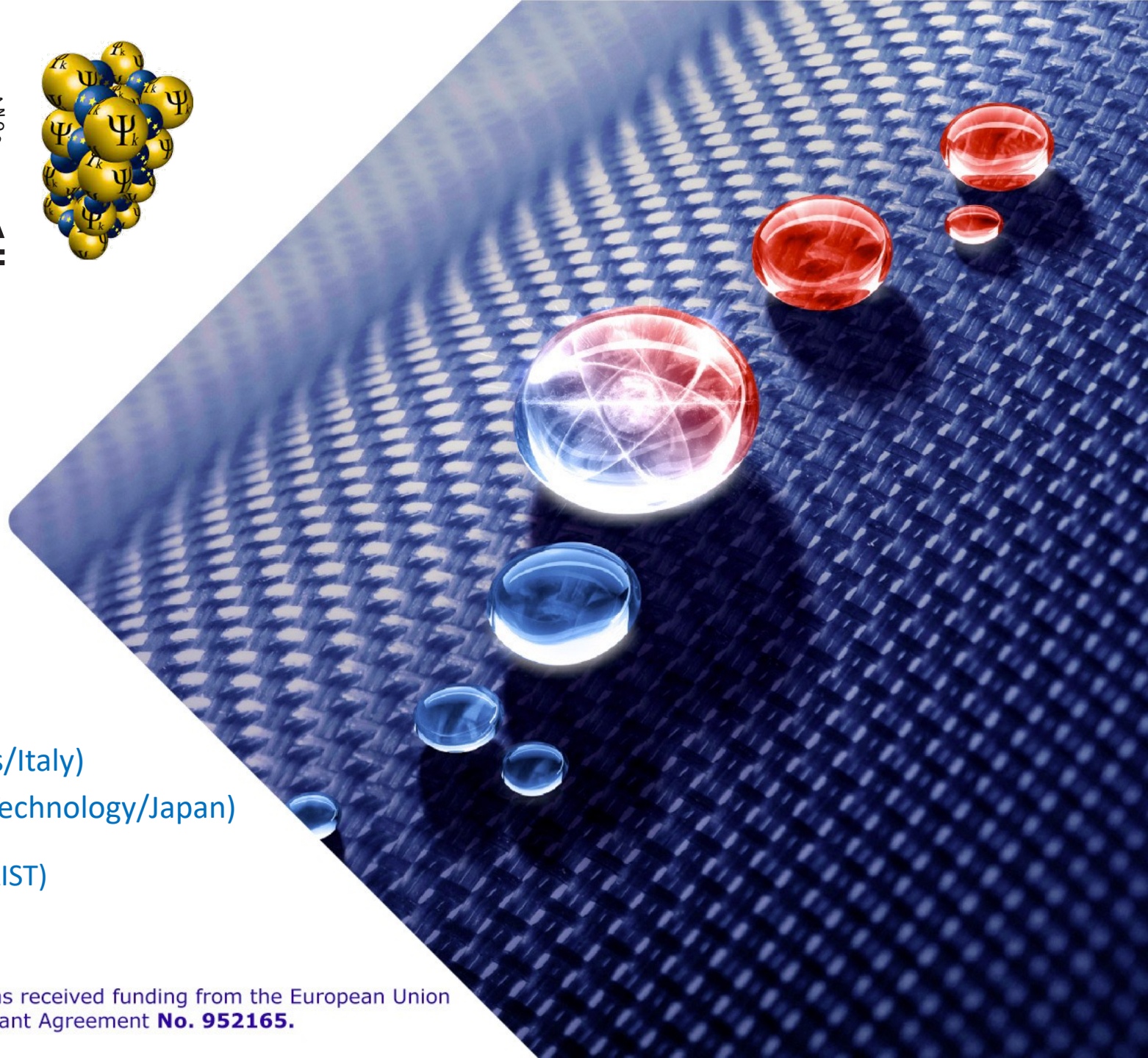
Targeting Real chemical accuracy at the EXascale

SISSA



# TurboRVB and Turbo-Genius: Overview and Workflow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(Prof. Sorella group/SISSA)  (Prof. Maezono group/JAIST)



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

# Day3:
# - Single-shot VMC
# - VMC force

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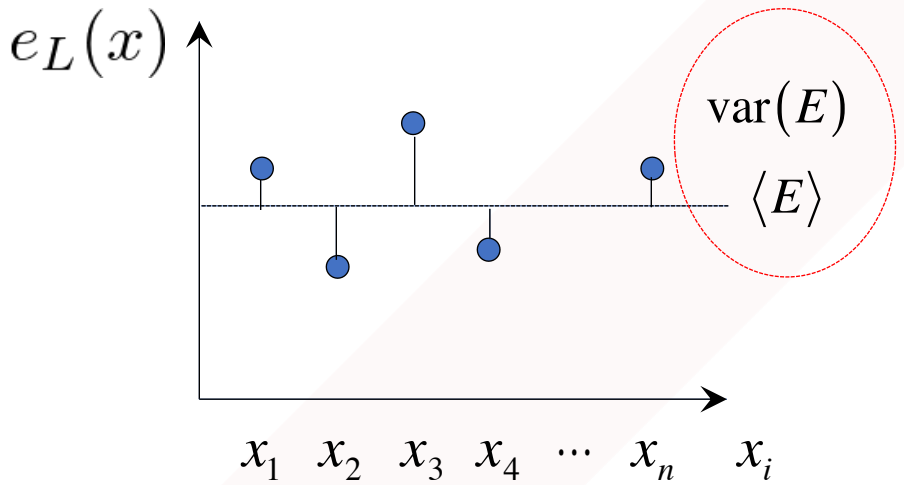
# VMC input file

```
&simulation
    itestr4=2
    ngen=10000
    maxtime=10800
    iopt=1
/

&pseudo
/

&vmc
    !epscut=0.0
/

&readio
    !iread=3
/

&parameters
    !ieskin=1
/
```

One-shot VMC




=

ngen × nw

ngen is the total number of Monte Carlo steps.

Default: nw is the number of MPI processes.

# All information

```python
from scipy.io import FortranFile
import numpy as np

# check length of fort.12
f = FortranFile('fort.12', 'r')
a = f.read_reals(dtype='float64')
column_length = len(a)
f.close()

# start reading fort.12
head = ("head", "<i")
tail = ("tail", "<i")
dt = np.dtype([head, ("a", "<{}d".format(column_length)), tail])
fd = open('fort.12', "r")
fort12 = np.fromfile(fd, dtype=dt, count=-1)
data_length=len(fort12)
fd.close()
# end reading fort.12

print(fort12)
```

```
# for ngen=10
>>> fort12
array([(40, [  1.        ,   1.        , -11.23924971, -11.23924971, 126.32073395], 40),
       (40, [  1.        ,   1.        , -11.4465321 , -11.4465321 , 131.02309712], 40),
       (40, [  1.        ,   1.        , -11.25058355, -11.25058355, 126.57563015], 40),
       (40, [  1.        ,   1.        , -11.88021352, -11.88021352, 141.13947319], 40),
       (40, [  1.        ,   1.        , -10.89686295, -10.89686295, 118.74162225], 40),
       (40, [  1.        ,   1.        , -11.8906161 , -11.8906161 , 141.38675112], 40),
       (40, [  1.        ,   1.        , -10.50040878, -10.50040878, 110.25858451], 40),
       (40, [  1.        ,   1.        , -10.85804034, -10.85804034, 117.89704005], 40),
       (40, [  1.        ,   1.        , -11.3042634 , -11.3042634 , 127.78637111], 40),
       (40, [  1.        ,   1.        , -10.86745849, -10.86745849, 118.10165397], 40)],
      dtype=[('head', '<i4'), ('a', '<f8', (5,)), ('tail', '<i4')])
```

e(L), etc… -> written in fort.12

# Reblocking

forcevmc.sh “bin”, “init”, “pulay”, or
turbo-genius.sh –j vmc -post -reb “bin”, -eq “init”

“bin”: the length of reblocking size

“init”: the length of equilibration steps (init * bin)

“pulay”: the ratio of the pulay term (1 is OK)

pip0.d=energy

```
#cat pip0.d

number of bins read =        1496
Energy =  -1.1379192772188327        1.7589095174214898E-004
Variance square =   1.7369139136828382E-003   2.7618833870090571E-005
Est. energy error bar =   1.7510470092362484E-004   3.9800256121536918E-006
Est. corr. time  =   2.6420266523220208       0.10738159557488412
```

forcevmc.dat=forces

```
Force component 1
Force    =  6.004763869201490E-003  4.997922374161991E-005
6.273565633363322E-007
Der Eloc =  6.927675852724724E-003  4.999242839793062E-005
<OH> =  0.557134685159244       7.437283601136703E-005
<O><H> = -0.557596141151006       7.447559481785158E-005
2*(<OH> - <O><H>) = -9.229119835232336E-004  2.922997214772288E-006
```

# General features

(i) It employs the Resonating Valence Bond (RVB) WF that includes static and dynamical correlation effects beyond the commonly used Slater determinant, while keeping the computational cost at the single-determinant level.

(ii) The code implements a VMC algorithm based on localized orbitals (e.g., Gaussians) and state-of-the-art optimization methods, such as the stochastic reconfiguration. Therefore, at the VMC level, one can optimize not only the amplitude of the WF (i.e., the Jastrow factor), but also the nodal surfaces (e.g., the Slater determinant). This leads to a better variational energy in general, and also improves the corresponding FN-DMC energy.

(iii) The energy derivatives (e.g., atomic forces) are calculated very efficiently thanks to an implementation based on the Adjoint Algorithmic Differentiation (AAD). As a consequence, one can perform structural optimizations and Langevin molecular dynamics.

(iv) The code implements the newly developed Lattice Regularized Diffusion Monte Carlo (LRDMC), a stable DMC algorithm that, very recently, has shown to have a better scaling with the atomic number Z, compared with standard DMC.

K. Nakano, C. Attaccalite, M. Barborini, L. Capriotti, M. Casula, E. Coccia, M. Dagrada, Y. Luo, G. Mazzola, A. Zen, and S. Sorella, ***J. Chem. Phys.*** 152, 204121 (2020)

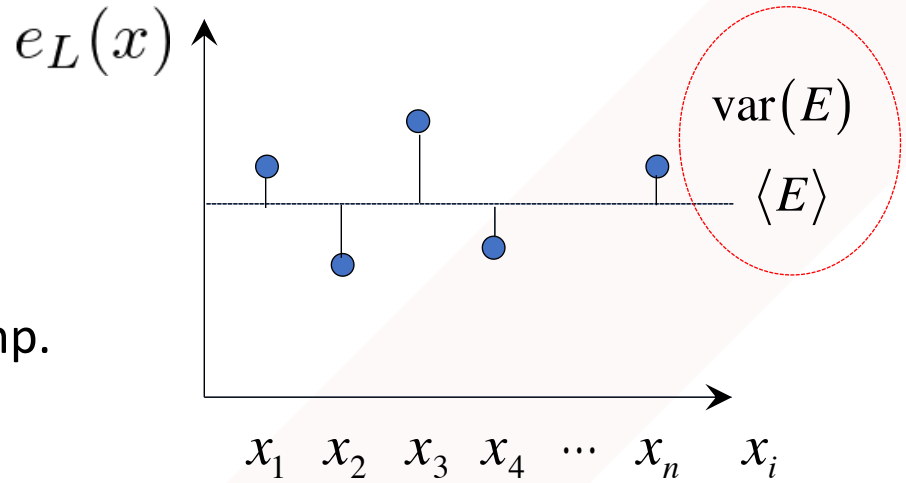
# VMC input file

```
&simulation
    itestr4=2
    ngen=10000
    maxtime=10800
    iopt=1
/

&pseudo
/

&vmc
    !epscut=0.0
/

&readio
    !iread=3
/

&parameters
    !ieskin=1
/
```

epsilon for a finite-variance samp.

Force!!

One-shot VMC




=

ngen × nw

ngen is the total number of Monte Carlo steps.

Default: nw is the number of MPI processes.

Ionic Forces:

```
# Constraints for forces: ion - coordinate
          1      1      3
```

# The number of forces, atom index, direction

F1,z for the first atom will be calculated.

```
# Constraints for forces: ion - coordinate
          2      1      1      2      -3
```

F1,x and F2,z will be calculated, assuming, F = F1,x = - F2,z.

The output value (forcevmc.dat) is the sum of two forces, i.e., (F = F1,x - F2,z. )

If you want to calculate forces, please set “ieskin=1” in the &parameter section in your VMC input.

forcevmc.dat=forces

```
Force component 1
Force    =  6.004763869201490E-003  4.997922374161991E-005
6.273565633363322E-007
Der Eloc =  6.927675852724724E-003  4.999242839793062E-005
<OH> =  0.557134685159244       7.437283601136703E-005
<O><H> = -0.557596141151006       7.447559481785158E-005
2*(<OH> - <O><H>) = -9.229119835232336E-004  2.922997214772288E-006
```

Force (total) $$F_\alpha = -\langle \frac{d}{d\mathbf{R}_\alpha} E_L \rangle - 2 \left( \langle E_L \cdot \frac{d}{d\mathbf{R}_\alpha} \log(J^{1/2}\Psi) \rangle - \langle E_L \rangle \cdot \langle \frac{d}{d\mathbf{R}_\alpha} \log(J^{1/2}\Psi) \rangle \right),$$

Der Eloc: (Hellmann-Feynman term)

2*(<OH> - <O><H>) (Pulay term)

where, J is the Jacobian of the warp transformation. S Sorella, L Capriotti, ***J. Chem. Phys.*** 133, 234111 (2010).

```
# Constraints for forces: ion - coordinate
          2      1      1      2      -3
```

The output value (forcevmc.dat) is the sum of two forces, i.e., (F = F1,x - F2,z. )

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

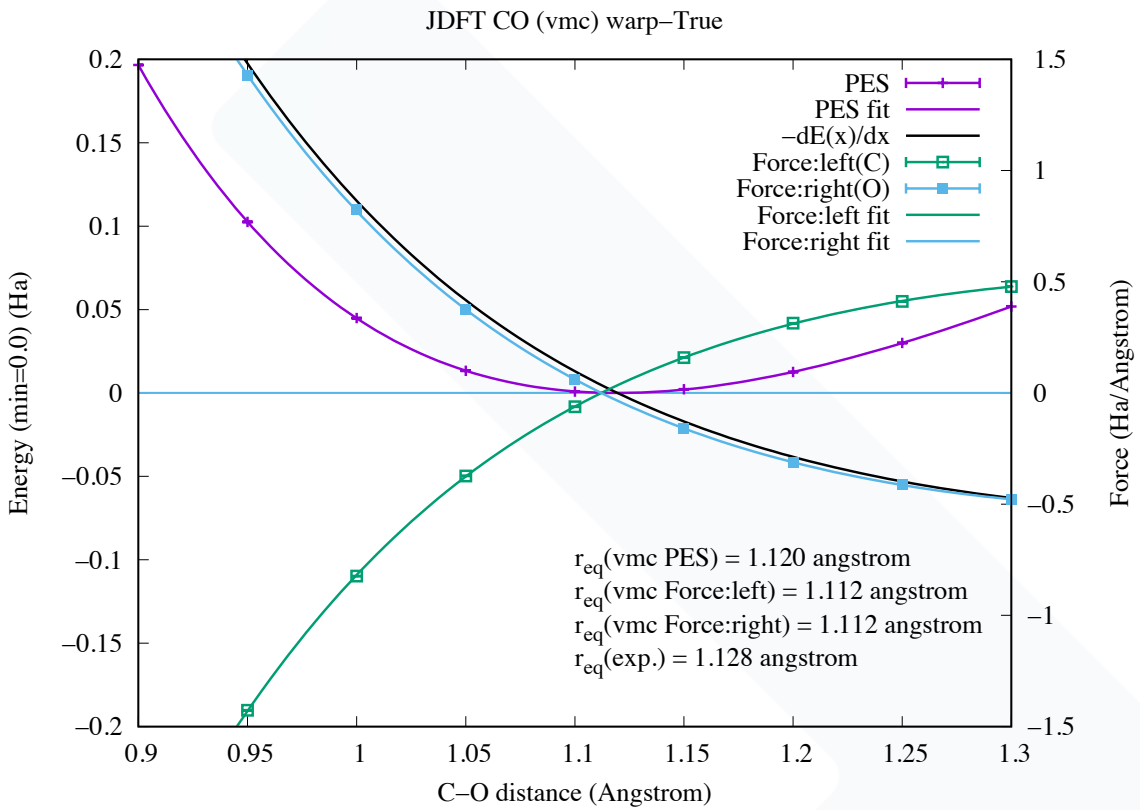
1. The system is already at a variational minimum. $\frac{\partial E}{\partial c_i} = 0$ → JAGPs ○

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

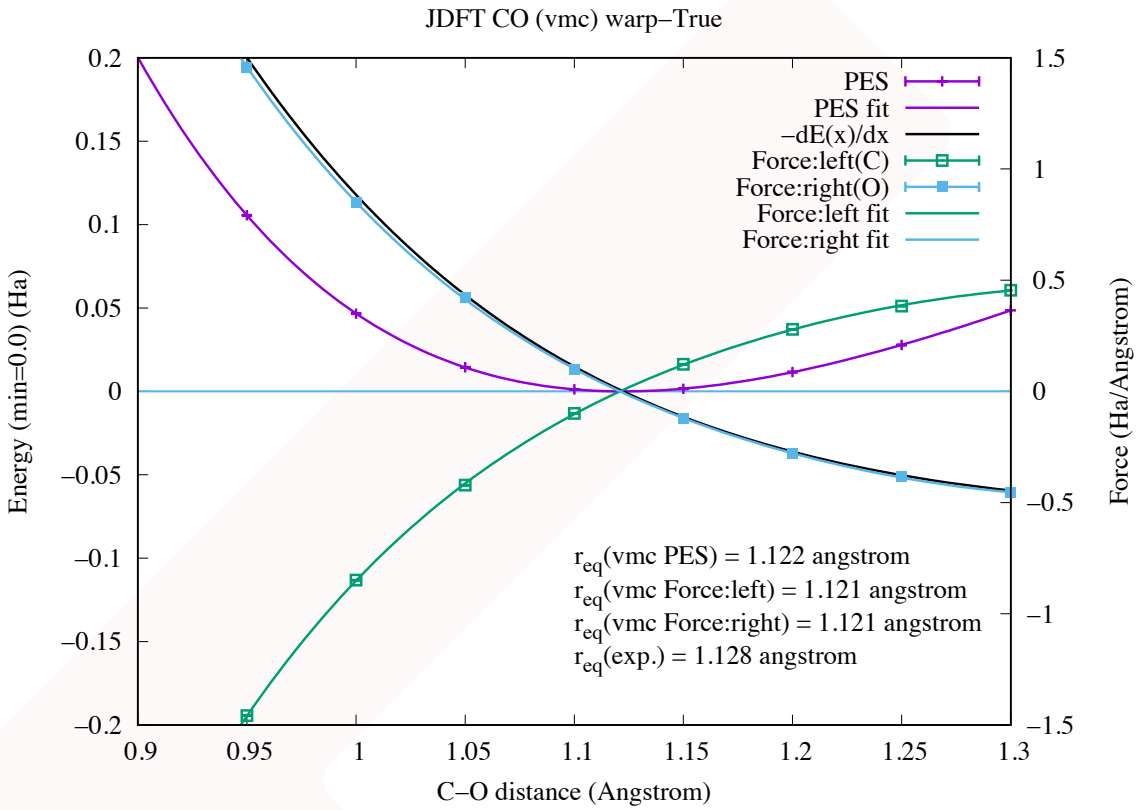
J. Tiihonen et al., ***J. Chem. Phys.*** 154, 204111 (2021)

# Carbon monoxide: PES v.s. Force

All-electron calculations, VMC (**JDFT**). Jastrow factors were optimized for each C-O distance.




Basis = cc-pVDZ




Basis = cc-pVQZ

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

TurboRVB employs the CRYSTAL periodic basis for PBC calculations:

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

-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.

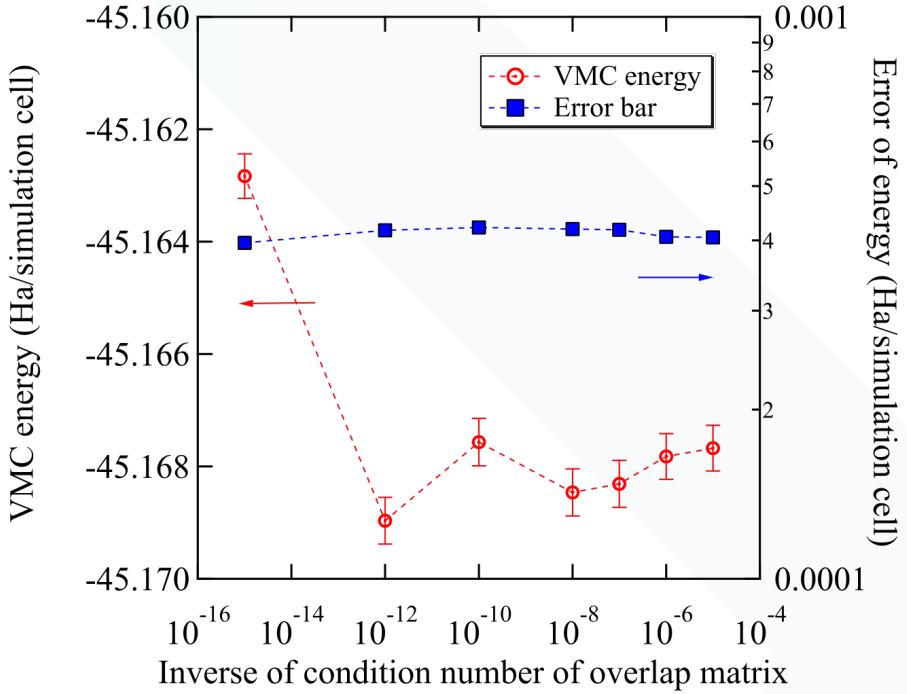
One can also use all-electron basis sets optimized for periodic systems such as ones provided in the CRYSTAL DFT code [https://www.crystal.unito.it/basis-sets.php].

# Basis set redundancy for periodic cases

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

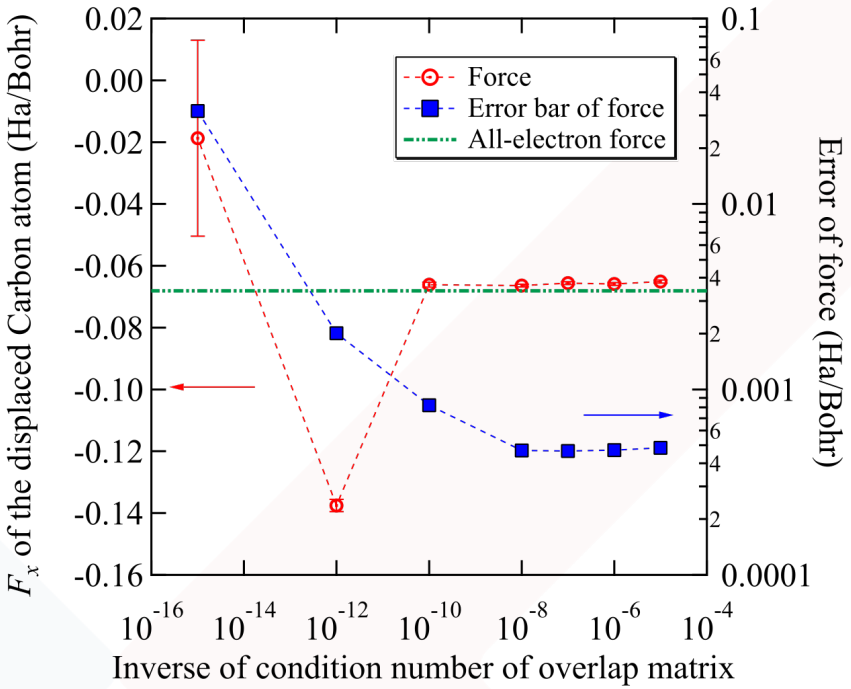
Linear dependency = the condition number of the overlap matrix (S).

- Diamond: Total Energy (E)

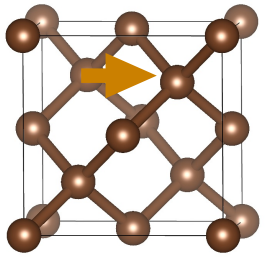



Large <- Lin. Dep. -> Small

- Diamond: Force (F)




Large <- Lin. Dep. -> Small



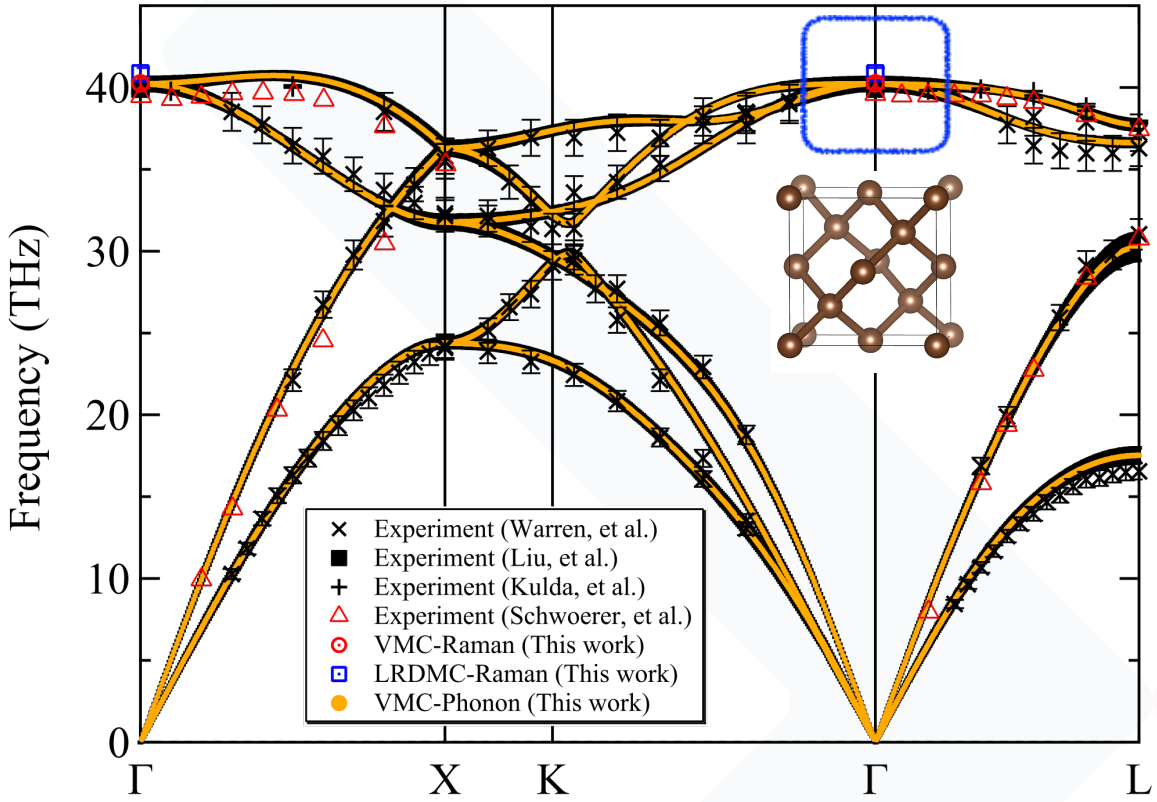
Only one C is displaced

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

# 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.

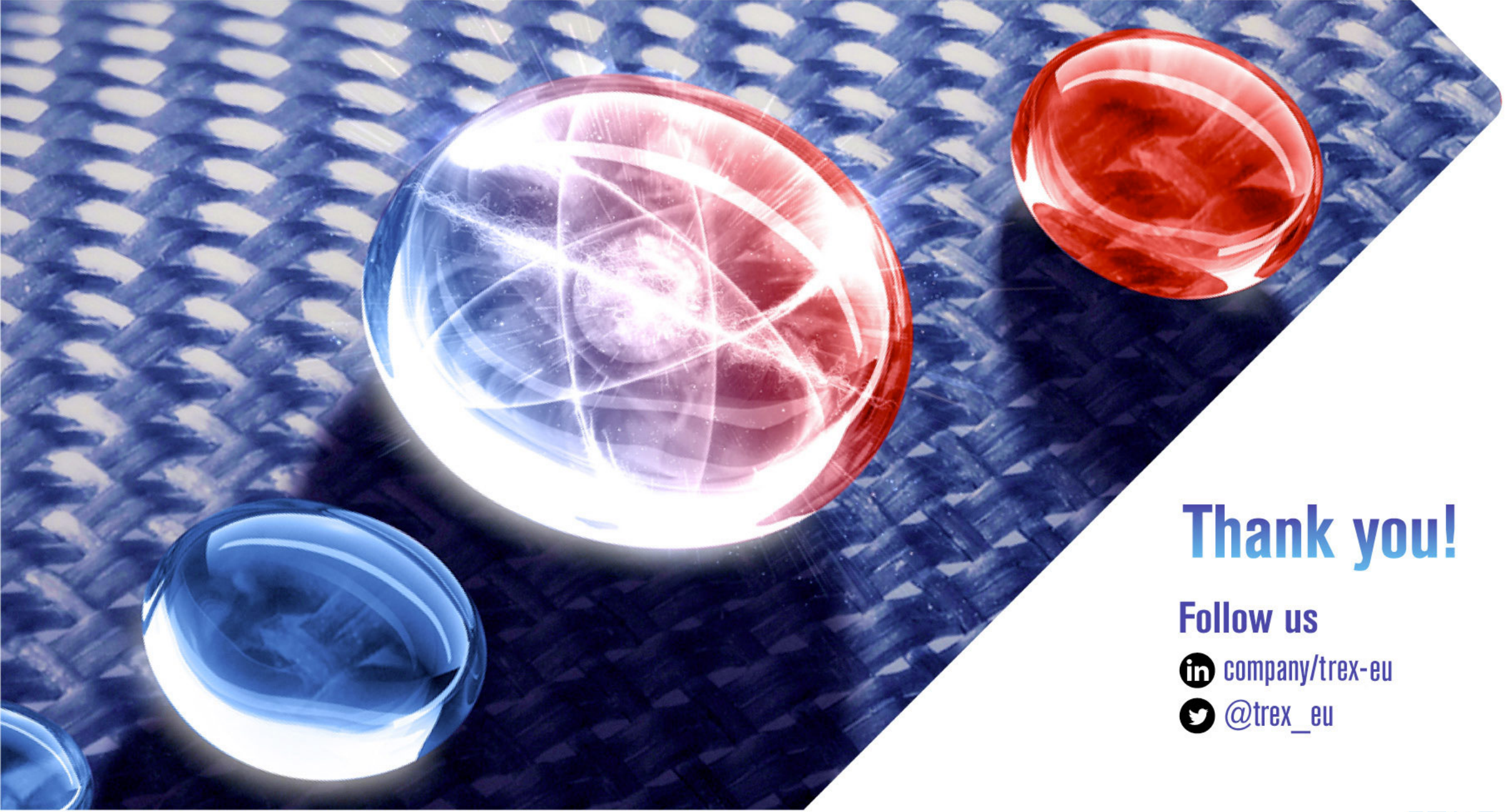
Raman Freq. (optical phonon at Γ)

| | |
|---|---|
| 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)

| | | Ansatz Level | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | JDFT | | | | JsAGPs | | | | JAGPu | | | | | JAGP(JPf) | | | |
| 1. $H_2$-dimer | $H_2$ | 01 DFT Day1 | 02 VMCo Day2,3 | 03 VMC Day3 | 04 DMC Day4 | 06 Conv. Day2 | 08 VMCo Day2,3 | 09 VMC Day3 | 10 DMC Day4 | NA | | | | | NA | | | |
| 2. $C_2$-dimer | $C_2$ | 01-01 01-05 DFT Day1 | 01-06 VMCo Day2,3 | 01-07 VMC Day3 | 01-08 DMC Day4 | 02-01 Conv. Day2 | 02-02 VMCo Day2,3 | 02-03 VMC Day3 | 02-04 DMC Day4 | 03-01 03-03 DFT Day1 | 03-04 Conv. Day2 | 03-05 VMCo Day2,3 | 03-06 VMC Day3 | 03-06 DMC Day4 | 04-01 Conv. Day3 | 04-03 VMCo Day4 | 04-03 VMC Day4 | 04-03 DMC Day4 |
| | C | | | | | | | | | 03-01 DFT Day1 | | | | | 04-02 Conv. Day3 | | | |
| 3. $H_2$ on graphene | $H_2$ + Graphene | 01 DFT Day1 | 02 VMCo Day2,3 | 03 VMC Day3 | 04 DMC Day4 | NA | | | | NA | | | | | NA | | | |
| | Graphene | 05 DFT Day1 | 06 VMCo Day2,3 | 07 VMC Day3 | 08 DMC Day4 | | | | | | | | | | | | | |
| | $H_2$ | 09 DFT Day1 | 10 VMCo Day2, 3 | 11 VMCo Day3 | 12 DMC Day4 | | | | | | | | | | | | | |



# Thank you!

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