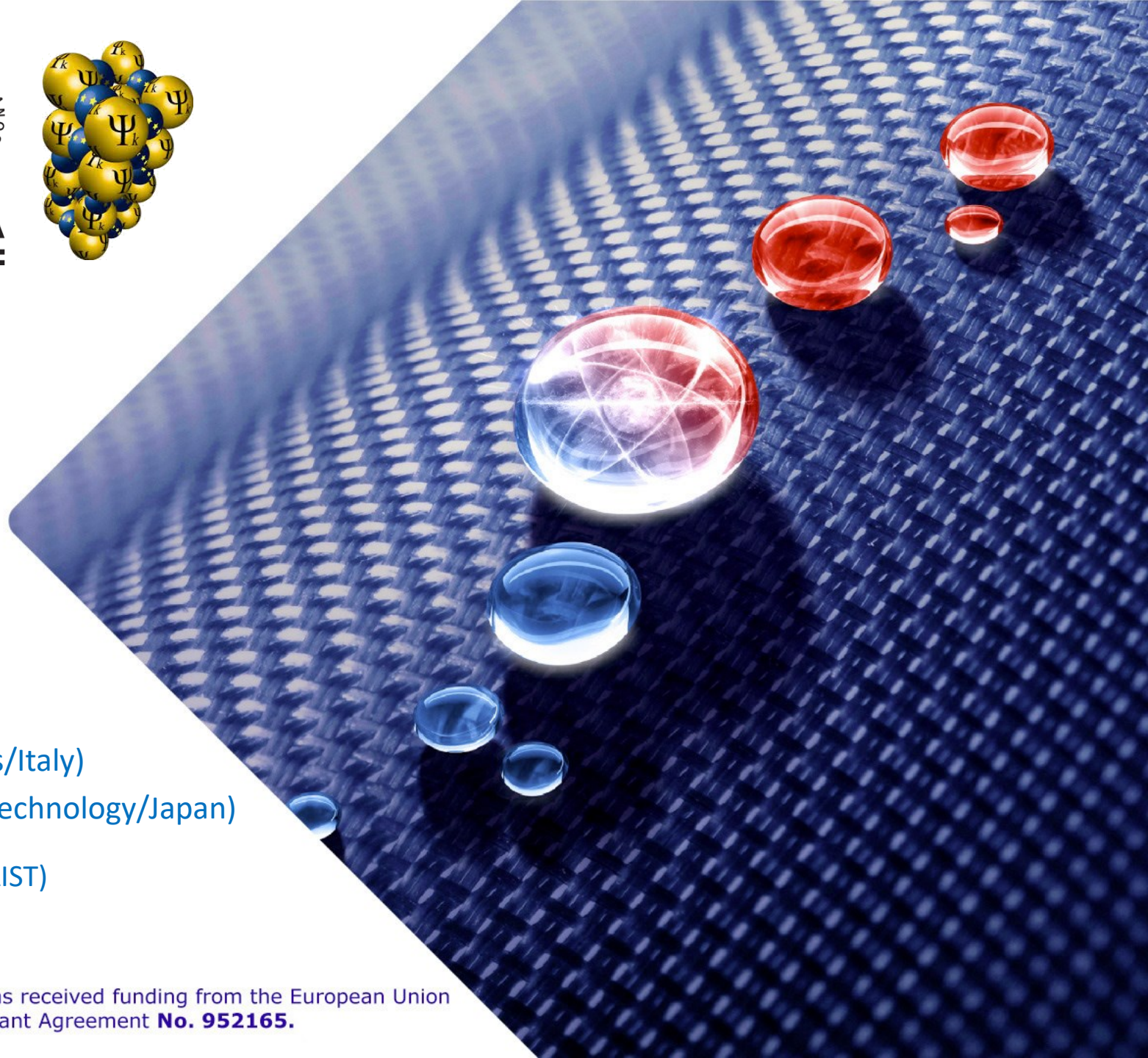
Targeting Real chemical accuracy at the EXascale

SISSA



TurboRVB and Turbo-Genius: Overview and Workflow

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Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizon 2020 research and innovation programme under Grant Agreement **No. 952165.**

Targeting Real chemical accuracy at the EXascale

SISSA

Day5:
- Applications (Phonon dispersion calc.)

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Phonon calculations based on VMC forces.

Phonon calculations play important roles in material science, e.g., for crystal stability.

We need the dynamical Matrix (i.e. the second derivatives of the energies with respect to atomic positions)

- 0. Fitting a Potential Energy Surface.

  Successful in molecules / Not reported for periodic systems.

  A. Zen, J. Chem. Theory Comput. 9, 4332 (2013), Ye Luo, et al. J. Chem. Phys. 141, 194112 (2014).

- 1. Direct evaluation of dynamical matrix (c.f., Linear response in DFT)

  Successful in molecules / Not reported for periodic systems.

  Y.Y.F. Liu et al., J. Chem. Phys. 150, 034104 (2019)

- 2. Finite Difference method (i.e., Frozen phonon)

  Successful in molecules / Not reported for periodic systems.

  A. Zen, J. Chem. Theory Comput. 9, 4332 (2013), Ye Luo, et al. J. Chem. Phys. 141, 194112 (2014).

We have implemented 0. and 2 so far. The strategy 2. was employed for the Diamond calculation.

We used Phonopy for the diamond phonon calculation. A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).

How to choose basis set for Force calc.? (PBC)

TurboRVB employs the CRYSTAL periodic basis for PBC calculations:

$$\psi^{\mathrm{PBC}}_{l,m,I}\left(\mathbf{r};\zeta\right) = \sum_{\mathbf{T}_s} \psi_{l,m,I}\left(\mathbf{r}+\mathbf{T}_s;\zeta\right) e^{-i\mathbf{k}_s\cdot\mathbf{T}_s}$$

-PBC, pseudo potential:

Unfortunately, provided basis sets for open systems are redundant for periodic cases, so we recommend that one should cut several smaller exponents, typically, smaller than 0.10.

-PBC, all-electron:

The same for all-electron cases. Basis sets provided for open systems such as Basis set exchange [https://www.basissetexchange.org] are usually redundant for a periodic case, so we recommend that one should cut several smaller exponents, typically, smaller than 0.10.

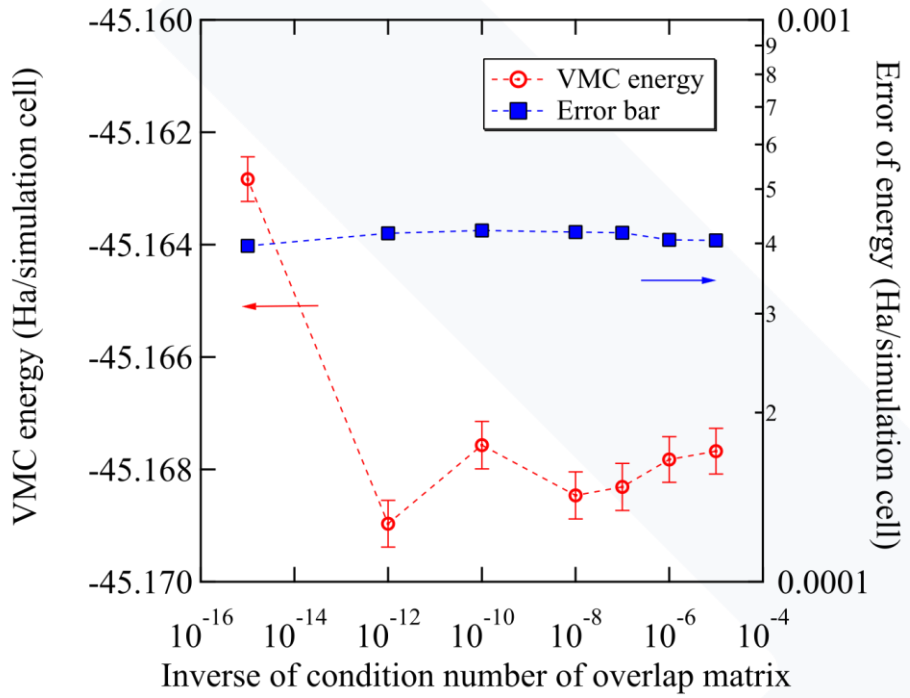
One can also use all-electron basis sets optimized for periodic systems such as ones provided in the CRYSTAL DFT code [https://www.crystal.unito.it/basis-sets.php].

Basis set redundancy for periodic cases

$$\Psi = J \times \Psi_{\mathrm{SD}} \qquad \phi_i^{\mathbf{R}} = \sum_{a,l} c_{i,\{a,l\}} \psi_{\{a,l\}}^{R_a}$$

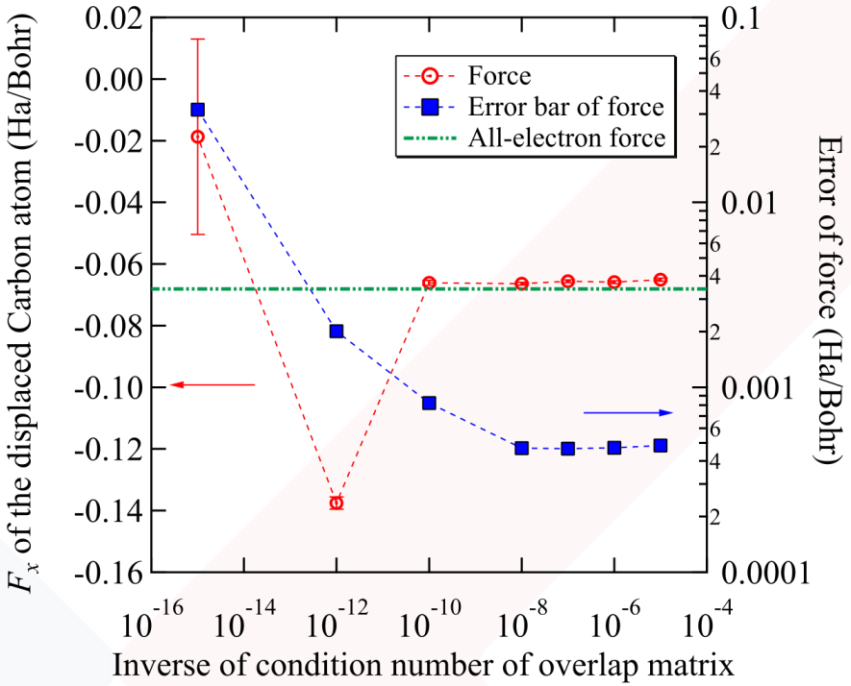
Linear dependency = the condition number of the overlap matrix (S).

- Diamond: Total Energy (E)

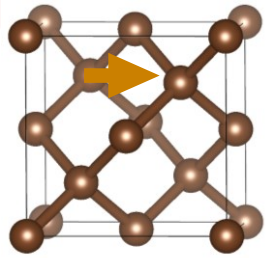


Large <- Lin. Dep. -> Small

- Diamond: Force (F)



Large <- Lin. Dep. -> Small



Only one C is displaced

"epsover" in prep.

K. Nakano *et al.*, ***Phys. Rev. B*** 103, L121110 (2021)

$$F_\alpha = \langle \frac{dE}{dR_\alpha} \rangle_{|\Psi^{\mathbf{R}}|^2} \simeq \langle \frac{E(\mathbf{R}+\Delta\mathbf{R}_\alpha) - E(\mathbf{R})}{\Delta R_\alpha} \rangle_{|\Psi^{\mathbf{R}}|^2},$$

By the algorithmic differentiation method.

- The method assumes that the WF does not change much as the atom is displaced.
- We confirmed that the linear dependency of the basis set deteriorated the overlap.

$$\langle \Psi^{\mathbf{R}+\Delta\mathbf{R}_\alpha} | \Psi^{\mathbf{R}} \rangle$$

$$\Delta\mathbf{R}_\alpha = 0.005\text{Bohr}$$

1.000 (Linear independent case)

0.973 (Linear dependent case)

K. Nakano *et al.*, *Phys. Rev. B* 103, L121110 (2021)

Energy derivative v.s. Force

$$\frac{dE}{dR_\alpha} = \langle \frac{\partial}{\partial R_\alpha} E_L \rangle + 2(\langle E_L \frac{\partial}{\partial R_\alpha} \log \Psi \rangle - \langle E_L \rangle \langle \frac{\partial}{\partial R_\alpha} \log \Psi \rangle)$$

$$+ \sum_{i=1}^{N_{\mathrm{par}}} \frac{\partial E}{\partial c_i} \frac{\partial c_i}{\partial R_\alpha}$$

Additional terms!!

JSD ? $\phi_i^{\mathbf{R}} = \sum_{a,l} c_{i,\{a,l\}} \psi_{\{a,l\}}^{R_a}$

1. The system is already at a variational minimum. $\frac{\partial E}{\partial c_i} = 0$ → JAGPs ○

2. The variational parameters are not allowed to vary with changing the atomic pos. $\frac{\partial c_i}{\partial R_\alpha} = 0$

J. Tiihonen et al., ***J. Chem. Phys.*** 154, 204111 (2021)

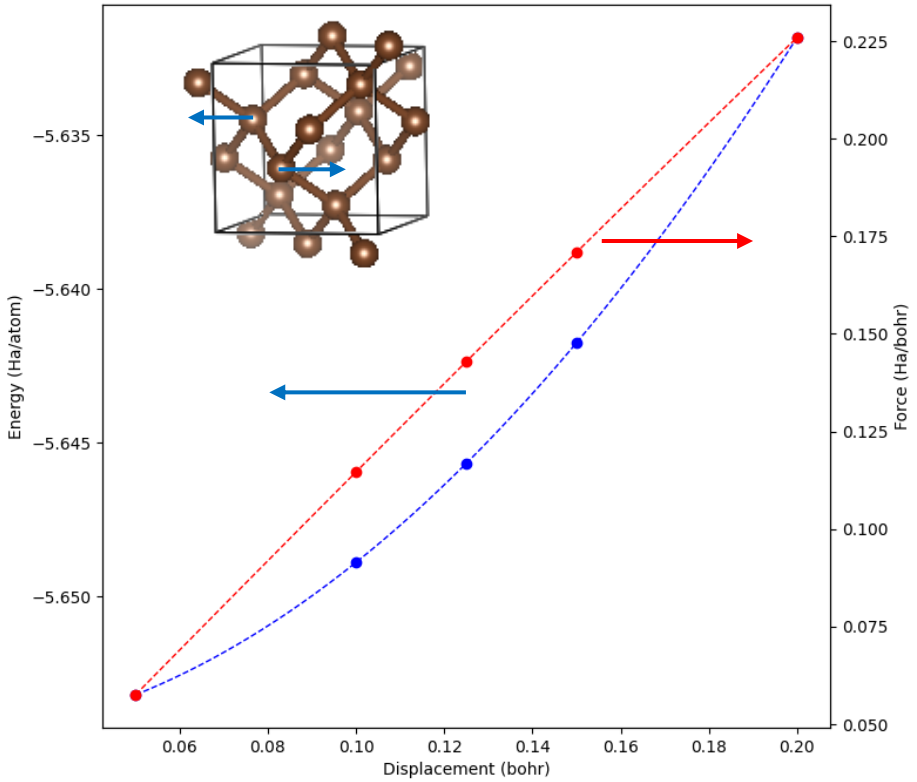
Diamond: PES v.s. Force

Phonon vib. at Gamma point T_{3g}

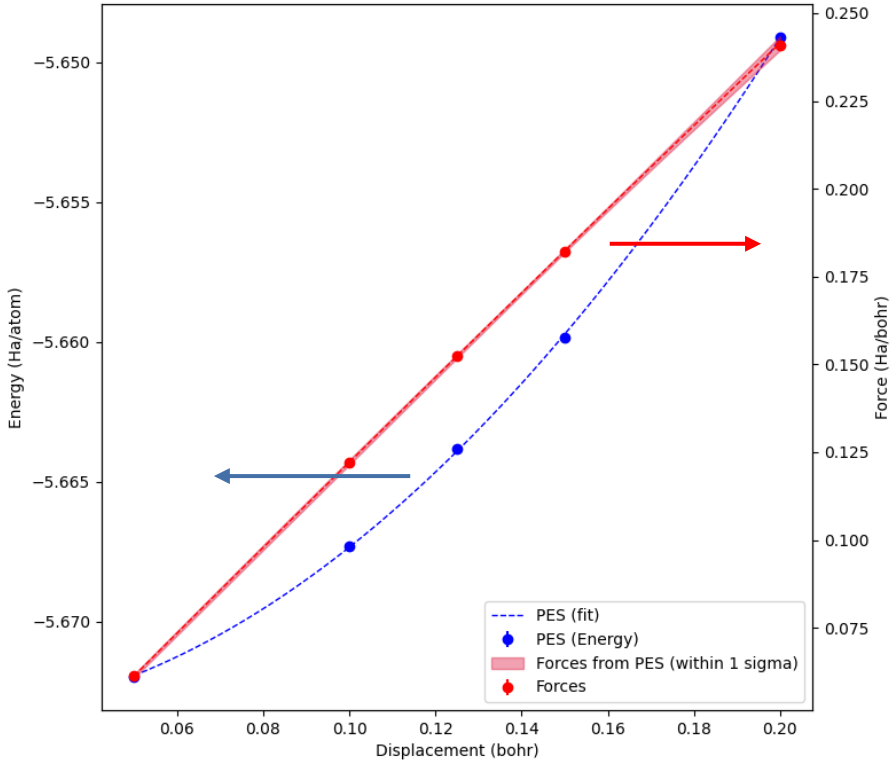
D. Vanderbilt, et al., Phys. Rev. Lett. 53, 1477 (1984).

σ symmetry remains. => only F_x

$1 \times 1 \times 1$ supercell = 8 atoms $k = \pi, \pi, \pi$



DFT (Quantum Espresso)

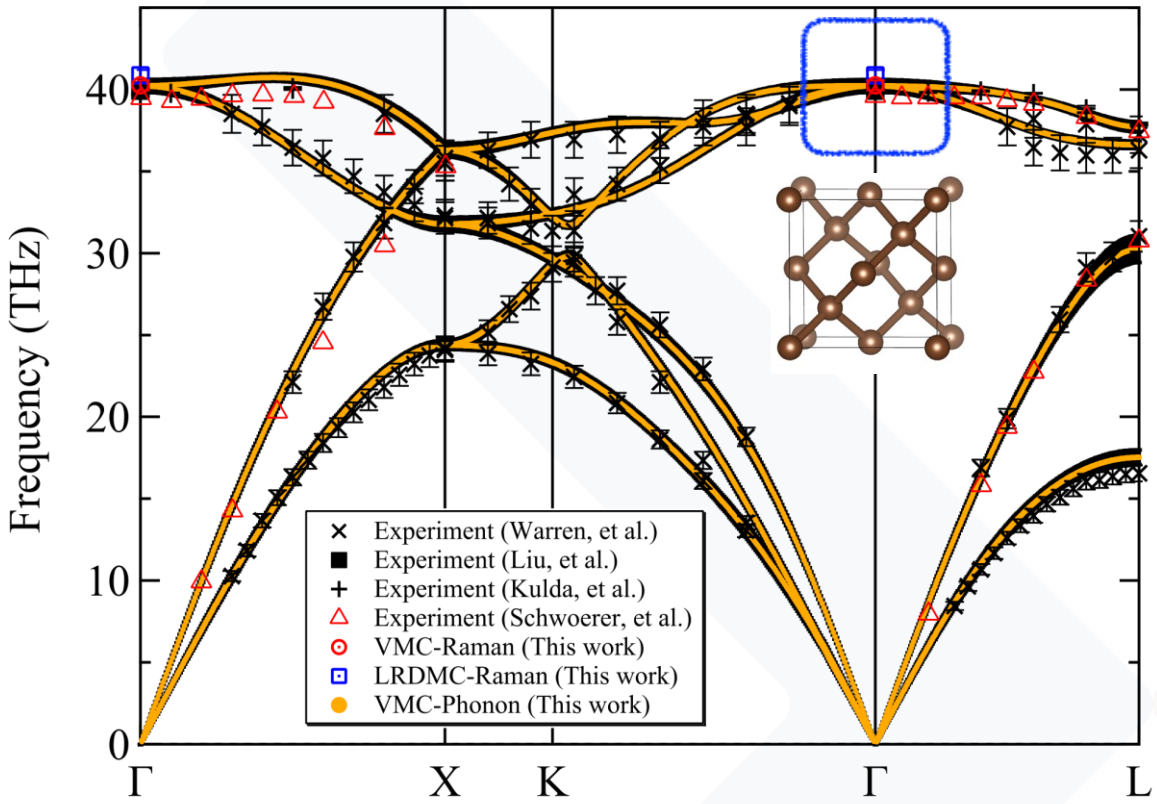


VMC-JDFT (TurboRVB)

Recent progress: Phonon dispersion calculations

- Diamond: the conventional 2x2x2 supercell with the experimental lattice parameter
- The frozen phonon method implemented in Phonopy package.

A. Togo and I. Tanaka, *Scr. Mater.* 108, 1 (2015).



* including anharmonic corrections.

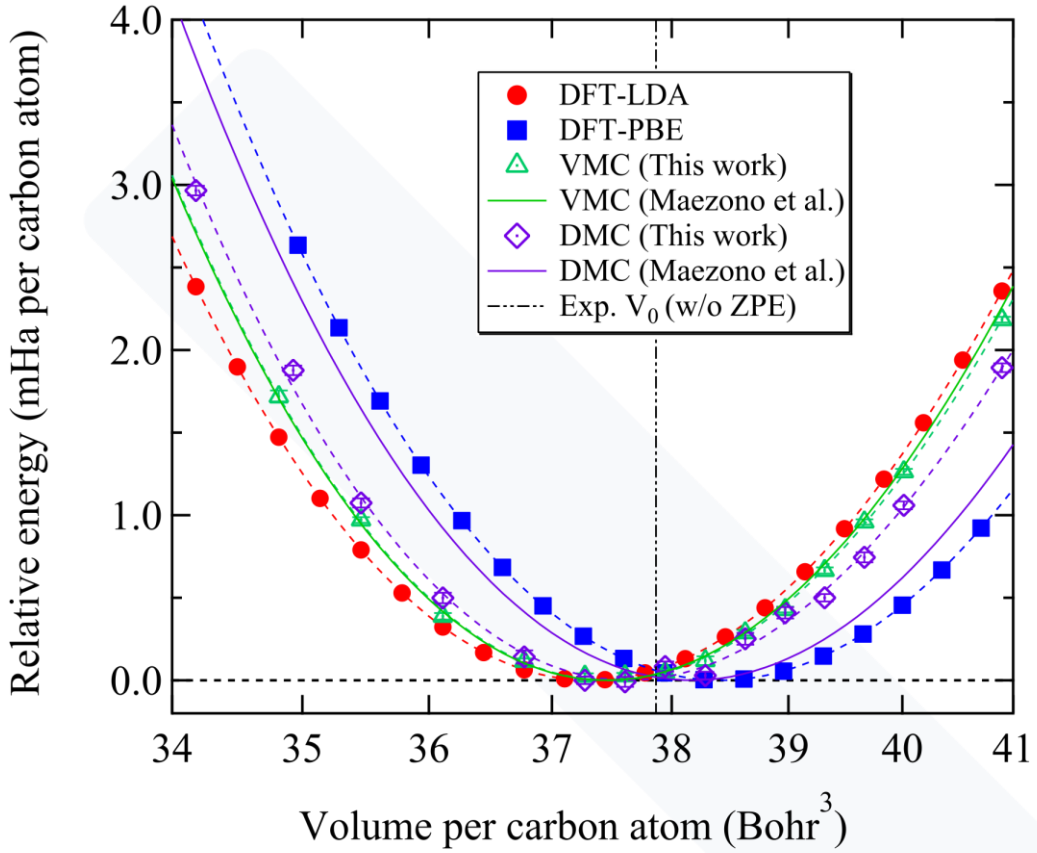
Raman Freq. (optical phonon at Γ)

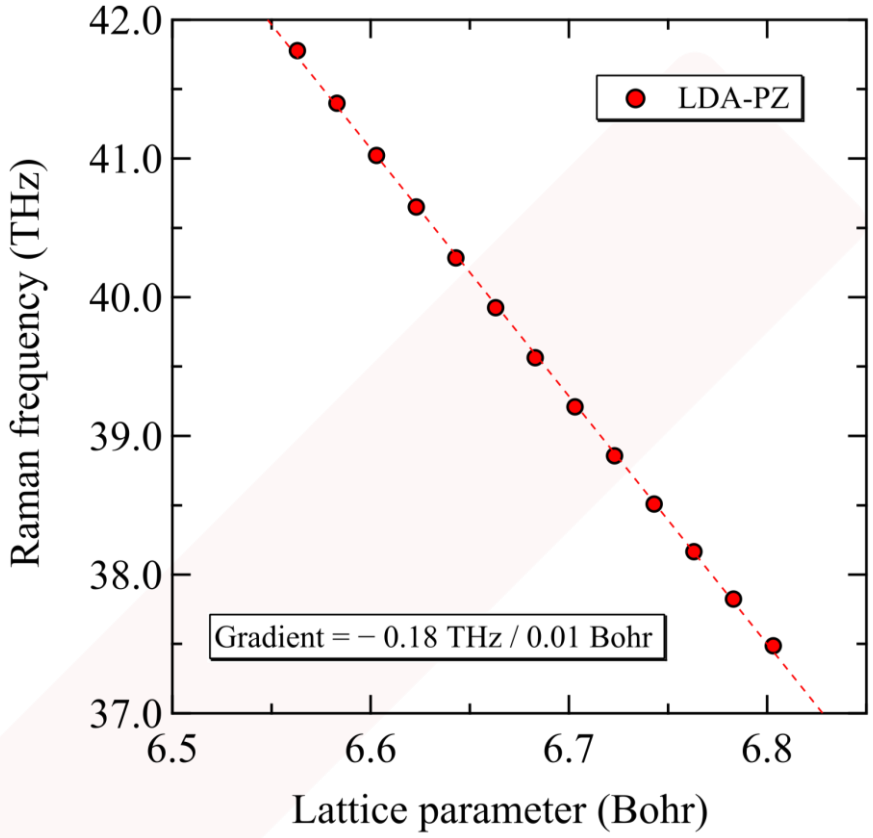
DFT-LDA	38.55 THz
VMC	40.65(38) THz
Exp.	40.35 THz

** These are harmonic frequencies

K. Nakano *et al.*, ***Phys. Rev. B*** 103, L121110 (2021)

Equation of State





Future work: the nodal surface optimization could solve the discrepancy at the (LR)DMC level.

K. Nakano *et al.*, *Phys. Rev. B* 103, L121110 (2021)

Limitations and future works

- Semiconductors with more than 2 elements (i.e., the LO-TO splitting effect is not taken into consideration)

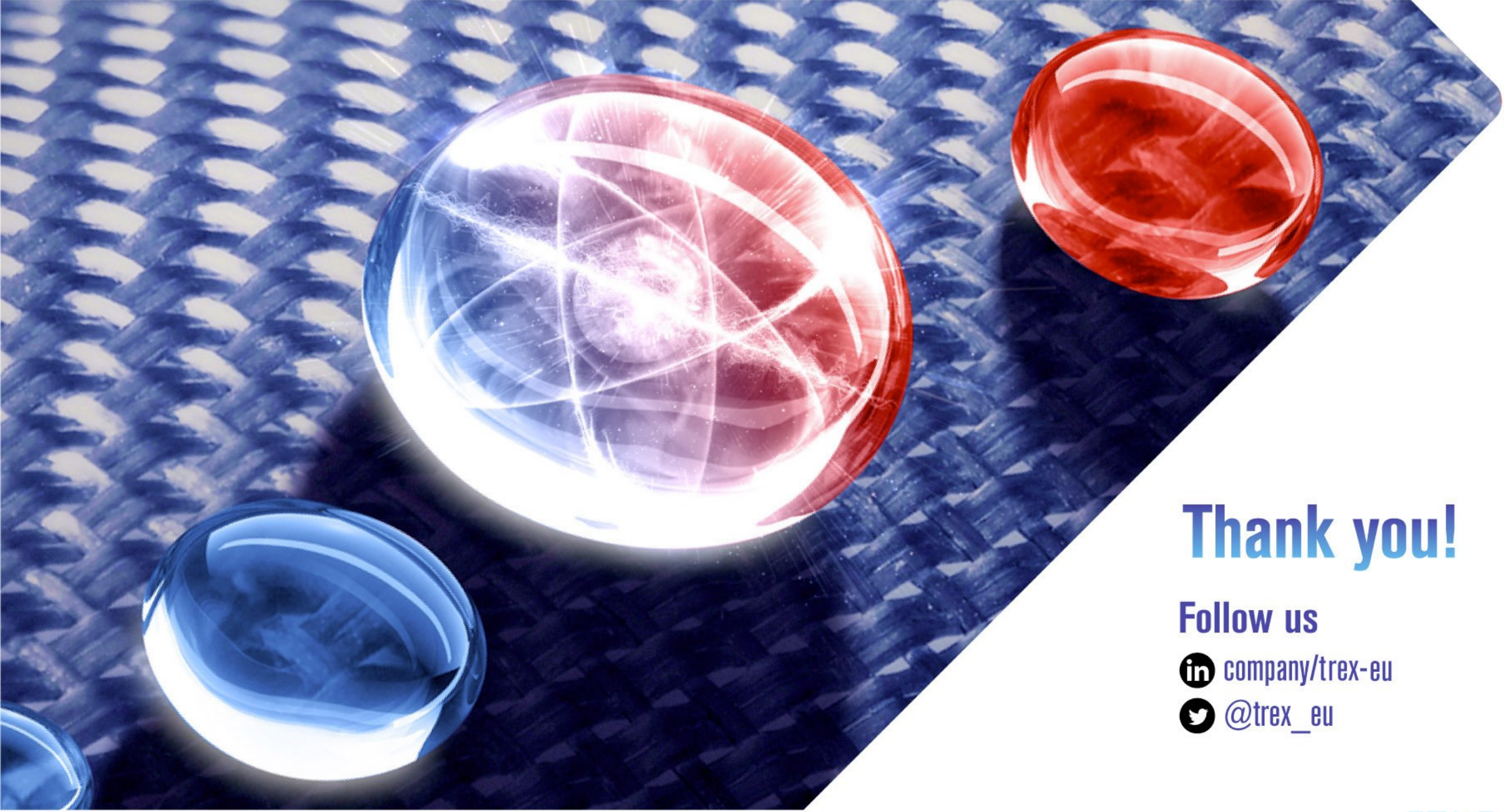
- We should be careful about compounds that have the degree of freedoms in their atomic (Wycoff) positions.

  i.e., we should search for equilibrium positions at the VMC level before a phonon calculation.

- The anharmonic effect is not taken into consideration.

- Turbo-Genius is under refactoring.

K. Nakano *et al.*, *Phys. Rev. B* 103, L121110 (2021)



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