Benchmark and application of density functional theory for superconductors

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Collaborators and papers :

- Benchmarks for Elemental bulks : M. Kawamura, Y. Hizume, and T. Ozaki, Phys. Rev. B **101**, 134511 (2020); arXiv:1911.06481.
- Effect of Spin-fluctuation in s-wave superconductors: K. Tsutsumi, Y. Hizume, M. Kawamura, R. Akashi, and S. Tsuneyuki, Phys. Rev. B **102**, 214515 (2020); arXiv:2010.06796.
- Compounds with latest SCDFT functional : In preparation
- Quaternary hydrides guided by sphere-packing : R. Koshoji, M. Fukuda, M. Kawamura, T. Ozaki, Phys. Rev. Materials **6**, 114802 (2022); arXiv:2206.04971.

DFT2022
One-Day Workshop
2022/12/12

Outline

- Introduction
  - Motivation for benchmark calculation of SCDFT
- Theory
  - SCDFT functional
  - Correction for ultrasoft pseudopotentials
- Benchmark for compounds with latest SCDFT functional
  - Elemental materials
  - Compounds
  - Verification : Sommerfeld coefficient and lattice constant
  - T_c
- Prediction of quaternary hydrides from sphere-packing guideline
- Summary

Intro

Motivation

First-principles calculation of superconducting state is used for

- Prediction of new superconductors
- Analysis of known superconductors (mechanism, characterization of electronic structure)

Theories for predicting the transition temperature (T_C)

- Eliashberg equation (Semi-empirical)

  G. M. Eliashberg, Sov. Phys.-JETP **11** 696(1960).

$$T_C = \frac{\omega_{\ln}}{1.20}\exp\left[-\frac{1.04\,(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]$$

  W. L. McMillan, PR 167, 331 (1968).

DFT → ($\lambda, \omega_{\ln}$) → DFPT/ Frozen

$$\lambda = \sum_{\mathbf{q}\nu}\lambda_{\mathbf{q}\nu}$$

$$\ln\omega_{\ln} = \frac{1}{\lambda}\sum_{\mathbf{q}\nu}\lambda_{\mathbf{q}\nu}\ln\omega_{\mathbf{q}\nu}$$

$$\lambda_{\mathbf{q}\nu} = \frac{2}{D(0)\omega_{\mathbf{q}\nu}}\sum_{\mathbf{k}nn'}\left|g^{\nu}_{n\mathbf{k}n'\mathbf{k}+\mathbf{q}}\right|^2 \times\delta(\xi_{n\mathbf{k}})\delta\left(\xi_{n'\mathbf{k}+\mathbf{q}}\right)$$

- Eliashberg equation (Non-empirical)

  W. Sano, *et al.*, PRB **93**, 094525 (2016).

  T. Wang, PRB **102**, 134503 (2020).

  Tackling the difficulty in Frequency integration

- Density functional theory for superconductors (SCDFT)

  Fully non-empirical

  M. Lüders *et al*, PRB 72, 024545 (2005).

Earlier Applications of SCDFT

	El-Ph	El-El	T_c (Calc.)	T_c (Exp.)	
Al	Averaged	Tomas-Fermi	0.90 K	1.18 K	Marques2005
Ta	Averaged	Tomas-Fermi	3.7	4.48	Marques2005
Pb	Averaged	Tomas-Fermi	6.9	7.2	Marques2005
Nb	Averaged	Tomas-Fermi	9.5	9.3	Marques2005
MgB_2	Band-dep.	RPA(static)	34.1	39	Floris2005
Pb	Full (n, k)	RPA(static)	5.25	7.2	Floris2007
CaC_6	Full (n, k)	RPA(static)	9.4	11.5	Sanna2007
H_2@450GPa	Full (n, k)	RPA(static)	242	–	Cudazzo2010
β -$Li_{0.5}ZrNCl$	Averaged	RPA(static)	4.3	10-15.2	Akashi2012
Cs_3C_{60}	Full (n, k)	RPA(static)	15.7	35	Akashi2013
Li@25GPa	Averaged	RPA(dynamical)	3.2	5-17	Akashi2013
Li@25GPa	Averaged	RPA(static)	6.8	5-17	Akashi2013
H_3S	Averaged	RPA(dynamical)	155	203	Akashi2015
YNi_2B_2C	Full (n, k)	ALDA	13.8	15.4	Kawamura2017
FeSe	Band-dep.	RPA(static) spin-fluctuation	8	3	Essenberger2016

No systematical verification

Purpose : To find where does it work well and where does it fail.

Improvement of SCDFT

Prepare for the materials exploration

Method

Density functional theory for superconductors (SCDFT)

Extension of DFT to the superconducting order parameter

Minimize $E[\rho]$ → $\Omega[\rho,\chi]$

$$\chi(\mathbf{r},\mathbf{r}') \equiv \langle \hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}') \rangle$$

- Band structure (Crystalline potential)
- Spin–orbit coupling
- Phonons and Electron–phonon interaction
- Inter–electron Coulomb interaction
- Spin–fluctuation

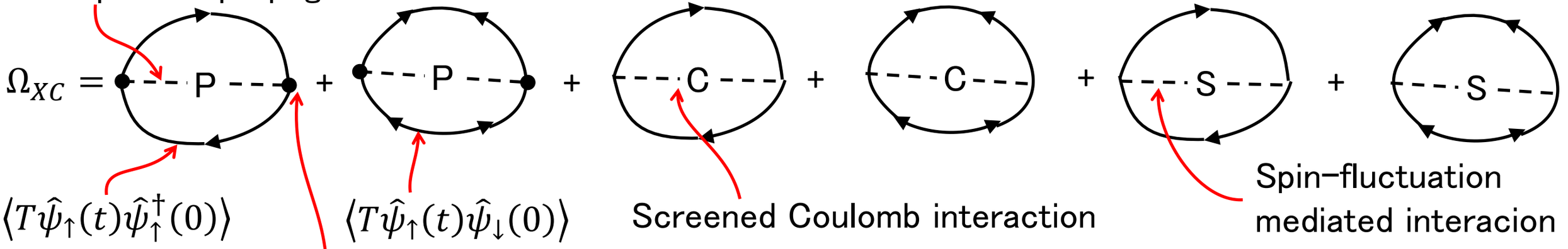
Universal functional (approximated)

For normal DFT, LDA $E_{XC}[\rho] = \int d^3r \varepsilon_{XC}(\rho(\mathbf{r}))$, GGA, ⋯ are used.

For SCDFT, Kohn–Sham Perturbation theory (like OEP) is used.

M. Lüders *et al.*, PRB **72**, 024545 (2005).

Free phonon propagator



R. Akashi, *et al.*, PRL **111**, 057006 (2013).
A. Davydov, *et al.*, PRB **102**, 214508 (2020).

F. Essenberger, *et al.* PRB 90, 214504 (2014).

Method

Gap eq. and kernel

SC order parameter : $\chi(\mathbf{r},\mathbf{r}') \equiv \langle \hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r}')\rangle = \sum_{nk} \chi_{nk}\varphi_{nk}(\mathbf{r})\,\varphi^*_{nk}(\mathbf{r}')$

$$\chi_{nk} = \frac{\Delta_{nk}}{2E_{nk}}\tanh\left(\frac{E_{nk}}{2T}\right)$$

$$E_{nk} \equiv \sqrt{\xi_{nk}^2 + |\Delta_{nk}|^2}$$

$$\xi_{nk} \equiv \varepsilon_{nk} - \varepsilon_F$$

Kohn–Sham gap eq.

$$\Delta_{nk} = -\frac{1}{2}\sum_{n'k'} K_{nkn'k'}\frac{\Delta_{n'k'}}{E_{n'k'}}\tanh\left(\frac{E_{n'k'}}{2T}\right) \qquad K_{nkn'k'} = \frac{\delta\Omega_{\mathrm{XC}}}{\delta\chi_{n'k'}\delta\chi^*_{nk}}\Big|_{\chi=0}$$

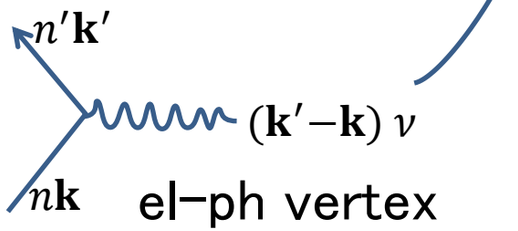
Find temperature where $\Delta_{nk} = 0 : T_c$

Kernel

$$K_{n\mathbf{k}n'\mathbf{k}'} = \frac{K^{ep}_{n\mathbf{k}n'\mathbf{k}'} + K^{se}_{n\mathbf{k}n'\mathbf{k}'} + K^{sf}_{n\mathbf{k}n'\mathbf{k}'}}{1 + Z^{ep}_{n\mathbf{k}} + Z^{se}_{n\mathbf{k}} + Z^{sf}_{n\mathbf{k}}}$$

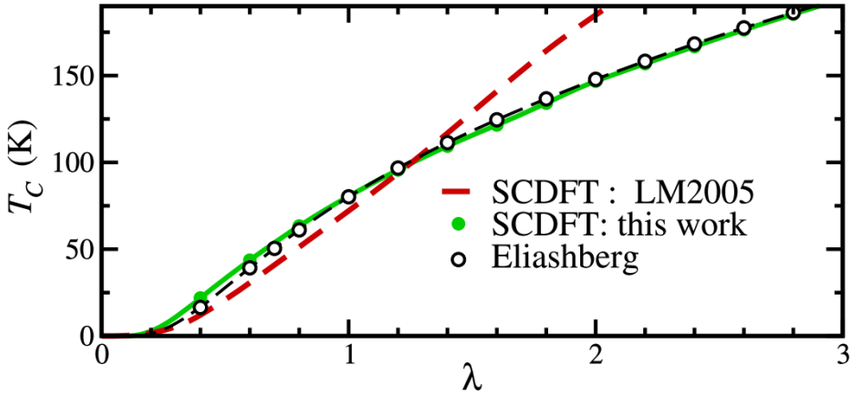
$$K^{\mathrm{ep}}_{n\mathbf{k}n'\mathbf{k}'} = -\sum_{\nu}\left|g^{(\mathbf{k}'-\mathbf{k})\,\nu}_{n\mathbf{k}n'\mathbf{k}'}\right|^2 F_K\left(\xi_{n\mathbf{k}},\xi_{n'\mathbf{k}'},\omega_{(\mathbf{k}'-\mathbf{k})\,\nu}\right) \quad \text{Attractive}$$

$$Z^{\mathrm{ep}}_{n\mathbf{k}} = \sum_{n'\mathbf{k}'\nu}\left|g^{(\mathbf{k}'-\mathbf{k})\,\nu}_{n\mathbf{k}n'\mathbf{k}'}\right|^2 F_Z\left(\xi_{n\mathbf{k}},\xi_{n'\mathbf{k}'},\omega_{(\mathbf{k}'-\mathbf{k})\,\nu}\right) \quad \text{Reductive}$$



el–ph vertex

$$\int d^3r\,\varphi^*_{n'\mathbf{k}+\mathbf{q}}(\mathbf{r})\varphi_{n\mathbf{k}}(\mathbf{r})\sum_R e^{i\mathbf{q}\mathbf{R}}\frac{\partial V_{\mathrm{KS}}(\mathbf{r})}{\partial R_\alpha}$$



A. Sanna, *et al.*, PRL **125**, 057001 (2020).

Eliashberg–combined functional

Reproducing T_c and self energy in the phonon–only model

Method

Screened exchange and spin-fluctuation

$$\hat{I}_{XC} \equiv \frac{\delta^2 E_{XC}}{\delta m(\mathbf{r})\delta m(\mathbf{r}')}$$

$$K^{se/sf}_{n\mathbf{k}n'\mathbf{k}'} = \frac{2}{\pi}\int_0^\infty d\omega \frac{|\xi_{n\mathbf{k}}| + |\xi_{n'\mathbf{k}'}|}{(|\xi_{n\mathbf{k}}|+|\xi_{n'\mathbf{k}'}|)^2 + \omega^2} V^{se/sf}_{n\mathbf{k}n'\mathbf{k}'}(i\omega)$$ Repulsive

$$Z^{se/sf}_{nk} = \mp \sum_{n'\mathbf{k}'} \frac{1}{\pi}\int_0^\infty d\omega \frac{(|\xi_{n\mathbf{k}}|+|\xi_{n'\mathbf{k}'}|)^2 - \omega^2}{[(|\xi_{n\mathbf{k}}|+|\xi_{n'\mathbf{k}'}|)^2 + \omega^2]^2} V^{se/sf}_{n\mathbf{k}n'\mathbf{k}'}(i\omega)$$ Reductive

Spin-fluctuation

$$\hat{V}^{sf}(\mathbf{q}, i\omega) = -3\hat{I}_{XC}\hat{\chi}_S\hat{I}_{XC}$$

$$\hat{\chi}_S(\mathbf{q}, i\omega) = \left(1 - \hat{I}_{XC}\hat{\Pi}_0\right)^{-1}\hat{\Pi}_0$$

Screened exchange

$$\hat{V}^{se}(\mathbf{q}, i\omega) = \left(1 - \hat{V}_{bare}\hat{\Pi}_0\right)^{-1}\hat{V}_{bare}$$

$$V^{se/sf}_{n\mathbf{k}n'\mathbf{k+q}}(i\omega) = \sum_{\mathbf{GG}'} \rho_{n\mathbf{k}n'\mathbf{k+q}}(\mathbf{G})\rho^*_{n\mathbf{k}n'\mathbf{k+q}}(\mathbf{G}')V^{se/sf}(\mathbf{G}, \mathbf{G}', \mathbf{q}, i\omega)$$

$$\Pi_0(\mathbf{G}, \mathbf{G}', \mathbf{q}, i\omega) = \sum_{\mathbf{k}nn'} \frac{\theta(-\xi_{n\mathbf{k}}) - \theta(-\xi_{n'\mathbf{k}'})}{\xi_{n\mathbf{k}} - \xi_{n'\mathbf{k}'} + i\omega} \rho_{n\mathbf{k}n'\mathbf{k+q}}(\mathbf{G})\rho^*_{n\mathbf{k}n'\mathbf{k+q}}(\mathbf{G}')$$

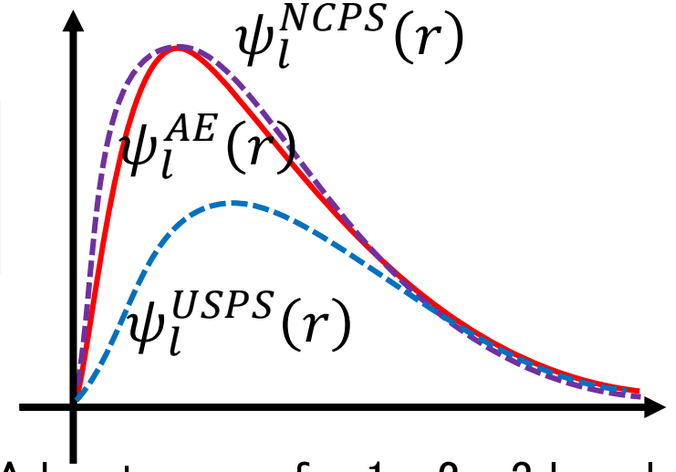
$$\rho_{n\mathbf{k}n'\mathbf{k+q}}(\mathbf{G}) = \mathrm{FFT}\left[\varphi^*_{n\mathbf{k}}(\mathbf{r})\varphi_{n'\mathbf{k+q}}(\mathbf{r}) + \sum_{\tau ij} Q_{\tau ij}(r)\langle\varphi_{n\mathbf{k}}|\beta_{\tau i}\rangle\langle\beta_{\tau j}|\varphi_{n'\mathbf{k+q}}\rangle\right]$$

Augmentation charge $Q_{\tau ij}(r) = \psi^{NC*}_{\tau i}(r)\psi^{NC}_{\tau j}(r) - \psi^{US*}_{\tau i}(r)\psi^{US}_{\tau j}(r)$

M. Gajdoš, *et al.*, PRB **73**, 045112 (2006). Polarizability, GW

Ultrasoft pseudopotential

D. Vanderbilt,
PRB **41**, 7892(R) (1990).



Advantageous for 1s, 2p, 3d, and 4f.

Benchmark for elemental materials

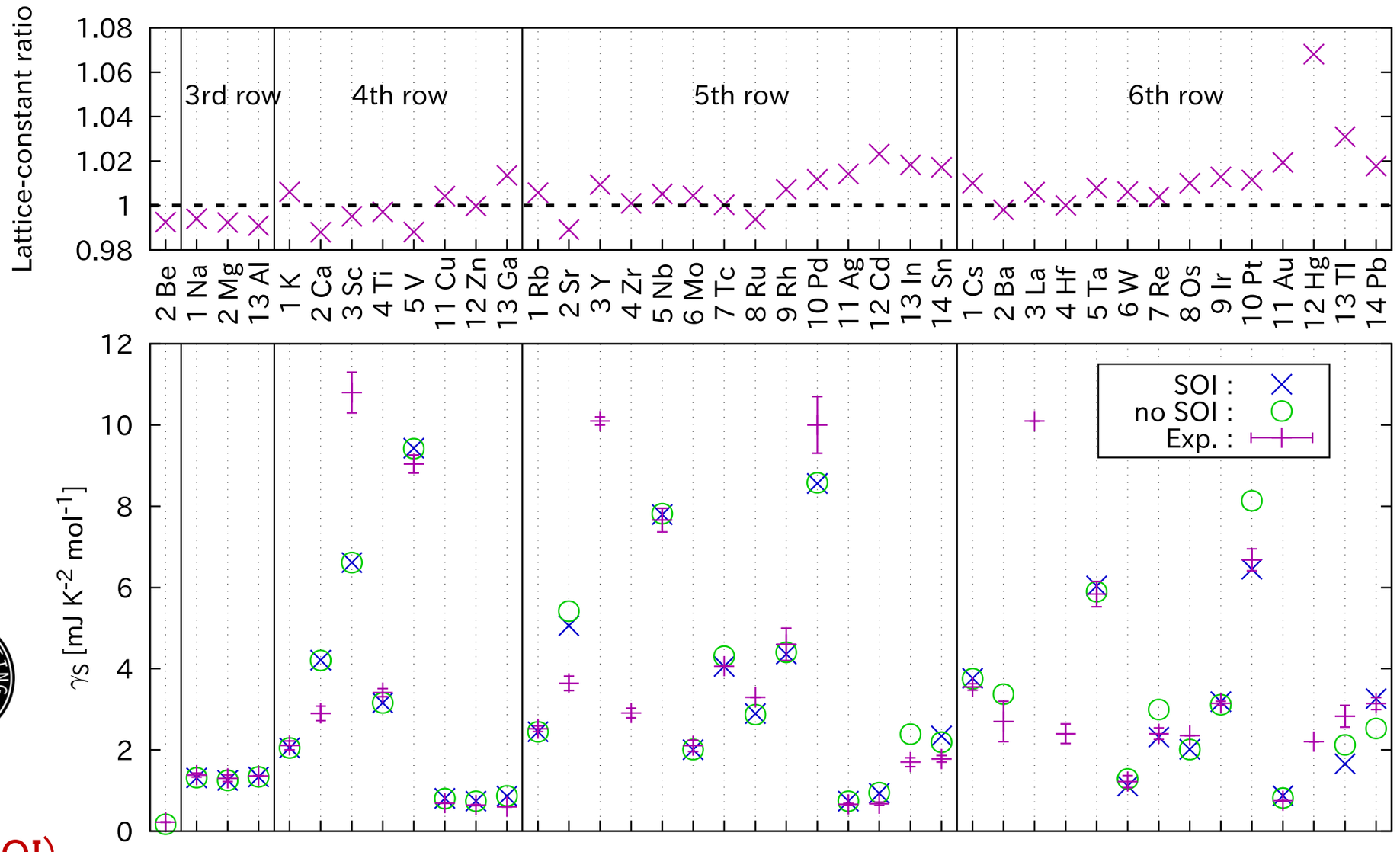
M. Kawamura, Y. Hizume, T. Ozaki,
PRB **101**, 134511 (2020).

Result

- Norm-conserving PP (SG15)
- Quantum ESPRESSO
- GGA-PBE functional
- Cutoff(WFC) : From SSSP criteria
- phonon $\mathbf{q}$-grid : Proportional to BZ size (8^3 for Al)
- $\mathbf{k}$-grid : $2 \times \mathbf{q}$-grid (SCF), $4 \times \mathbf{q}$-grid (DOS, $\hat{\Pi}_0$),
- Empty bands:
  $20 \times N_{\mathrm{atom}}$ (without SOI)
  $40 \times N_{\mathrm{atom}}$ (with SOI)
- No Z_C, Lüders2005 functional

Include/exclude

- Spin-fluctuation (SF)
- Spin-orbit interaction (SOI)

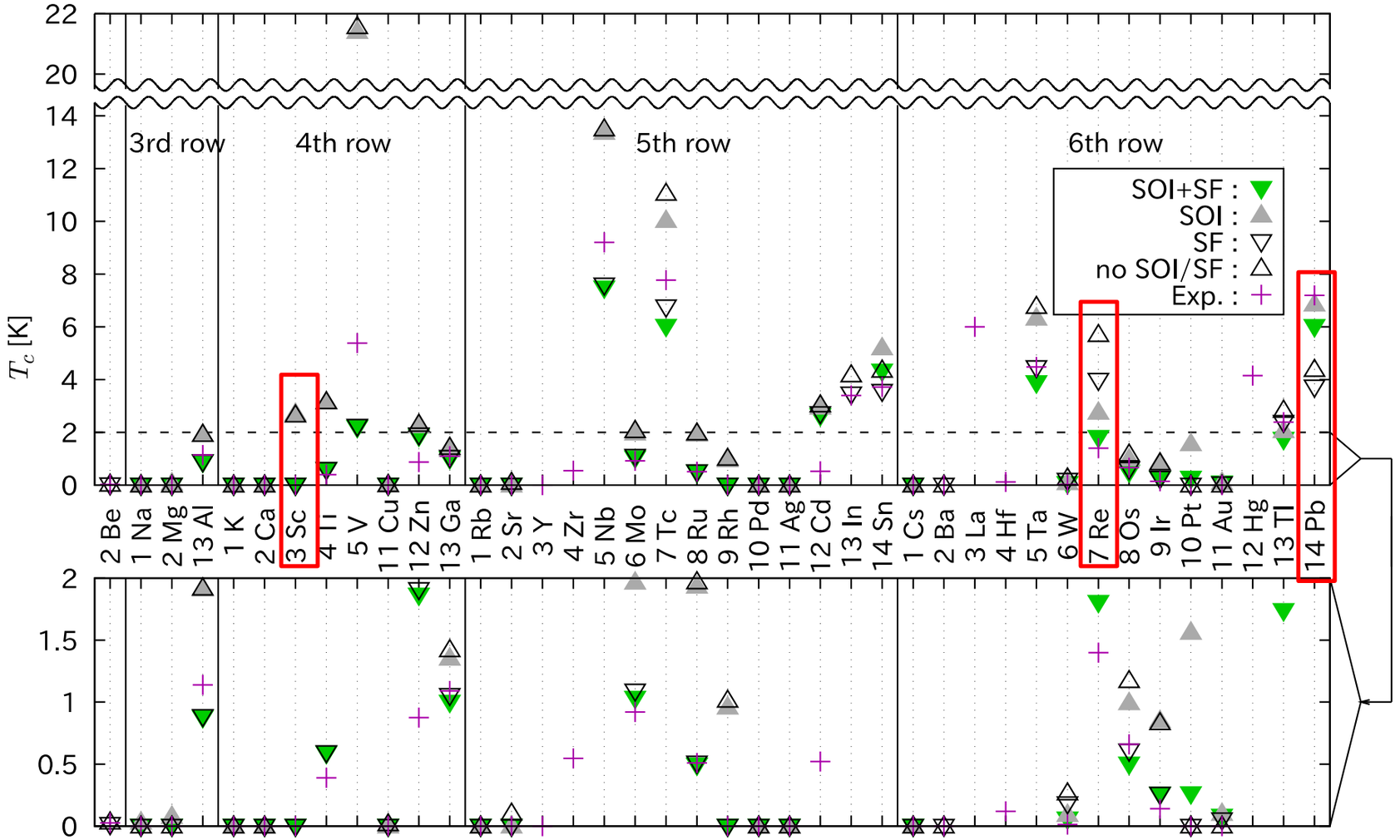


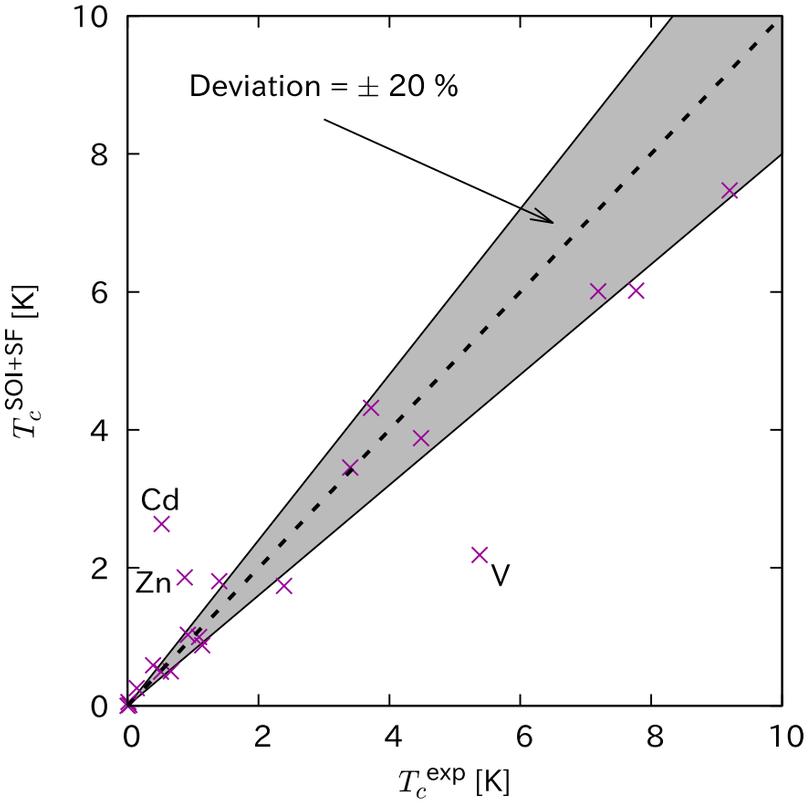
$$C_v = \gamma_S T + O(T^3) \quad \gamma_S = \frac{\pi^2 D(0)}{3}(1+\lambda) \quad \lambda = \sum_{\mathbf{q}\nu\mathbf{k}nn'} \frac{2}{D(0)\omega_{\mathbf{q}\nu}} \left| g^{\nu}_{n\mathbf{k}n'\mathbf{k}+\mathbf{q}} \right|^2 \delta(\xi_{n\mathbf{k}})\delta(\xi_{n'\mathbf{k}+\mathbf{q}})$$

Result

T_c for elemental bulks

M. Kawamura, Y. Hizume, T. Ozaki,
PRB **101**, 134511 (2020).





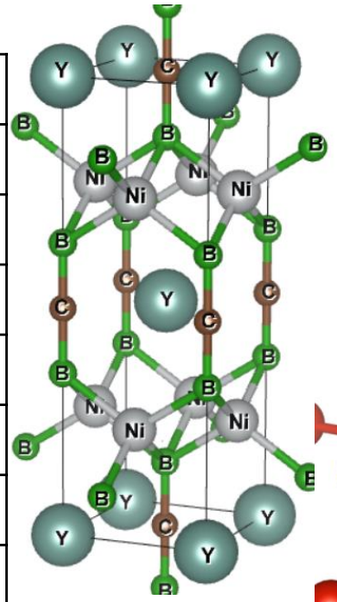
- SF always reduces T_cs for the elemental systems.
- SOI is significant only for Tc, Sn, Re, Tl, and Pb.
- Reproducing the noSC in alkaline, alkaline-earth, noble metals, and Sc (with SF).

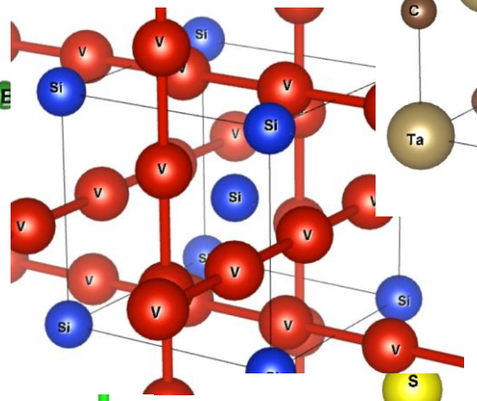
Result

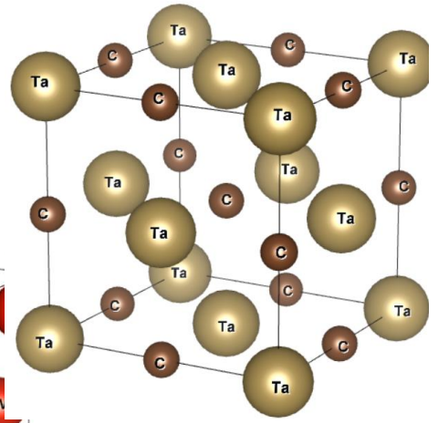
Benchmark calculation for compounds

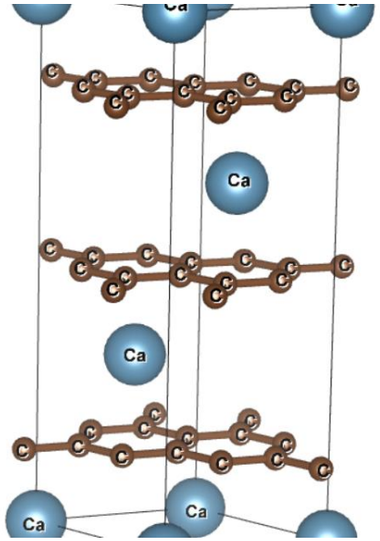
- Quantum ESRPRESSO
- GGA-PBE
- $20 \times N_{atom}$ empty bands
- $N_{\mathbf{k}} = 2^3 N_{\mathbf{q}}$
- SSSP(NCPP/USPP/PAW)
- $E_{cut}[\rho_{n\mathbf{k}n'\mathbf{k}'}] = E_{cut}[\text{density}]/2$
- $E_{cut}[n] = 4E_{cut}[\varphi]$ for NCPP
- $E_{cut}[n] = 8E_{cut}[\varphi]$ for NCPP

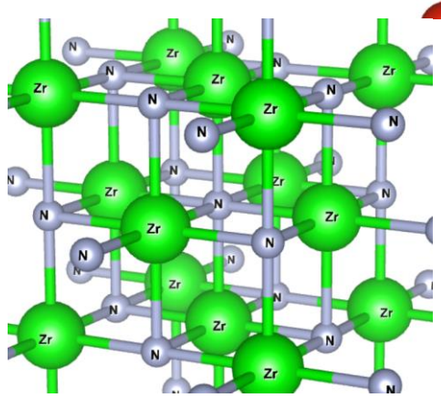
Material	N_{atom}	$N_{\mathbf{k}}$	$E_{cut}[\varphi]$[Ry]
Al	1	16^3	30
V	1	18^3	35
Nb	1	16^3	40
Ta	1	16^3	45
In	1	14^3	50
Zn	2	$18^2 \times 10$	40
Cd	2	$16^2 \times 8$	60
Sn	2	10^3	60
ZrN	2	14^3	60
TaC	2	16^3	45
MgB_2	3	$16^2 \times 14$	35
H_3S	4	18^3	60
YNi_2B_2C	6	8^3	45
CaC_6	7	10^3	45
V_3Si	8	10^3	35

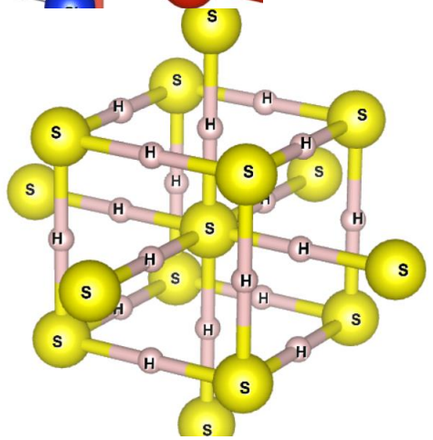


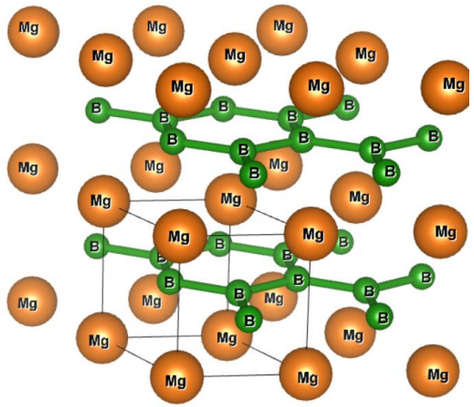






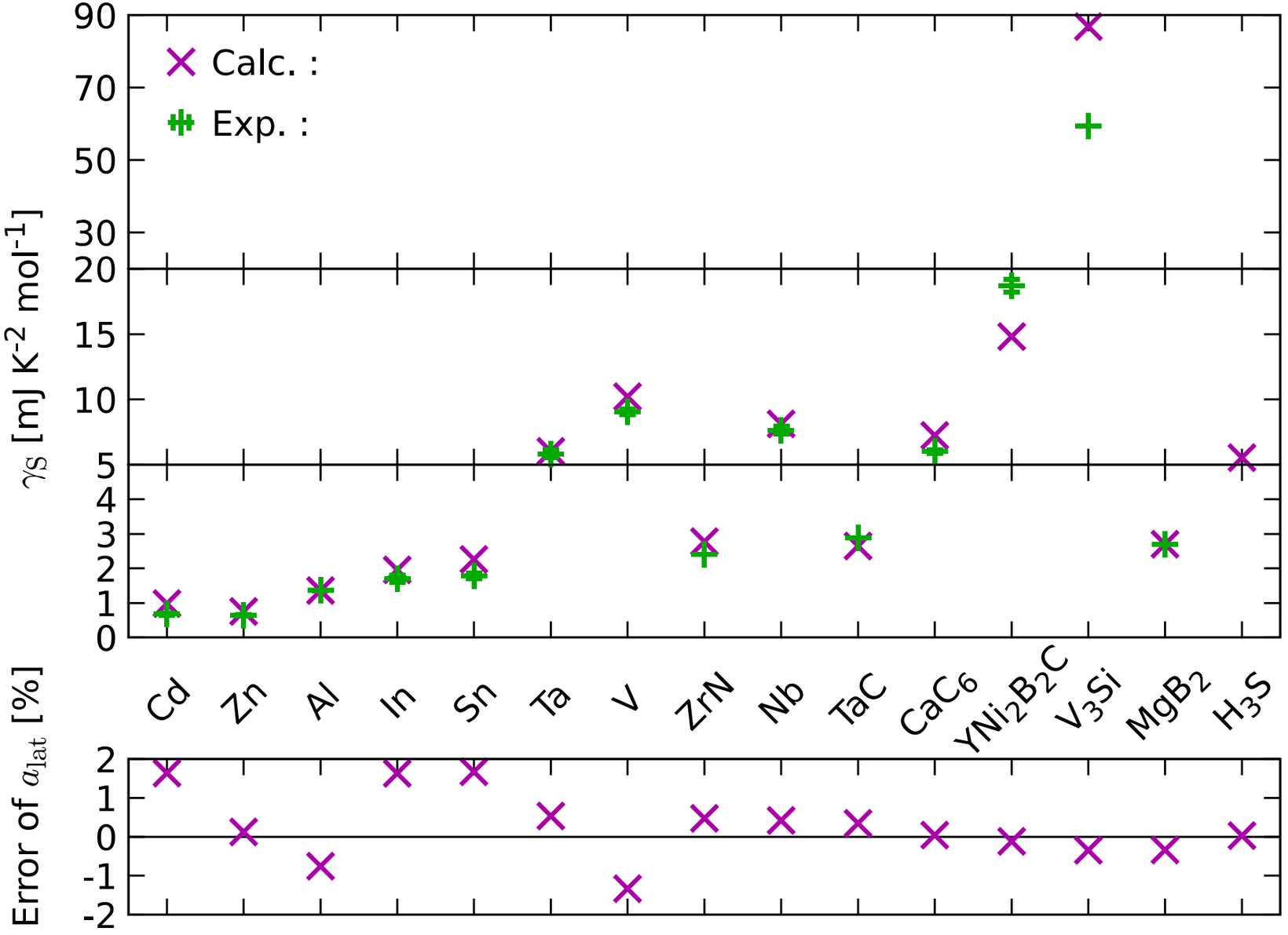






Result

Verify calculation with lattice constant and Sommerfeld coefficient



Normal-state specific heat at low-temperature including electron-phonon coupling

$$C_v = \gamma_S T + O(T^3)$$

$$\gamma_S = \frac{\pi^2 D(0)}{3}(1+\lambda)$$

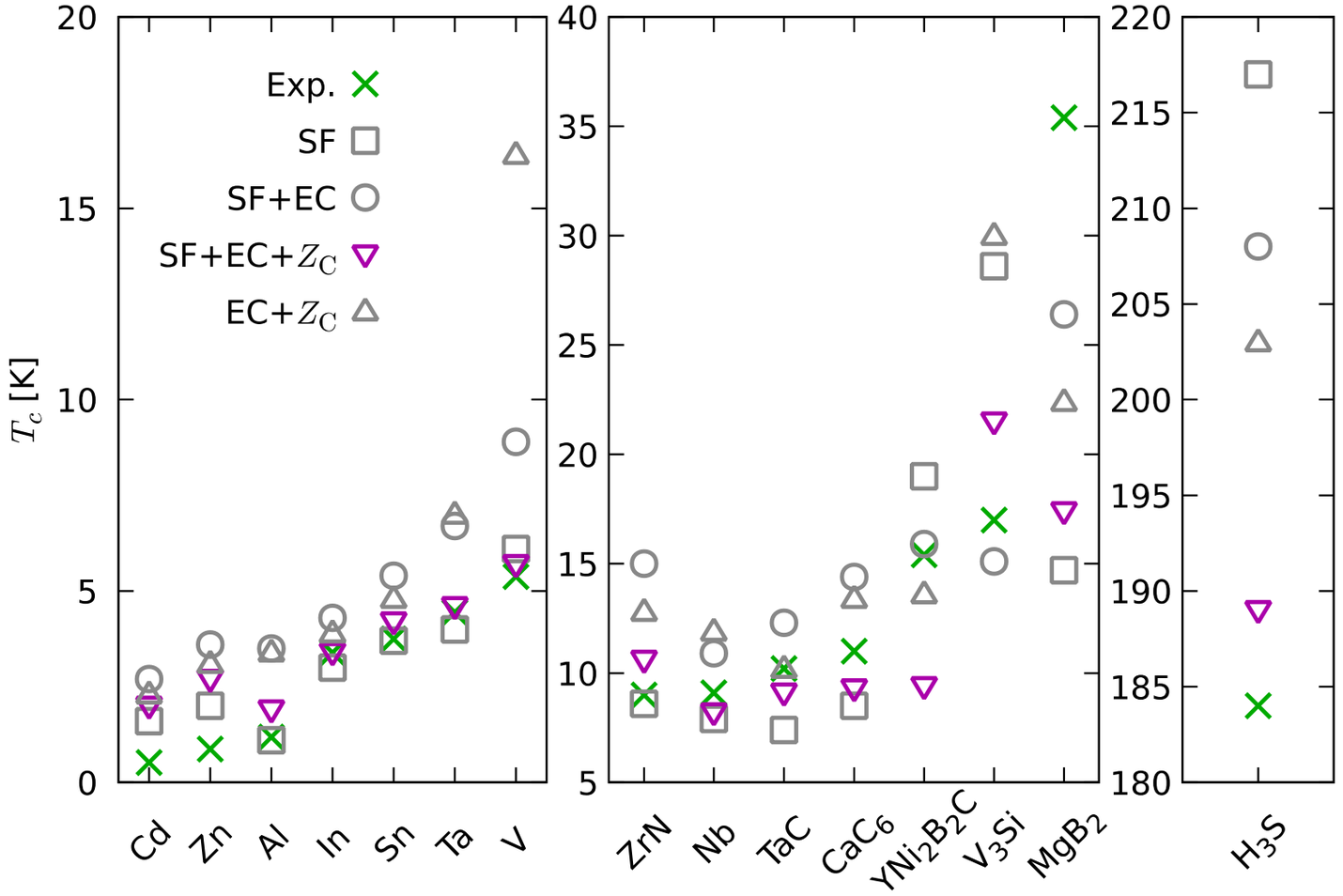
$$\lambda = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu}$$

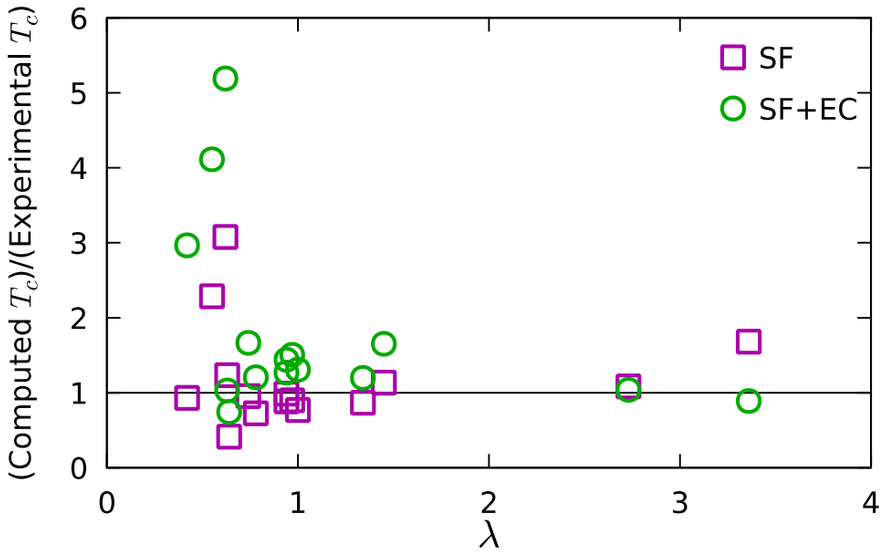
$$\lambda_{\mathbf{q}\nu} = \frac{2}{D(0)\omega_{\mathbf{q}\nu}} \sum_{\mathbf{k}nn'} \left| g^{\nu}_{n\mathbf{k}n'\mathbf{k}+\mathbf{q}} \right|^2 \times \delta(\xi_{n\mathbf{k}})\delta(\xi_{n'\mathbf{k}+\mathbf{q}})$$

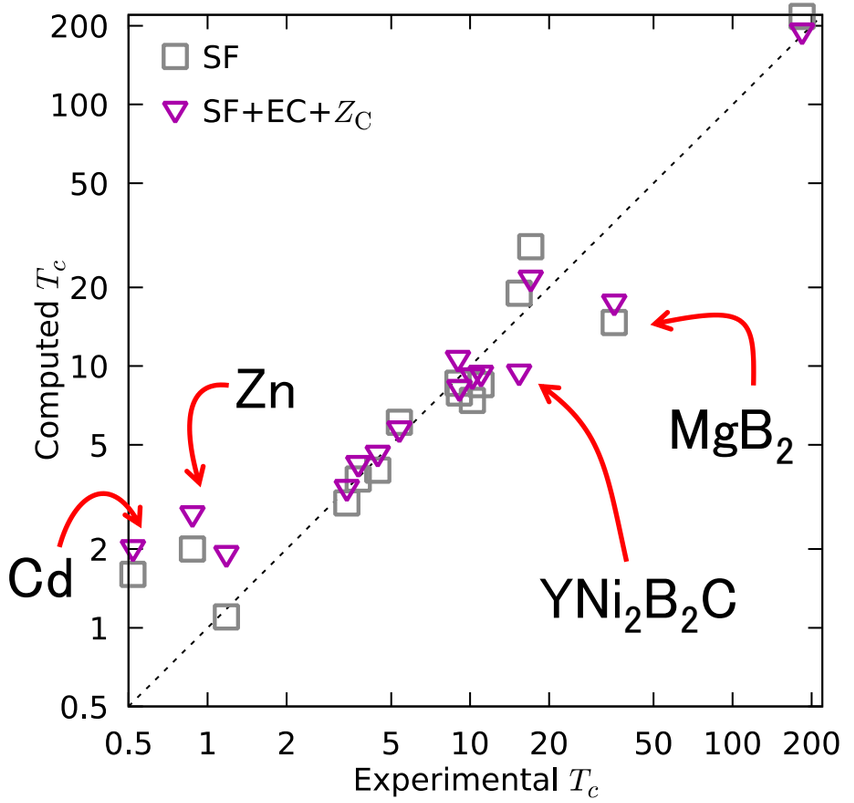
Result

T_c

Z_C : Davydov2020.
EC : Eliashberg-combined (Sanna2020)





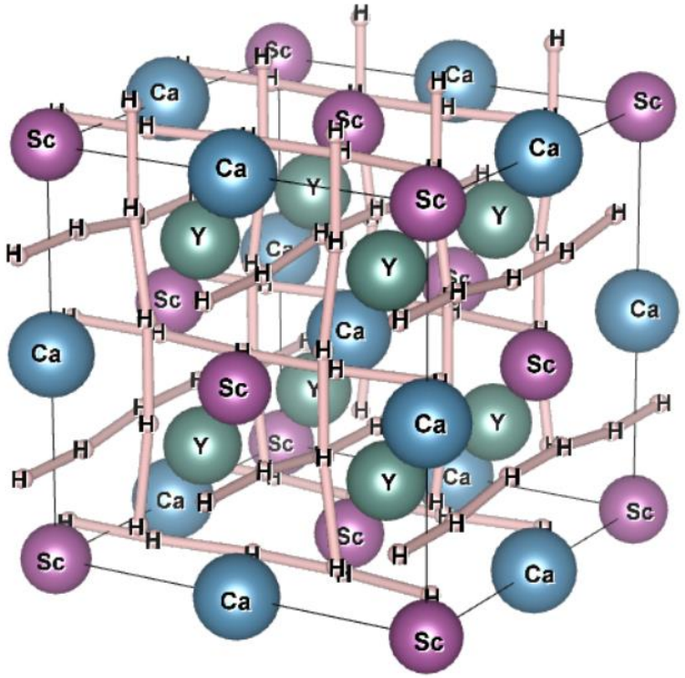


- Eliashberg-combined functional (EC) enhance (reduce) T_c for small (large) λ
- Overestimate T_c for small-T_c systems, and underestimate for materials including boron ?

Result

Prediction of quaternary hydrides

R. Koshoji, M. Fukuda, M. Kawamura, T. Ozaki, Phys. Rev. Materials **6**, 114802 (2022); arXiv:2206.04971.



- Finding new hydride superconductors
- Relatively low pressure (10 GPa)
- 23 compounds found

- Structure prototype by sphere packing
- Insert elements
- Metallic
- Hole-doped
- Less anharmonic

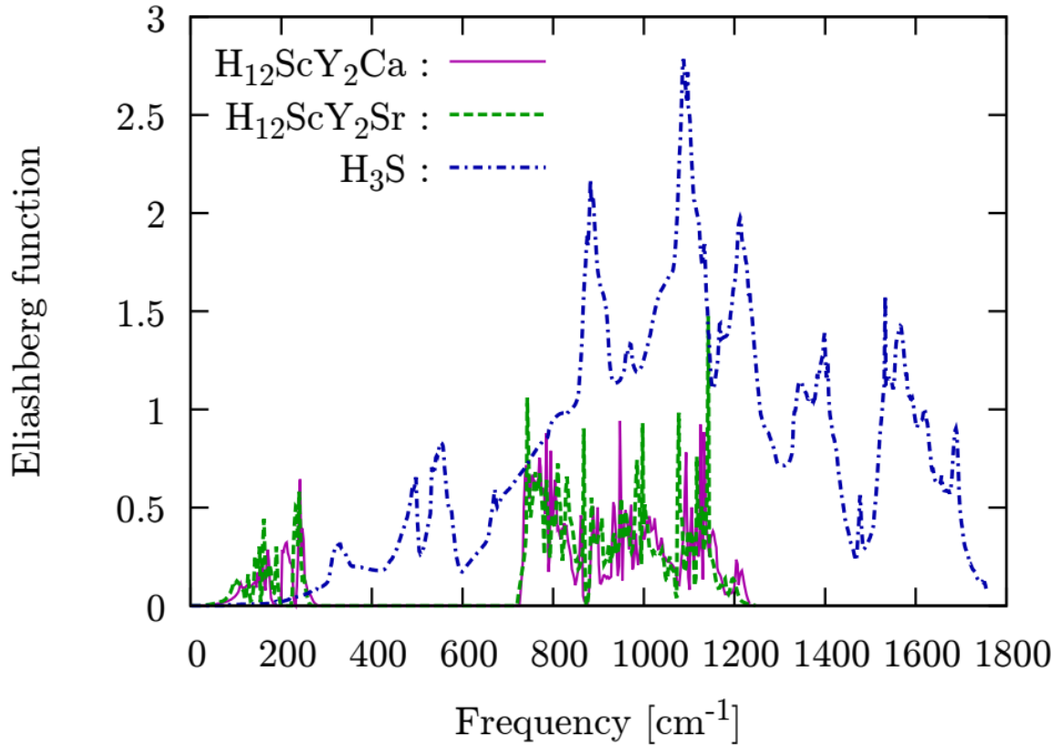
SEFs (eV/f.u.)	Material names	Valence
−12.20	$H_{12}ScY_2La$	±0
−11.87	$H_{12}ScSc_2Y$	± 0
−11.60	$H_{12}ScY_2Zr$	+1
−11.58	$H_{12}ScY_2Hf$	+1
−11.45	$H_{12}ScSc_2Hf$	+1
−11.12	$H_{12}ScY_2Ca$	−1
−11.05	$H_{12}ScY_2Sr$	−1
−10.82	$H_{12}TiY_2Ca$	± 0
−10.78	$H_{12}TiY_2Sr$	± 0
−10.49	$H_{12}ScLa_2Sr$	−1
−10.26	$H_{12}ScLa_2Ba^*$	−1
−10.15	$H_{12}CaZr_2Zr$	+2
−10.15	$H_{12}TiLa_2Sr$	± 0
−10.13	$H_{12}TiSc_2Zr$	+2
−10.12	$H_{12}TiY_2Ba$	± 0
−10.00	$H_{12}TiLa_2Ba$	± 0

Result

Numerical conditions

- Quantum ESPRESSO, DFPT
- 8^3 k-grid, 4^3 q-grid
- WFC cutoff: 60 Ry
- Standard Solid-State Pseudopotential, ultrasoft
- GGA-PBE、Eliiashberg-combined (Sanna2020)、plasmon Z_C、SF

	$H_{12}ScY_2Ca$	$H_{12}ScY_2Sr$	H_3S
DOS [/spin/eV/atom]	0.076	0.079	0.079
λ	0.65	0.68	2.73
$\omega_{\ln}$ [K]	591	550	1248
T_c ($\mu^* = 0.13$)	12.4	13.7	32.1
T_c (no SF)	10.6	11.5	203
T_c (SF)	5.7	6.7	190

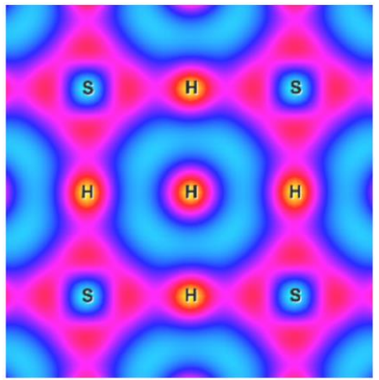


- Relatively low freq.←small pressure
- Why is the el-ph coupling small?
  We can see the shape of electronic states around Femi level (±1eV).

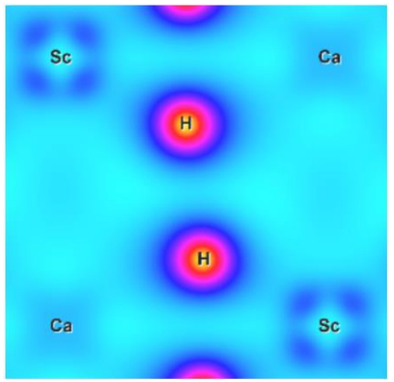
Integrated local density of states (ILDOS)

$$\rho(\mathbf{r}, \varepsilon_F - \Delta, \varepsilon_F + \Delta) \equiv \int_{\varepsilon_F - \Delta}^{\varepsilon_F + \Delta} d\varepsilon \sum_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) |\varphi_{n\mathbf{k}}(\mathbf{r})|^2$$

H_3S



$H_{12}ScY_2Ca$



Summary

Method and Implementation

- We developed method for treating SOI together with SF.
- We applied the formalism of susceptibilities etc. with ultrasoft pseudopotential.
  Especially for the spin-fluctuation integral (new).
- Implemented them to Superconducting-Toolkit (SCTK)

Benchmark for elemental materials

- The calculations, including SOI and SF, reproduce quantitatively the experimental T_cs.
  and absence of the superconductivity in the alkaline, alkaline earth, and noble metals and Sc.
- SF is essential especially for the transition metals, and the effect of SOI is small for elemental systems excepting Tc, Sn, Re, Tl, and Pb.

Benchmark for compounds

Phys. Rev. B **101**, 134511 (2020). arXiv:1911.06481.

- Eliashberg-combined functional (EC) enhance (reduce) T_c for small (large) λ
- Overestimate T_c for small-T_c systems, and underestimate for materials including boron ?

Quaternary hydrides

- We predict new hydride SC. It has weak el-ph because of its ionic nature.