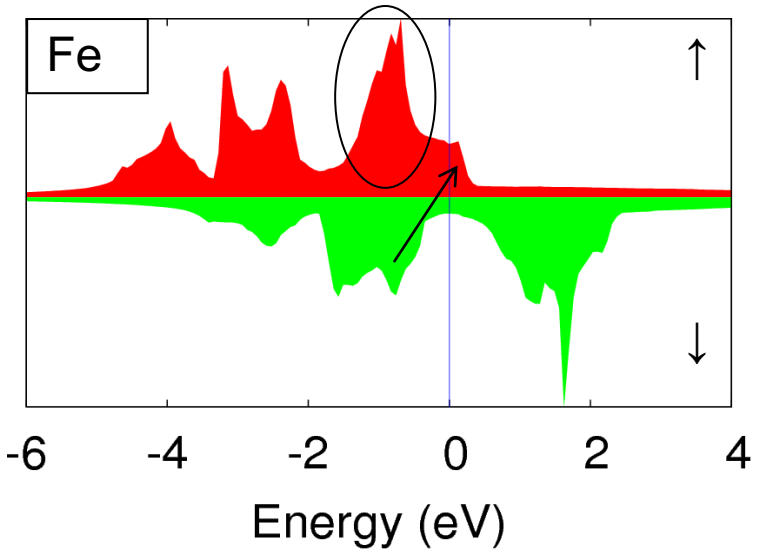


exp: Mlynczak et al., Nature Comm. **10**, 1 (2019)
theo: Nabok et al., npj Comput. Mater. **7**, 178 (2021)

HIGH-ENERGY BAND ANOMALY (IRON)



Mlynczak *et al.*, Nature Communications 10, 505 (2019)



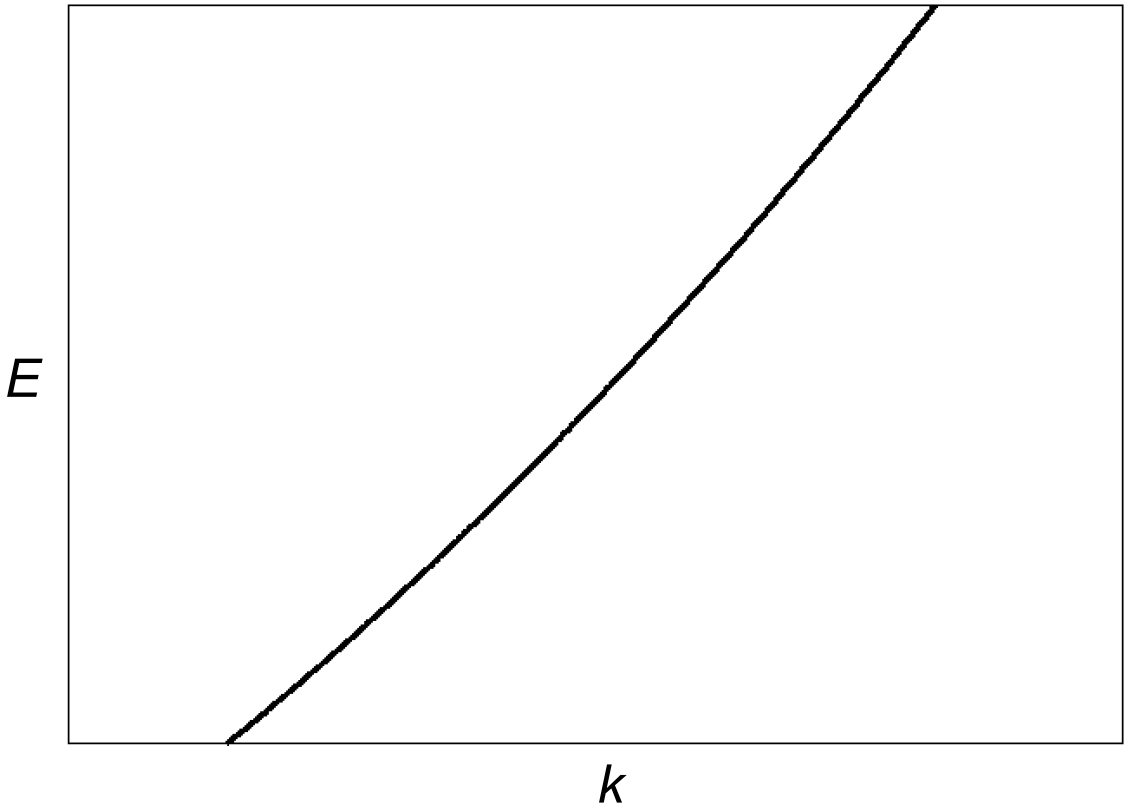
≈0.8eV ≈0.7eV

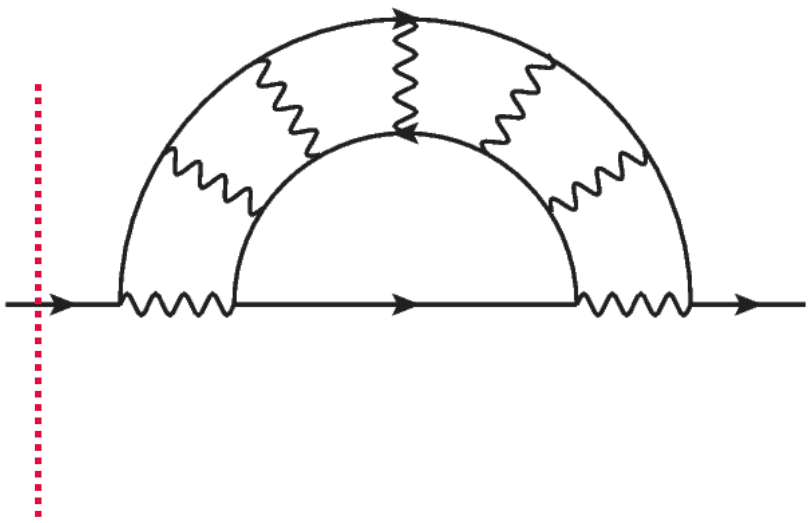
$$\Sigma_{GT} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{1}{\omega - \omega' - \epsilon - \mathrm{i}\eta}\,\frac{1}{\omega' - \epsilon_{\mathrm{M}} - \mathrm{i}\eta}\,d\omega'$$

$$= \frac{\mathrm{i}}{\omega - (\epsilon + \epsilon_{\mathrm{M}}) - \mathrm{i}\eta}$$

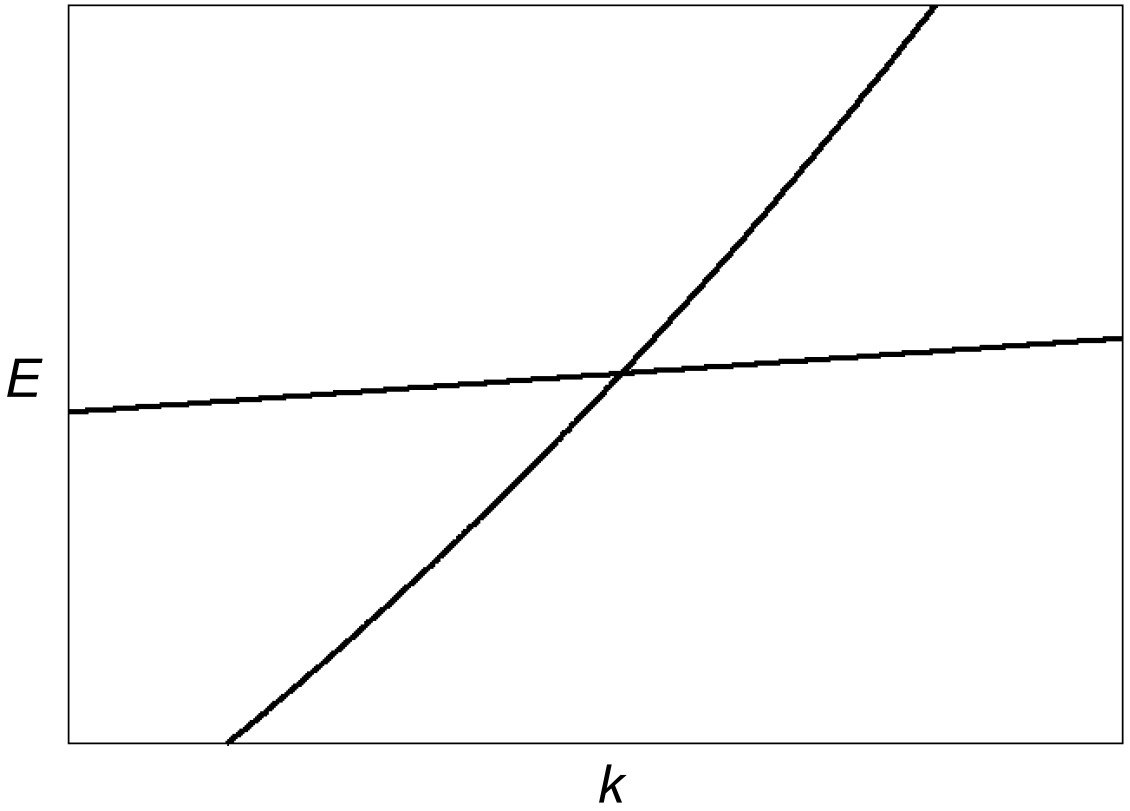
≈1.5eV

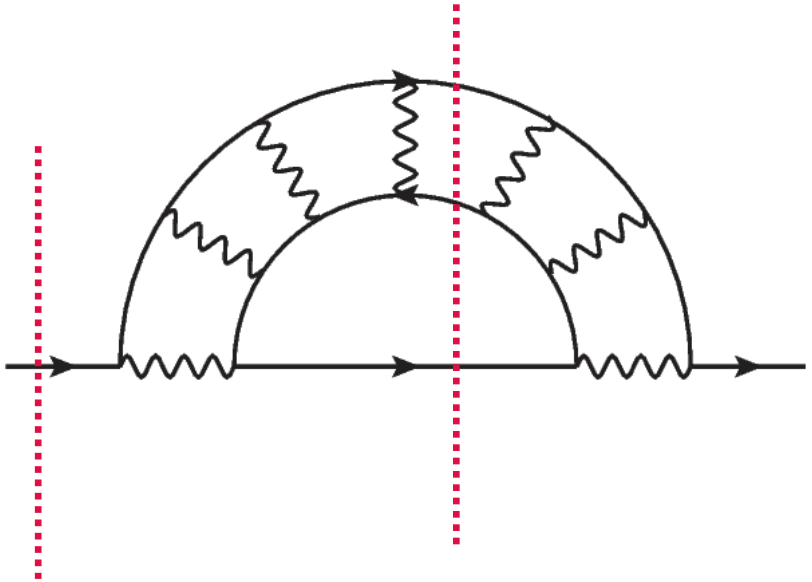
BAND ANOMALY (WATERFALL)



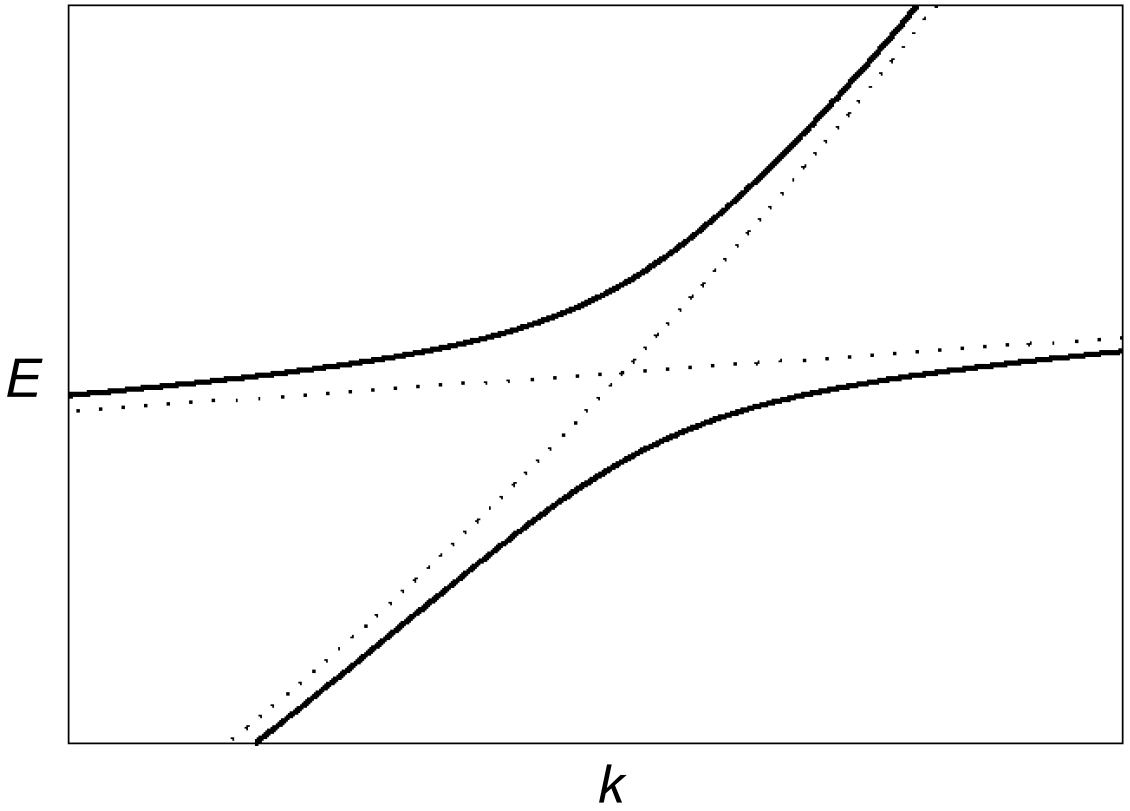


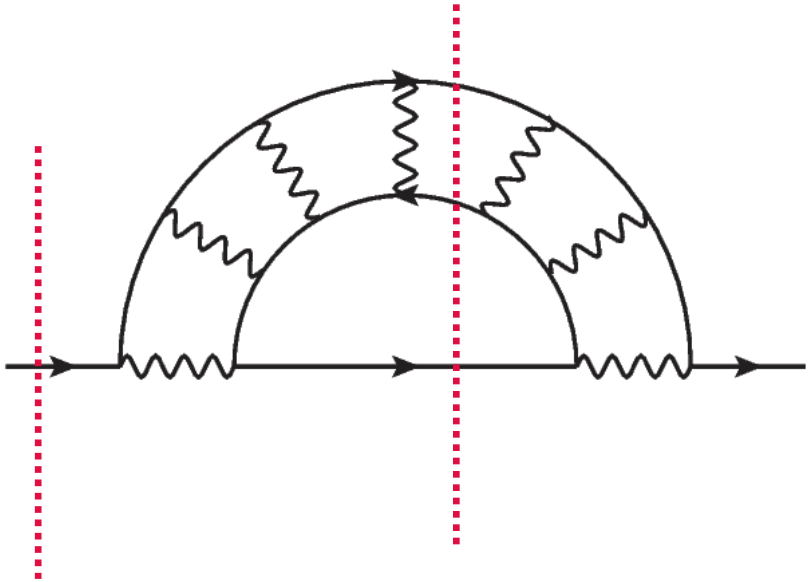
BAND ANOMALY (WATERFALL)





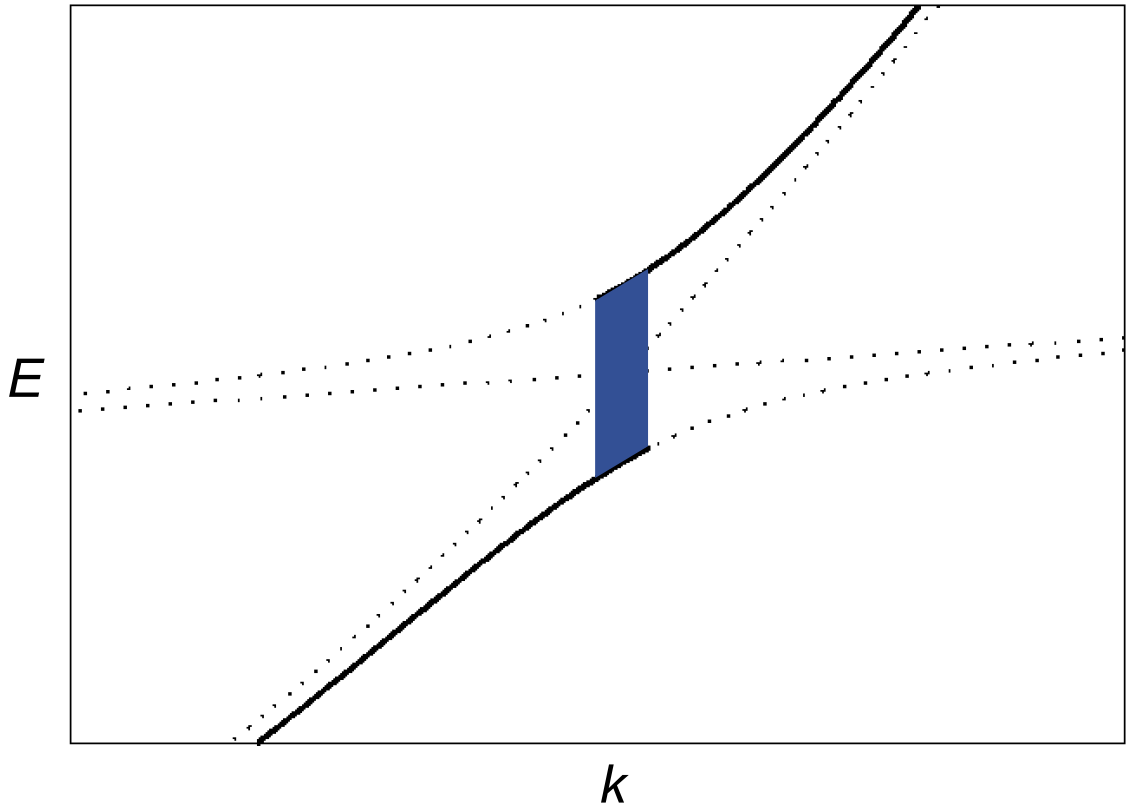
BAND ANOMALY (WATERFALL)

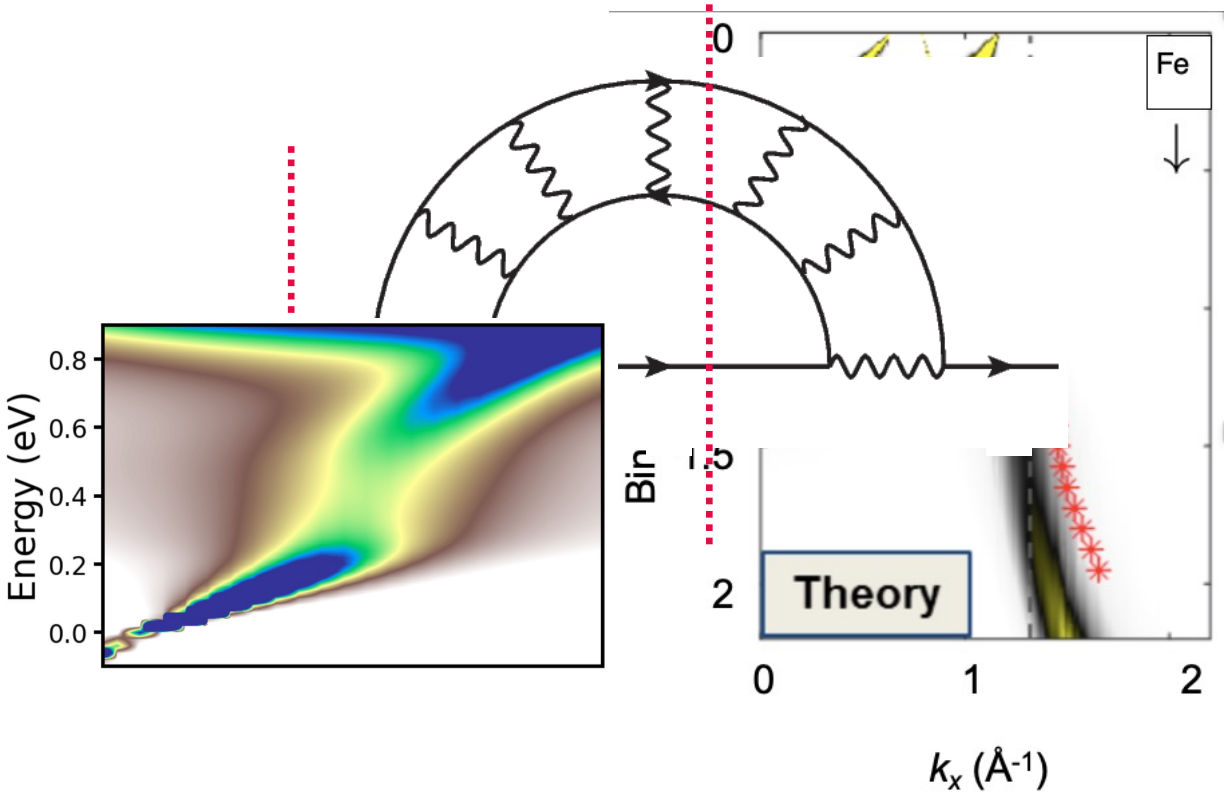




$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\psi_n^{N-1}(\mathbf{r})\psi_n^{N-1\,*}(\mathbf{r}')}{\omega - \epsilon_n^{N-1} - i\eta} + ...N+1...$$

BAND ANOMALY (WATERFALL)





$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\psi_n^{N-1}(\mathbf{r})\psi_n^{N-1\,*}(\mathbf{r}')}{\omega - \epsilon_n^{N-1} - i\eta} + ...N+1...$$

TABLES (IRON)

Table 1. Electron spin magnetic moments (in μ_B) of Fe, Co, and Ni computed with different techniques.

	LSDA	*GW*	*GT*	*GWT*	exp[1]
Fe	2.15	2.12 (2.17)	2.00	2.09	2.08
Co	1.58	1.57 (1.65)	1.28	1.54	1.52
Ni	0.58	0.59 (0.65)	0.49	0.59	0.52

GW values in brackets are calculated without the Δ_x correction (see text).
[1]Table 12 of ref. [52].

Table 2. *d* bandwidths (in eV) for bcc Fe, fcc Co, and fcc Ni obtained from LSDA, *GW*, *GT*, and *GWT* and compared with experimental data.

W_d	LSDA	*GW*	*GT*	*GWT*	exp
Fe $N_{1\uparrow}$	4.74	4.29 (4.30)	5.10	4.67	4.50 ± 0.23[1]
Fe $N_{1\downarrow}$	3.54	3.46 (3.35)	3.96	3.57	3.60 ± 0.20[1]
Co $\langle L_1 \rangle$	4.64	4.18 (4.33)	4.67	4.40	3.8 ± 0.5[2]
					> 4.0[3]
Ni $\langle L_1 \rangle$	4.58	4.12 (4.18)	4.56	4.12	3.9 ± 0.2[4]

The bandwidths are estimated, as in the experiment, based on the specified states. The *GW* values in brackets are computed without the Δ_x correction (see text).
[1]Ref. [53].
[2]Ref. [37].
[3]Ref. [36].
[4]Ref. [16] (based on experimental data from ref. [2]).

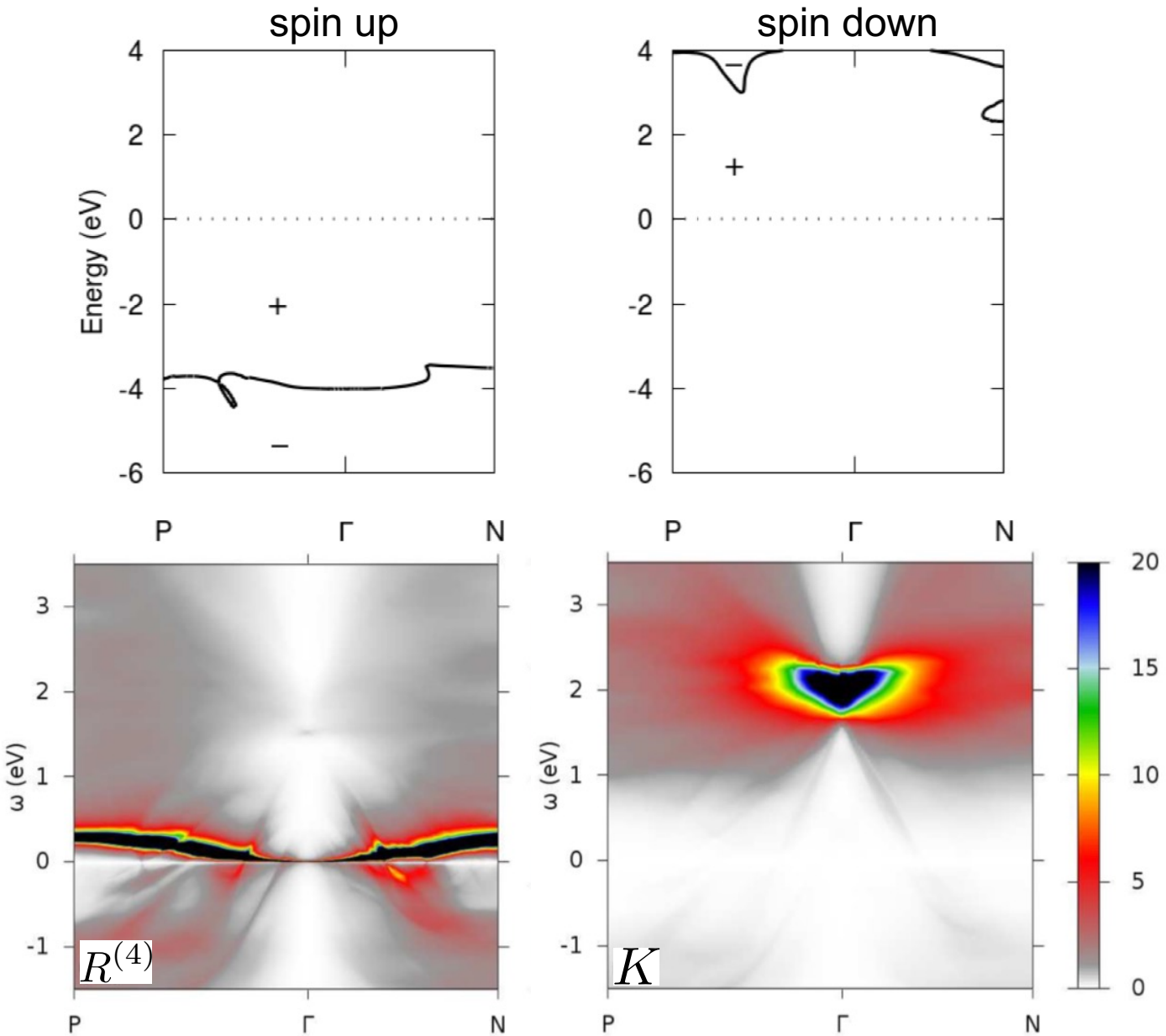
Table 3. The exchange splitting ΔE_x at special **k** points computed with different techniques and compared with available experimental values.

ΔE_x	LSDA	*GW*	*GT*	*GWT*	exp
Fe					
Γ_{25}	1.77	1.41 (1.55)	2.09	1.90	2.08 ± 0.10[1]
H_{12}	1.56	1.06 (1.19)	1.64	1.51	1.30 ± 0.30[1]
P_4	1.36	0.96 (1.08)	1.50	1.19	1.35 ± 0.10[1]
N_2	1.60	1.19 (1.32)	1.78	1.49	1.60 ± 0.15[1]
Co					
Γ_{25}	1.44	0.98 (1.24)	1.39	1.18	1.20 ± 0.30[2]
Γ_{12}	1.66	1.20 (1.48)	1.49	1.04	0.85 ± 0.20[2]
L_3	1.48	1.00 (1.26)	1.33	1.18	1.15 ± 0.40[2]
Ni					
L_3	0.56	0.37 (0.51)	0.51	0.37	0.31 ± 0.03[3]
X_2	0.52	0.30 (0.45)	0.44	0.31	~ 0.2[4]

GW values in brackets are calculated without the Δ_x correction in the reference system (see text).
[1] Ref. [53].
[2] Ref. [37].
[3] Ref. [54].
[4] Ref. [55].

Nabok, Blügel, Friedrich, npj Comput. Mater. **7**, 178 (2021)

VIOLATION OF CAUSALITY (*GT*)



There are regions where the *GT* spectral function turns negative!

Can be traced back to the imag. part of the *T*-matrix having negative sign.

$$T = T_{\geq 2} - T_2$$
$$= W[R^{(4)} - K]W$$

→ difference is negative

***GW* restores correct sign.**

SUMMARY

JÜLICH Forschungszentrum

- Calculation of spin excitations (spin waves and Stoner excitations) implemented within FLAPW through the solution of the Bethe-Salpeter equation.

- Goldstone condition violated in the limit $\mathbf{q}\to 0$ and $\omega\to 0$ due to inconsistency of Green functions (LSDA vs. self-consistent); self-consistent COHSEX recovers Goldstone mode.

- Electron-magnon scattering described by *GT* self-energy.

- Double-counting-free combination with *GW* self-energy gives the *GWT* self-energy.

- Strong spin asymmetry of lifetime broadening in agreement with experiment. Majority *d* bands strongly renormalized (quasiparticle character lost) due to coupling to many-body spin excitations.

- Band anomalies due to many-body renormalization through coupling to spin-wave and Stoner excitations (the latter seen in recent ARPES experiment).

- *GWT* band structure of Fe is similar to DMFT spectral function but with improvements in the details:
  - quasiparticle band at 2.34 eV (Γ) and 3.2 eV (P),
  - 1.5 eV band anomaly,
  - no false prediction of hole pocket at N

http://spex.readthedocs.org SPEX

ACKNOWLEDGMENTS

Dmitrii Nabok

Mathias C. T. D. Müller

Stefan Blügel

Experiments:

Ewa Mlynczak

Lukas Plucinski