



# Recent developments and Future Perspectives of ab initio Quantum Monte Carlo Methods

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# Outline

- Introductions: Why QMC is needed?
- Basics of Variational and Green Function Monte Carlo
- Practical Tips for QMC calculations (software etc...)

# Outline

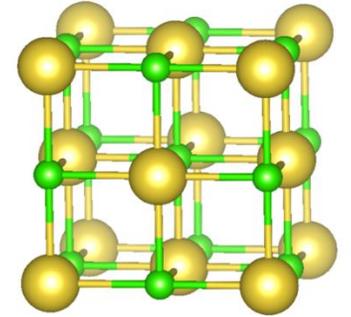
- Introductions: Why QMC is needed?

# Reliability of Density Functional Theory (DFT)

Based on electron density:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\vec{r}) \right\} \cdot \psi_i(\vec{r}) = \epsilon_i \cdot \psi_i(\vec{r})$$

Kohn-Sham equation  
(one-particle description)



Solving the eq. (SCF)

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\vec{r}) \right\} \cdot \psi_i(\vec{r}) = \epsilon_i \cdot \psi_i(\vec{r}) \longrightarrow n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$$

$$v(\vec{r}) = v_{ext}(\vec{r}) + e^2 \int d^3r' \cdot \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[n(\vec{r})]$$

Biggest drawback:

**Depending on a functional we choose (e.g., LDA, PBE, meta-GGA, etc...)**

# Ab initio Quantum Monte Carlo (QMC)

Solving the many-body Schrödinger eq. without the one-particle approximation.  $\hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \dots, \vec{r}_N)$

Variational Monte Carlo Method

VMC

$$E(\vec{\alpha}) = \frac{\langle \Psi_{\vec{\alpha}} | \hat{H} | \Psi_{\vec{\alpha}} \rangle}{\langle \Psi_{\vec{\alpha}} | \Psi_{\vec{\alpha}} \rangle}$$

$J(\vec{\alpha}) \times |\Psi_{AS}(\vec{\alpha})\rangle$   
with a chosen ansatz

Evaluating by MCMC. Minimizing the variational parameters  $\alpha_k$  such that the total energy goes down.

Green Function Monte Carlo Method

GFMC/DMC



Projecting out the ground state from a given trial wavefunction.

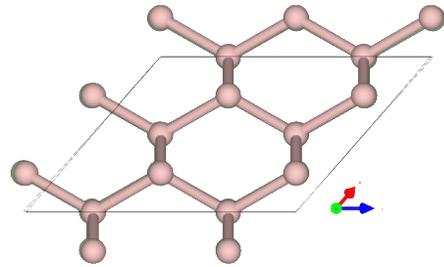
The exact solution with a given nodal surface

It does not need the exchange-correlational functional in the framework.

QMC suffers from error bars intrinsic in the method. However, supercomputers such as Fugaku nowadays allow one to study realistic materials (e.g., perovskites).

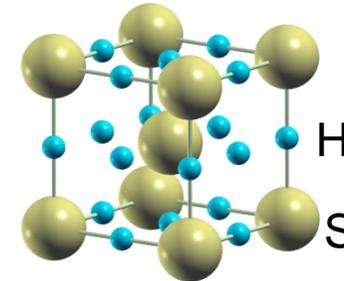


# Applications of QMC in materials science



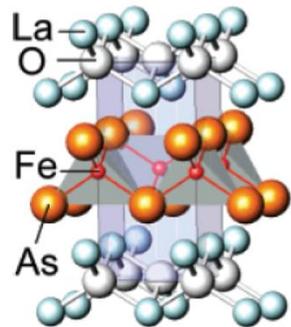
Liquid and Solid hydrogens at high pressures

L. Monacelli et al., *Nat. Phys.* **19**, 845-850 (2023)



Hydrides superconductors at high pressures

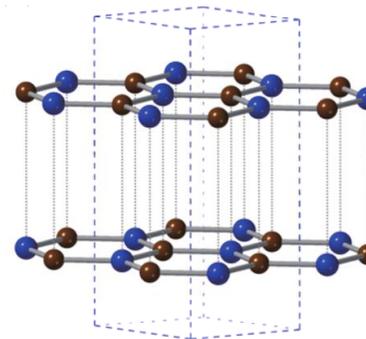
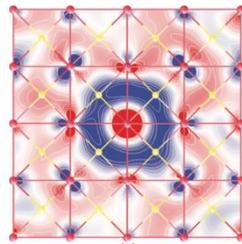
R. Taureau, et al., *npj Comput. Mater.* **10**, 56 (2024)



Y. Kamihara, et al.: *JACS* **130** (2008) 3296.

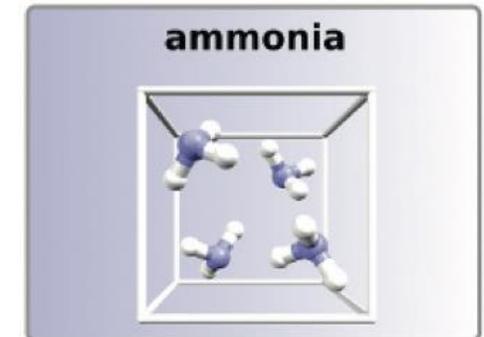
Unconventional Superconductors

M. Casulla et al., *Phys. Rev. B* **88**, 155125 (2013)



Two-dimensional compounds  
(graphene, BN, TMDCs)

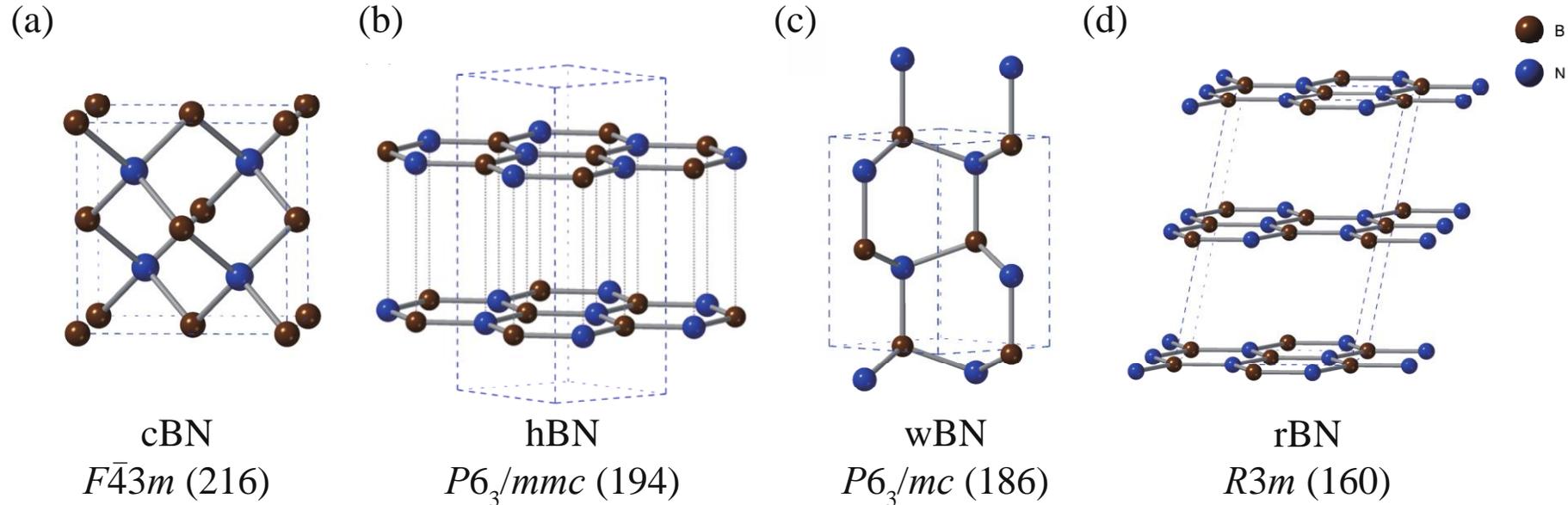
Y. Nikaido, et al., *J. Phys. Chem. C* **126**, 6000-6007 (2022)



Molecular Crystals

A. Zen, *PNAS.* **115**, 1724-1729 (2018)

e.g., the most stable polymorph of BN ?



- DFT-LDA
- RPA
- CCSD(T)
- **QMC (DMC)**

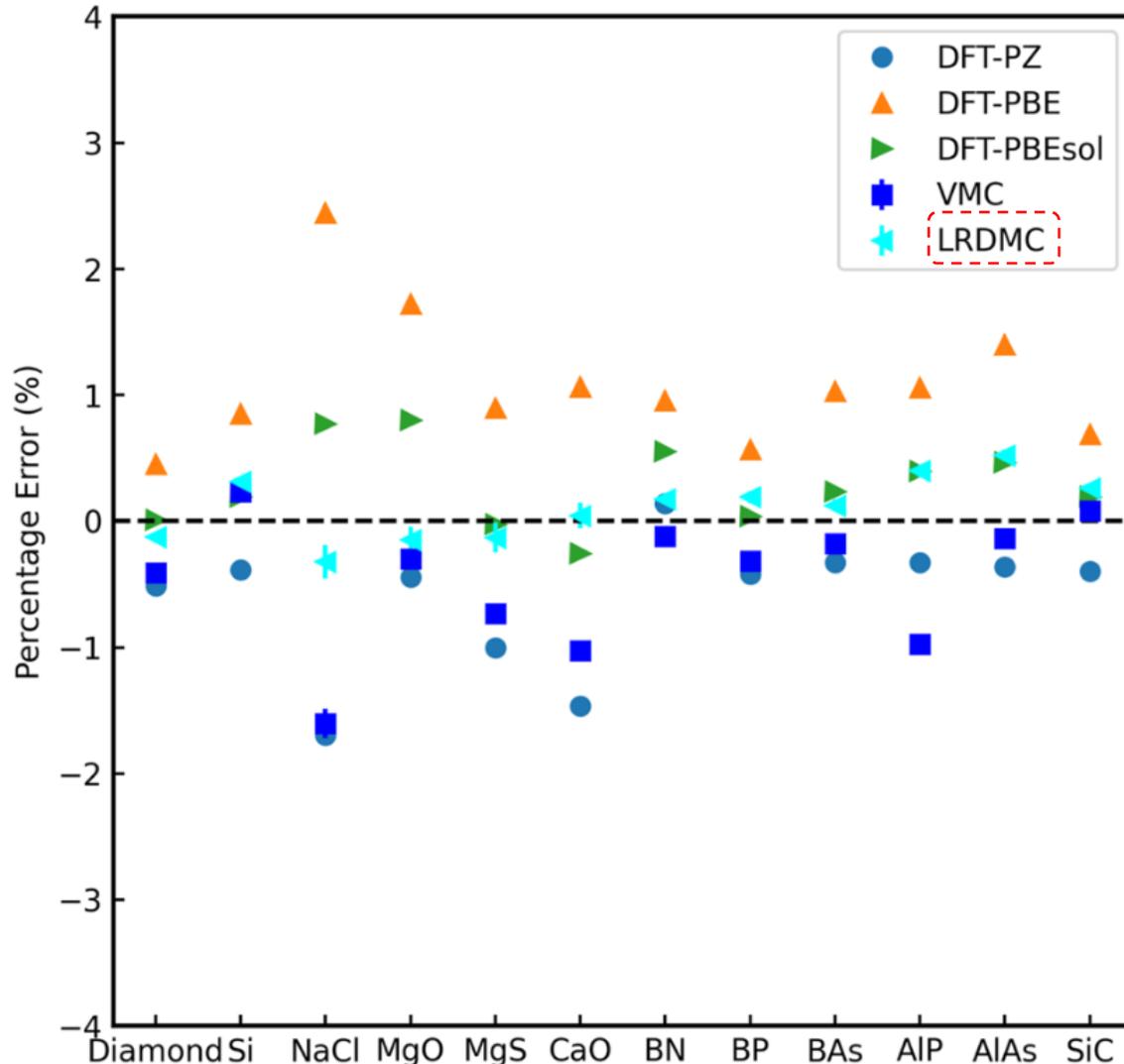
cBN (agree with Solozhenko *et al.* experiment)

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**hBN** (agree with Corrigan *et al.* and Fukunaga experiments)

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# e.g., Lattice constant at 0 K by QMC



Compound	Equilibrium lattice parameter (Å)					Exp.
	DFT (PZ)	DFT (PBE)	DFT (PBEsol)	VMC	LRDMC	
Diamond	3.5368	3.5711	3.5552	3.540 43(45)	3.550 55(49)	3.555
Si	5.4011	5.4681	5.4323	5.4346(11)	5.4390(11)	5.422
NaCl	5.4707	5.7009	5.6080	5.4758(32)	5.5472(37)	5.565
MgO	4.1695	4.2602	4.2214	4.1756(12)	4.1819(21)	4.188
MgS	5.1361	5.2346	5.1867	5.1502(16)	5.1814(29)	5.188
CaO	4.7111	4.8320	4.7688	4.7318(11)	4.7832(23)	4.781
BN	3.5991	3.6282	3.6139	3.589 74(51)	3.600 33(55)	3.594
BP	4.5080	4.5528	4.5287	4.512 71(56)	4.5356(11)	4.527
BAs	4.7486	4.8130	4.7752	4.7556(11)	4.7700(12)	4.764
AlP	5.4322	5.5077	5.4714	5.3969(12)	5.4718(14)	5.450
AlAs	5.6287	5.7281	5.6753	5.6412(13)	5.6784(13)	5.649
SiC	4.3309	4.3780	4.3565	4.351 53(60)	4.359 48(62)	4.348
MAE (Å)	0.0307	0.0537	0.0158	0.025 60(39)	0.011 47(53)	...
MARE (%)	0.6219	1.0947	0.3271	0.5087(75)	0.229(11)	...

- VMC predicts it with  $\sim 0.5\%$  accuracy.
- DMC shows the best performance,  $\sim 0.3\%$  accuracy.

K. Nakano\*, et al., *J. Chem. Phys.* **159**, 224801 (2023)

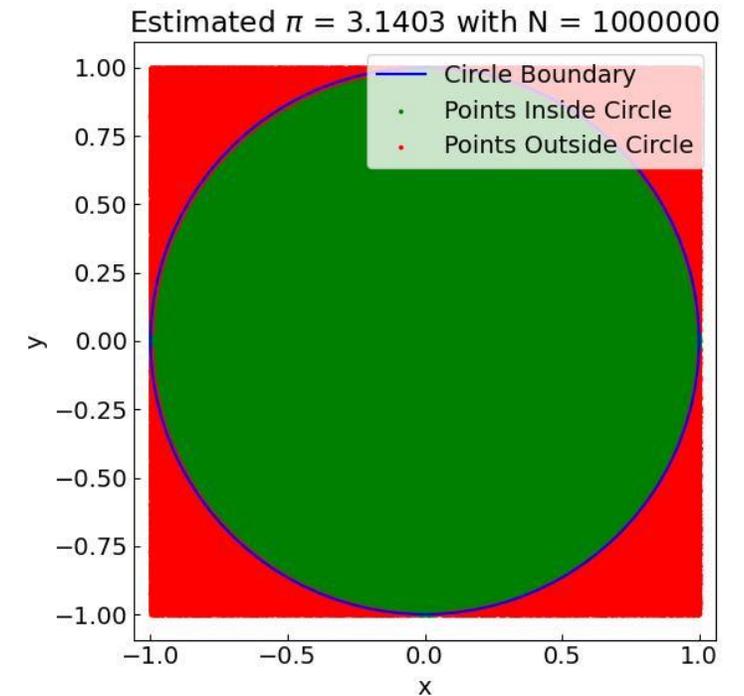
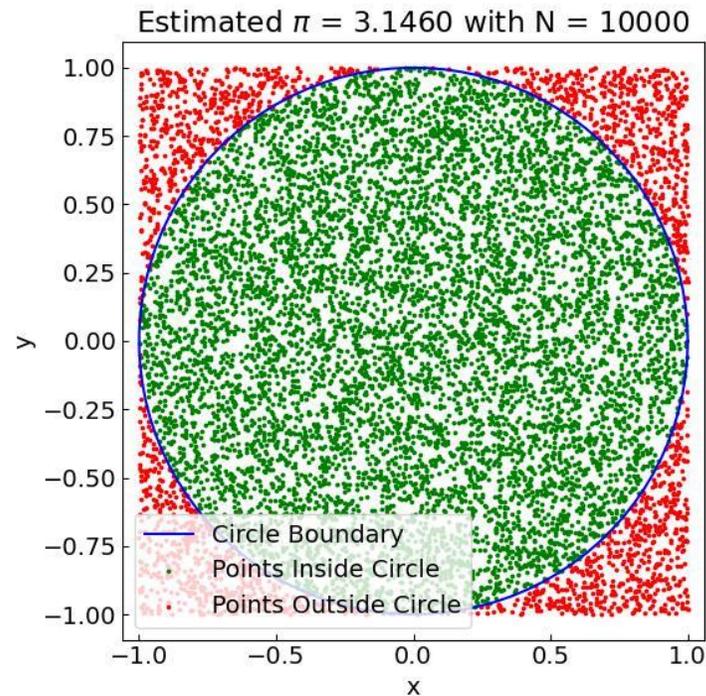
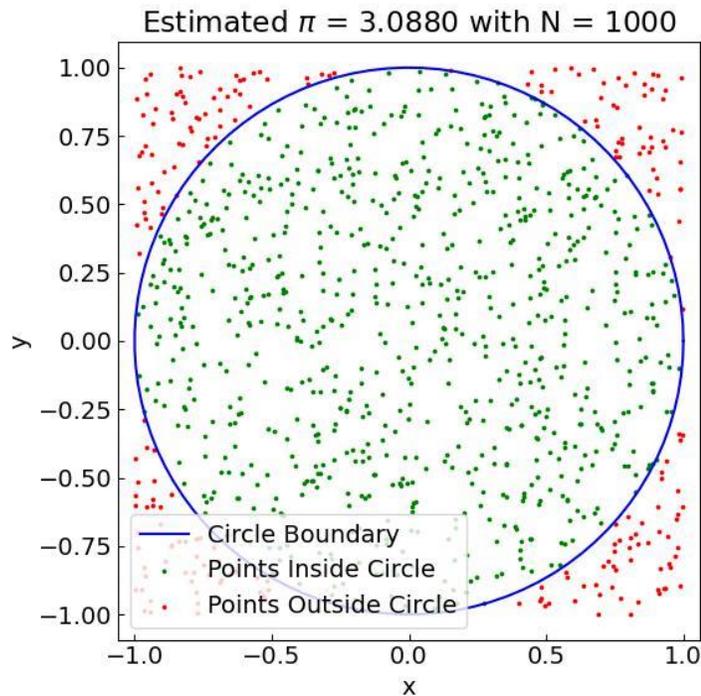
# Outline

- Basics of VMC and GFMC
  - Variational Monte Carlo (VMC)
  - Green Function Monte Carlo (GFMC)

# Why is Monte Carlo needed for physics?

The Monte Carlo method is a general term referring to a method exploiting random numbers.

Estimation of  $\pi$      Scatter points randomly and count the number of points inside the circle.  
(Uniform distribution)



The more random numbers are generated, the more accurate estimation we get (Important point!!)

# Why is Monte Carlo needed for ab initio?

In ab initio Quantum Monte Carlo framework:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad \equiv \quad E = \frac{\int d\vec{r}_1 \cdots d\vec{r}_N \Psi^*(\vec{r}_1 \cdots \vec{r}_N) \hat{H} \Psi(\vec{r}_1 \cdots \vec{r}_N)}{\int d\vec{r}_1 \cdots d\vec{r}_N |\Psi(\vec{r}_1 \cdots \vec{r}_N)|^2}$$

Requires  $3N$ -dimensional integrals ( $N$ : # of electrons)

Analytical Integration?  $\rightarrow$  Impossible because the functional form of a WF is complicated.

Numerical integration?  $\rightarrow$  Very inefficient for a high-dimensional integration ( $N > 5$ ).

(quadrature)

No choice but to do it stochastically. Monte Carlo Integral.

What we need to estimate  $E$  (total energy)?

$$E = \frac{\int d\vec{X} |\Psi(\vec{X})|^2 \frac{\hat{H}\Psi(\vec{X})}{\Psi(\vec{X})}}{\int d\vec{X} |\Psi(\vec{X})|^2} = \int d\vec{X} \pi(\vec{X}) e_L(\vec{X}) \sim \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i)$$

Local energy

$X = (\vec{r}_1, \dots, \vec{r}_N)$   $3N$ -dim. electron coordinates

If one can generate electron coordinates ( $X$ ) according to  $\pi(\vec{X}) = \frac{|\Psi(\vec{X})|^2}{\int d\vec{X} |\Psi(\vec{X})|^2}$

Then, the total energy is the mean of the local energy  $E = \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i)$

( $\vec{X}_1, \dots, \vec{X}_i, \dots, \vec{X}_M$ )

What we need to estimate E (total energy)?

$$E = \frac{\int d\vec{X} |\Psi(\vec{X})|^2 \frac{\hat{H}\Psi(\vec{X})}{\Psi(\vec{X})}}{\int d\vec{X} |\Psi(\vec{X})|^2} = \int d\vec{X} \pi(\vec{X}) e_L(\vec{X}) \sim \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i)$$

Local energy

$$X = (\vec{r}_1, \dots, \vec{r}_N) \quad 3N\text{-dim. electron coordinates}$$

If one can generate electron coordinates (X) according to  $\pi(\vec{X}) = \frac{|\Psi(\vec{X})|^2}{\int d\vec{X} |\Psi(\vec{X})|^2}$

Then, the total energy is the mean of the local energy  $E = \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i)$

with an error bar!!

$$(\vec{X}_1, \dots, \vec{X}_i, \dots, \vec{X}_M)$$

# Zero-Variance Zero-Bias property

The local energy has an essential property, Zero-Variance Zero-Bias property.

$$e_L(\vec{X}) = \frac{\hat{H}\Psi_0(\vec{X})}{\Psi_0(\vec{X})} = \frac{E_0\Psi_0(\vec{X})}{\Psi_0(\vec{X})} = E_0$$

because  $|\Psi_0\rangle$  is an eigenstate of  $\hat{H}$

$$E = \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i) = E_0 \pm 0$$

If one finds the exact ground-state WF (zero-bias), the MCMC gives the value without statistical uncertainty (zero-variance). -> Smaller error bar with a better WF.

# What is Markov Chain Monte Carlo (MCMC)?

Markov chain Monte Carlo (MCMC) methods create samples from a continuous random variable, with a target probability density.

$$(\vec{X}_1, \dots, \vec{X}_i, \dots, \vec{X}_M) \text{ according to } \pi(\vec{X}) = \frac{|\Psi(\vec{X})|^2}{\int d\vec{X} |\Psi(\vec{X})|^2}$$



Markov chain Monte Carlo (MCMC) allows us to compute  $3N$ -dimensional integrals very efficiently using random numbers.

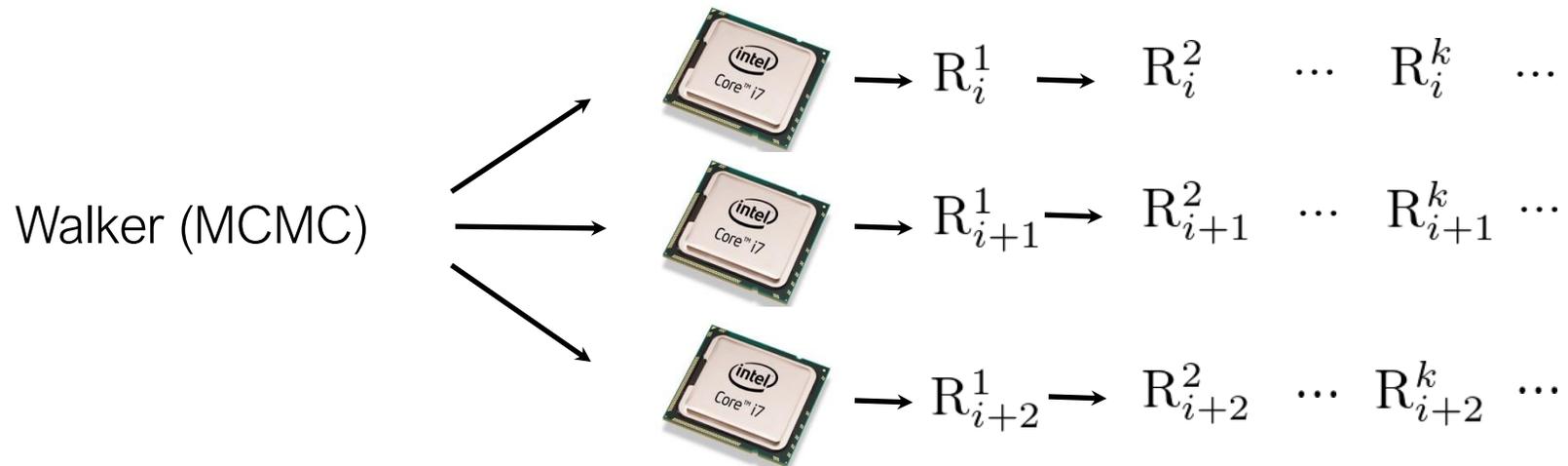
Applied in: Bayesian statistics, condensed matter physics, computational finance ...

# Suitable for exa-scale supercomputers

$$E = \frac{\int d\vec{X} |\Psi(\vec{X})|^2 \frac{\hat{H}\Psi(\vec{X})}{\Psi(\vec{X})}}{\int d\vec{X} |\Psi(\vec{X})|^2} = \int d\vec{X} \pi(\vec{X}) e_L(\vec{X}) \sim \frac{1}{M} \sum_{i=1}^M e_L(\vec{X}_i)$$

Local energy

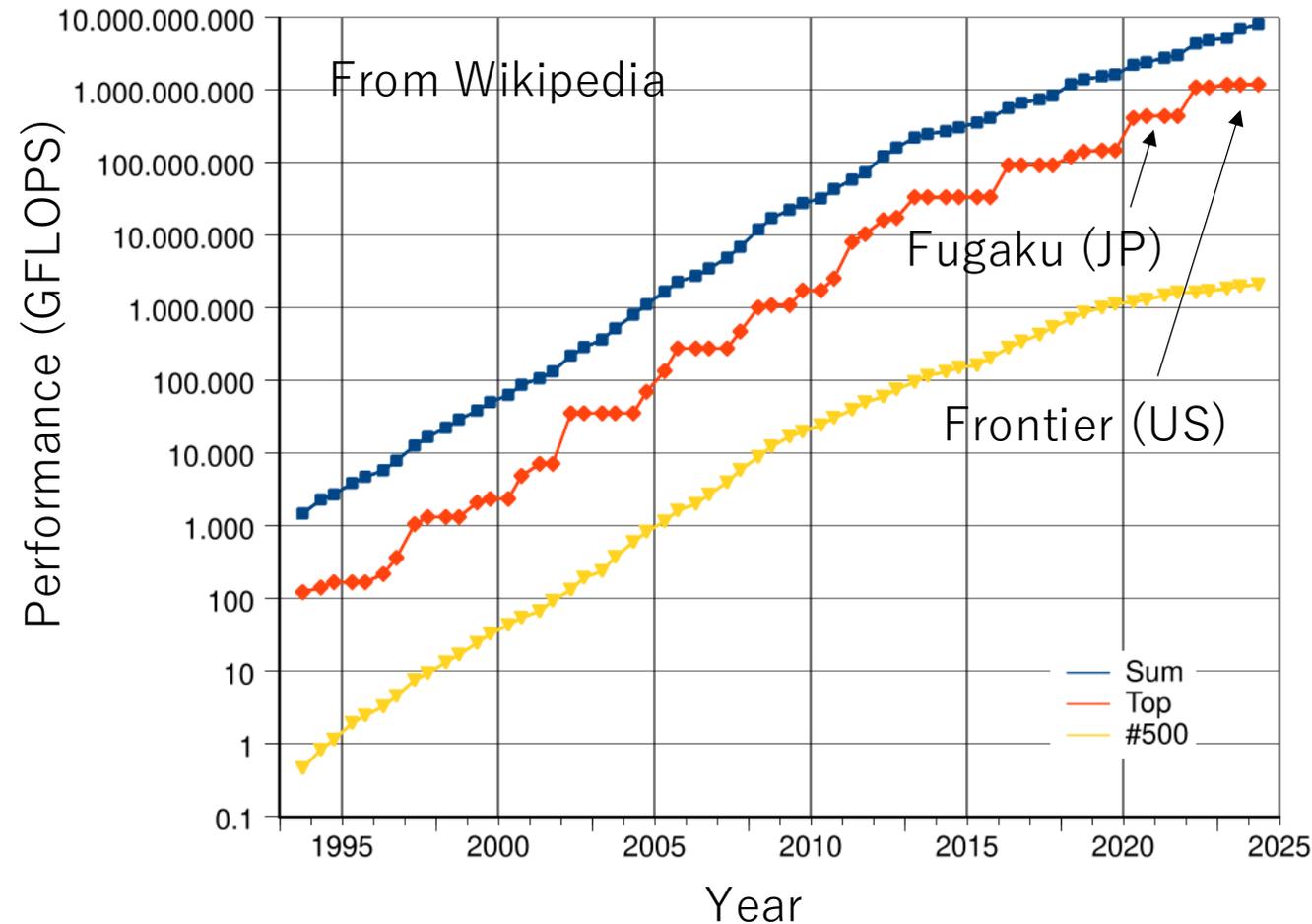
The statistical error ( $\sigma$ ) is inversely proportional to the number of samples ( $M$ ).  $\sigma \propto \frac{1}{\sqrt{M}}$



The computation is spent on decreasing the error bar of the estimation.

# QMC makes the most of exascale computers.

## TOP500 supercomputers



The computer power grows exponentially.

(Moore's law)

However, DFT does not scale due to the difficulties of parallelization (Amdahl's law).

The parallelization efficiency of QMC is 100 % because it relies on MCMC, making the most of the power of exascale computers.

The complexity of QMC is  $O(M^3)$ , where  $M$  is the number of electrons in a system.

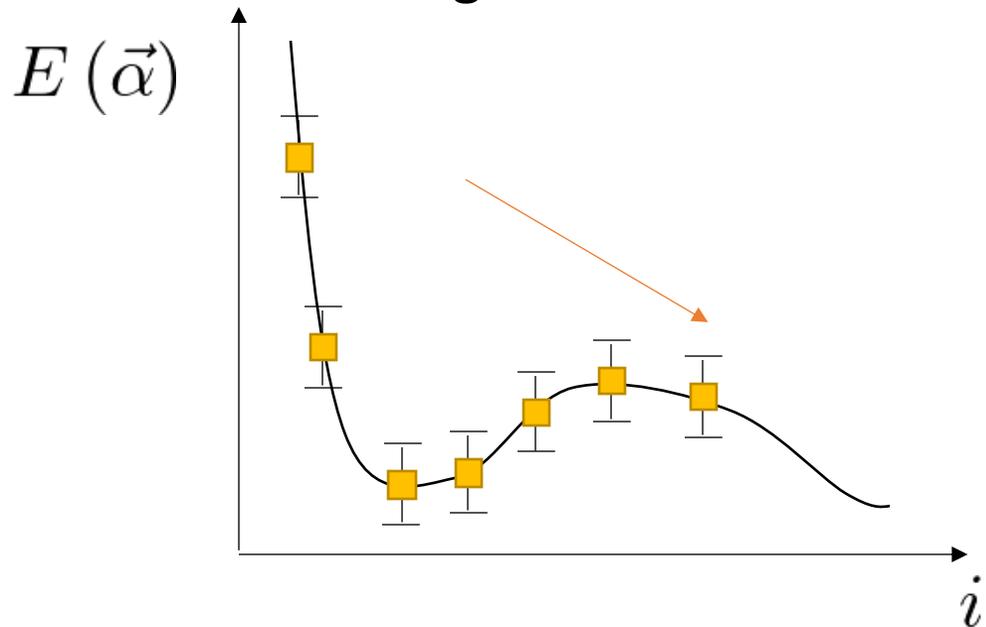
(in 10 years: triple; in 20 years: 10 times; in 30 years: 30 times.)

# Variational Principle $\rightarrow$ Variational Monte Carlo

$$E(\vec{\alpha}) = \frac{\int d\vec{X} \Psi^*(\vec{X}, \vec{\alpha}) \hat{H} \Psi(\vec{X}, \vec{\alpha})}{\int d\vec{X} |\Psi(\vec{X}, \vec{\alpha})|^2} \geq E_0 \quad \text{Variational principle}$$

$X = (\vec{r}_1, \dots, \vec{r}_N)$

This integral is evaluated using the MCMC method.



Variational parameters are updated!

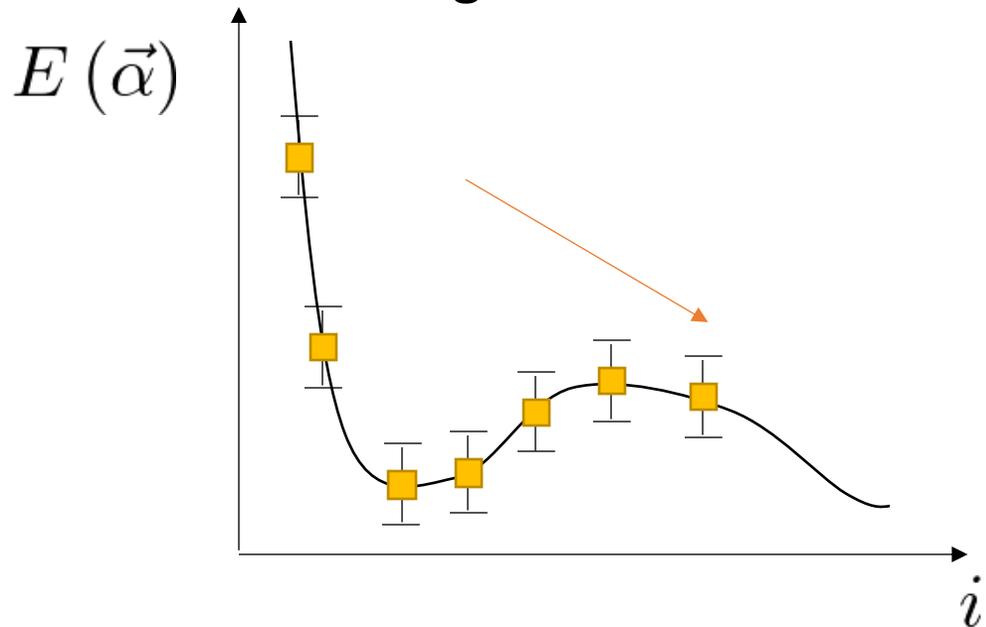
$$\vec{\alpha}_{i+1} \leftarrow \vec{\alpha}_i + \Delta \vec{\alpha}$$

# Variational Principle $\rightarrow$ Variational Monte Carlo

$$E(\vec{\alpha}) = \frac{\int d\vec{X} \Psi^*(\vec{X}, \vec{\alpha}) \hat{H} \Psi(\vec{X}, \vec{\alpha})}{\int d\vec{X} |\Psi(\vec{X}, \vec{\alpha})|^2} \geq E_0 \quad \text{Variational principle}$$

$X = (\vec{r}_1, \dots, \vec{r}_N)$

This integral is evaluated using the MCMC method.



Variational parameters are updated!

$$\vec{\alpha}_{i+1} \leftarrow \vec{\alpha}_i + \Delta \vec{\alpha}$$

but...

- How to parametrize the WF?
- How to optimize the WF?

# Two questions

- How to parametrize the WF?
- How to optimize the WF?

# The common choice of WF: Slater determinant

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  should be anti-symmetric under exchange of electrons. (positions and spins)

Otherwise, optimization makes the WF bosonic.

Slater determinant (SD): the most straightforward ansatz. **The solution of Hartree-Fock.**

$$\Psi(\{\vec{r}_i, \sigma_i\}) = \frac{1}{\sqrt{N_\alpha! N_\beta!}} \underbrace{\begin{vmatrix} \phi_1(\vec{r}_1) & \cdots & \phi_1(\vec{r}_{N_\alpha}) \\ \vdots & \ddots & \vdots \\ \phi_{N_\alpha}(\vec{r}_1) & \cdots & \phi_{N_\alpha}(\vec{r}_{N_\alpha}) \end{vmatrix}}_{\text{up electrons } (\sigma=\uparrow)} \underbrace{\begin{vmatrix} \phi_{N_\alpha+1}(\vec{r}_{N_\alpha+1}) & \cdots & \phi_{N_\alpha+1}(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\vec{r}_{N_\alpha+1}) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix}}_{\text{dn electrons } (\sigma=\downarrow)}$$

where  $\phi_k(\vec{r})$  is k-th molecular orbital (MO). MOs are expanded by atomic orbitals (AOs)

$$\phi_k(\vec{r}) = \sum_{i=1}^M c_{i,k} \psi_i(\vec{r}) \quad c_{i,k} \text{ are (variational) parameters.}$$

# Slater determinant lacks two correlations

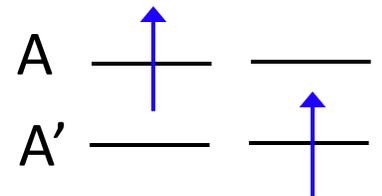
The electron correlation is defined as the difference between the exact and HF solutions.

The correlations are categorized as:

$$E_{\text{corr}} \equiv E_{\text{exact}} - E_{\text{HF}}$$

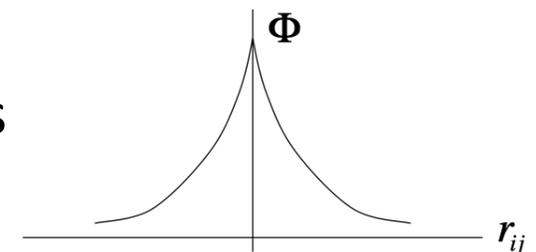
- Static correlation (e.g., 3d-transition metals)

When a single electronic configuration (i.e., a single Slater determinant) is insufficient to describe a quantum system accurately because multiple configurations have comparable importance.



- Dynamical correlation (e.g., Van der Waals force)

When two electrons approach each other, the Coulomb repulsion is divergent ( $+\infty$ ). The divergence should be compensated by an equal and opposite divergence in the kinetic term (cusp condition).



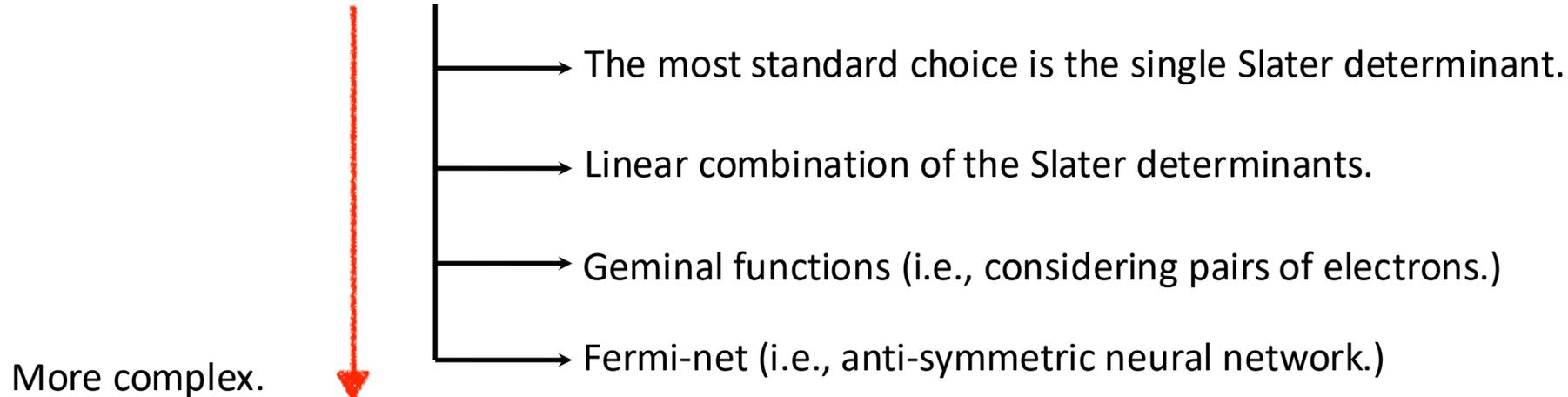
# Wavefunction ansatz considering correlations

The many-body WF is parametrized as:  $\Psi_{AS}(\vec{R}) \times \exp(J(\vec{R}))$

Antisymmetric term      Jastrow factor

Jastrow factor  $\exp(J(\vec{R}))$  To satisfy Kato's cusp conditions and to consider the further correlations.

Antisymmetric term  $\Psi_{AS}(\vec{R})$  To satisfy the Fermion statistics (antisymmetric under exchange of electrons.)



**One can employ any functional form as far as the antisymmetry is satisfied.**  
**The best WF form is still under debate.**

# Antisymmetric part (Antisymmetrized Geminal)

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  should be antisymmetric under exchange of electrons. (positions and spins)

Antisymmetrized Geminal Power (AGP):

$$\Psi(\{\vec{r}_i, \sigma_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} f(\vec{r}_1^\uparrow, \vec{r}_1^\downarrow) & \cdots & f(\vec{r}_{N^\uparrow - N^\downarrow}^\uparrow, \vec{r}_1^\downarrow) & \cdots & \Phi(\vec{r}_{N^\uparrow}^\uparrow) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ f(\vec{r}_1^\uparrow, \vec{r}_{N^\downarrow}^\downarrow) & \cdots & f(\vec{r}_{N^\uparrow - N^\downarrow}^\uparrow, \vec{r}_{N^\downarrow}^\downarrow) & \cdots & \Phi(\vec{r}_{N^\uparrow}^\uparrow) \end{vmatrix}$$

where  $f(\vec{r}_i, \vec{r}_j) = \sum_{(a,l), (b,m)} A_{\{a,l\}, \{b,m\}} \psi_{a,l}(\vec{r}_i) \psi_{b,m}(\vec{r}_j)$  is the geminal function  
Atomic Orbitals (AOs)

c.f.) It is equivalent to multi-determinant wavefunction.  $\longrightarrow$  Static correlation.

# Jastrow part (cusp conditions)

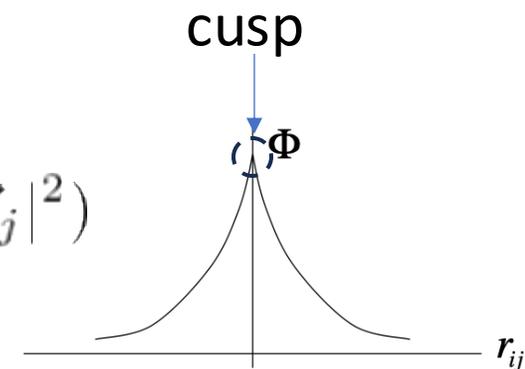
Conditions on the shape of the wave function such that the divergence of the Coulomb interaction is compensated by an equal and opposite divergence in the kinetic term.

Electron-Ion coalescence:

$$\frac{\Psi(\dots \vec{r}_i \simeq \vec{R}_J \dots)}{\Psi(\dots \vec{r}_i = \vec{R}_J \dots)} = 1 - Z_J |\vec{r}_i - \vec{R}_J| + O(|\vec{r}_i - \vec{R}_J|^2)$$

Electron-Electron coalescence:

$$\frac{\Psi(\dots \vec{r}_i \simeq \vec{r}_j \sigma_i = -\sigma_j \dots)}{\Psi(\dots \vec{r}_i = \vec{r}_j \sigma_i = -\sigma_j \dots)} = 1 + \frac{1}{2} |\vec{r}_i - \vec{r}_j| + O(|\vec{r}_i - \vec{r}_j|^2)$$



# Jastrow part (functional forms)

One-body Jastrow (Electron-Ion coalescence):

$$J_1(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i=1}^N \sum_{a=1}^{N_a} \left( -(2Z_a)^{3/4} u_a \left( (2Z_a)^{1/4} \left| \vec{r}_i - \vec{R}_a \right| \right) \right), \quad u_a(r) = \frac{1}{2b(1 - e^{-br})}$$

Two-body Jastrow (Electron-Electron coalescence):

$$J_2(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) = \sum_{i < j} v_{\sigma_i, \sigma_j}(|\vec{r}_i - \vec{r}_j|) \quad v_{\sigma_i, \sigma_j}(r) = \begin{cases} \frac{r}{4} \cdot (1 + br)^{-1} & (\sigma_i = \sigma_j) \\ \frac{r}{2} \cdot (1 + br)^{-1} & (\sigma_i \neq \sigma_j) \end{cases}$$

Three/Four-body Jastrow

$$J_{3/4}(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \sum_{i, j > i} \left( \sum_{(a,l), (b,m)} M_{(a,l), (b,m)}^{\sigma_i, \sigma_j} \chi_{(a,l)}(\mathbf{r}_i) \chi_{(b,m)}(\mathbf{r}_j) \right)$$

# Example: C<sub>2</sub>-dimer

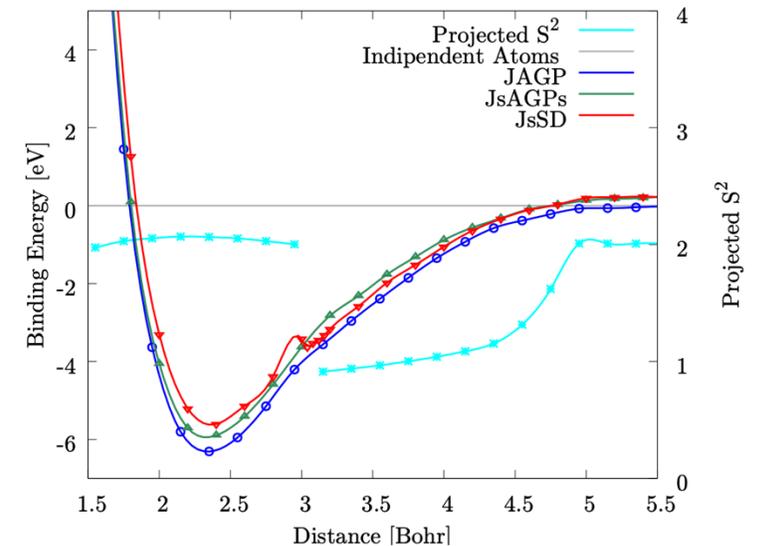
Double-bond?? Quadruple-bond??, spin-singlet. S. Shaik, et al. Nat. Chem. 4 195–200 (2012)

LRDMC results

Wavefunction	C atom (Ha)	C <sub>2</sub> molecule (Ha)	Binding (eV)
Jastrow Slater	-37.82966(4)	-75.8672(1)	5.656(3)
Jastrow Geminal (Singlet)	-37.8364(1)	-75.8938(2)	6.01(1)
Jastrow Geminal (Singlet + Triplet)	-37.8364(1)	-75.8935(2)	6.00(1)
Jastrow Geminal (All-pairings, Pfaffian)	-37.8363(1)	-75.9045(2)	<b>6.31(1)</b>
Estimated exact	-37.8450	-75.9045(2)	<b>6.44(2) (Exp.)</b>



More complex.



C.Genovese et al., *J. Chem. Theory Comput.* **16**, 6114 (2020)

CCSD(T) with the V5Z basis = 6.24 eV

The LRDMC gives a more accurate result than CCSD(T) for the challenging molecule!

# Two questions

- How to parametrize the WF?
- How to optimize the WF?

# Initial guess of WF

Initial guesses are taken from mean-field calculations, such as HF/DFT.



MOs

SD

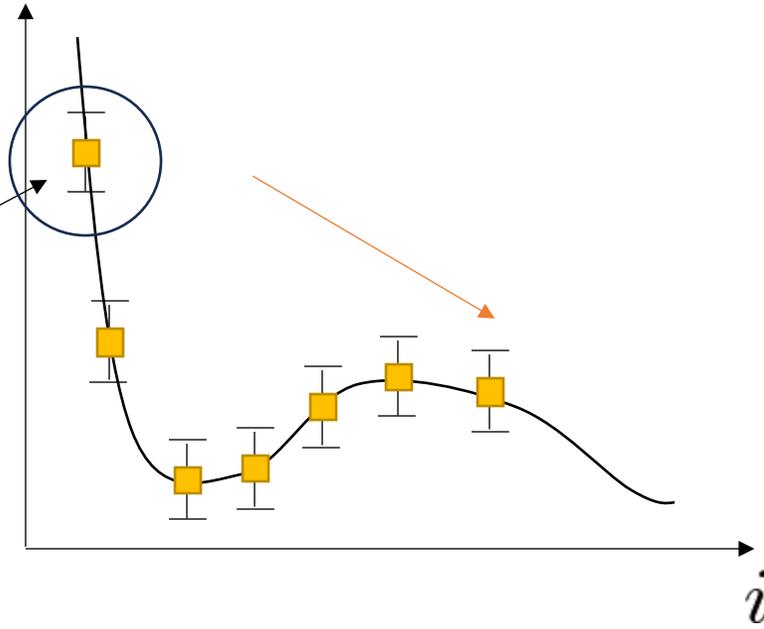
JSD

$E(\vec{\alpha})$

$$\phi_i(r)$$

$$\Phi_{SD}$$

$$e^J \Phi_{SD}$$



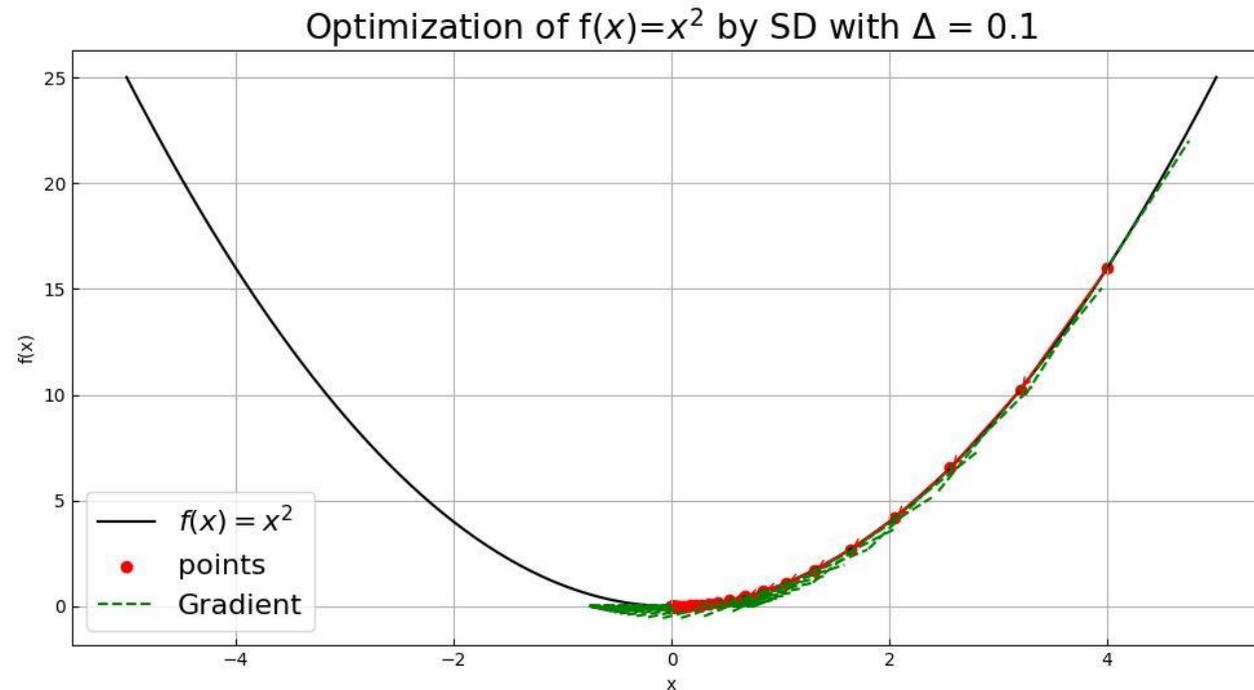
A research question:  
Can we make a database?

# The simplest Gradient method is the SD

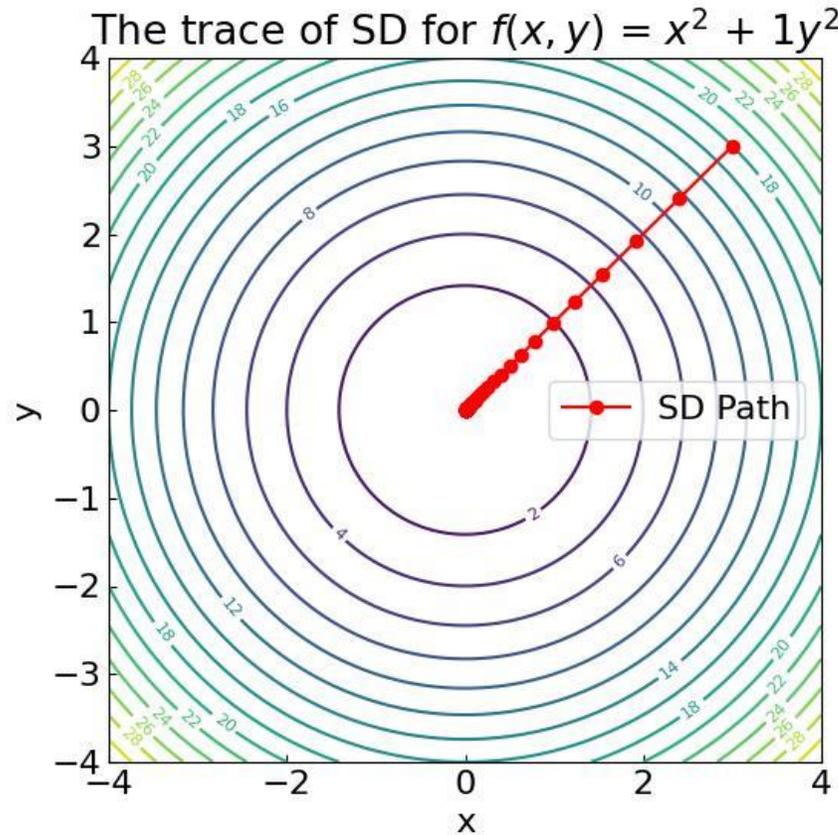
The steepest-decent (SD) is the simplest gradient-based optimization method.

$$\vec{f} = -\frac{\partial E}{\partial \vec{\alpha}} \quad \text{then,} \quad \vec{\alpha} \leftarrow \vec{\alpha} + \Delta \cdot \vec{f}$$

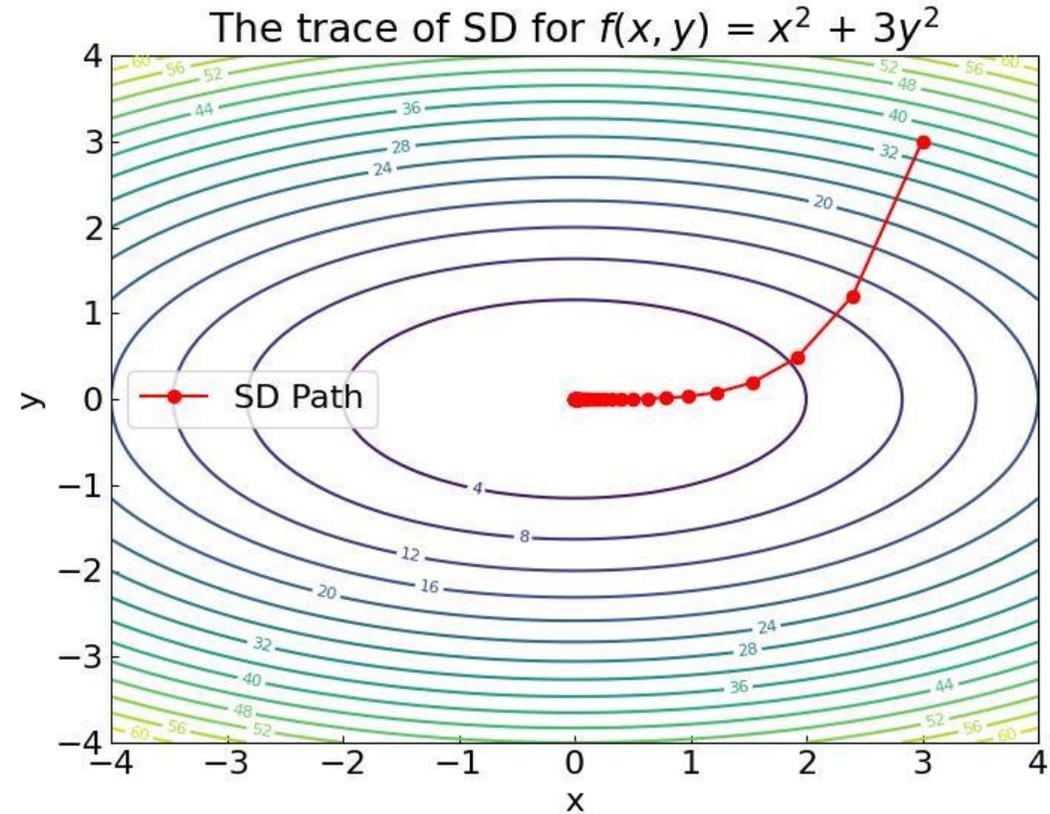
$\Delta$  is called the 'learning rate'



# Why does not SD work for many parameters?



It works.

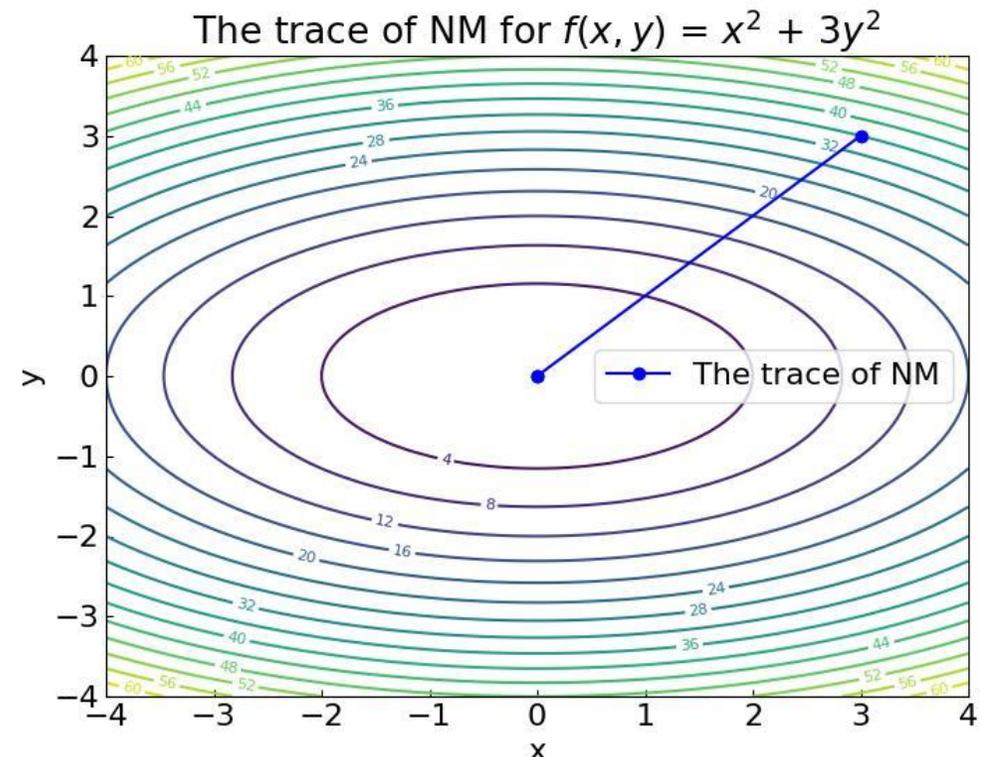
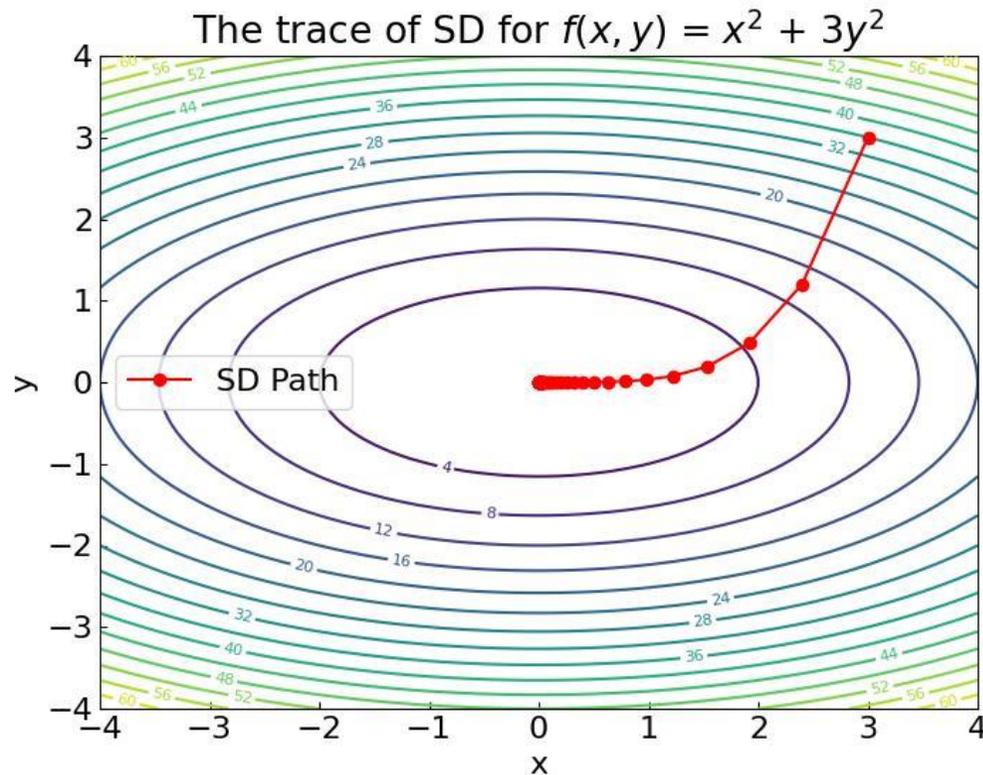


It works, but very slow.

# Newton Method (NM) works better

The Newton method (NM) is a more efficient gradient-based optimization using Hessian.

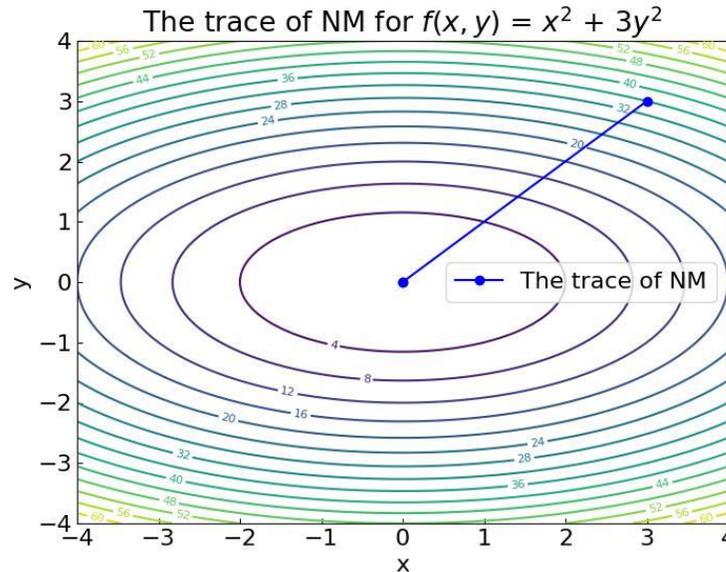
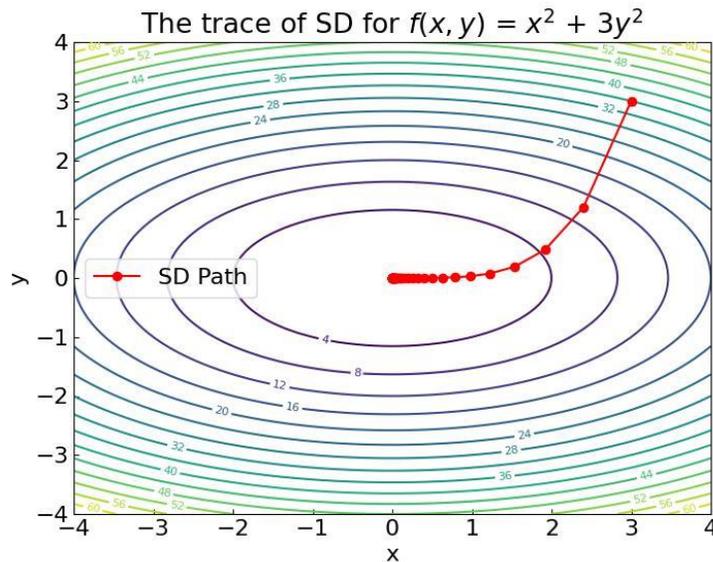
$$\vec{f} = -\frac{\partial E}{\partial \vec{\alpha}} \quad H_{k,k'} = \frac{\partial^2 E}{\partial \alpha_k \partial \alpha_{k'}} \quad \text{then,} \quad \vec{\alpha} \leftarrow \vec{\alpha} + \mathbf{H}^{-1} \vec{f}$$



# Newton Method (NM) works, why?

SD assumes that all the parameters affect the function equivalently.

NM considers the difference through Hessian (i.e., the metric of param. space)  
(curvature)



However, the computation of Hessian is heavy, thus not practical.

Is there a way to estimate the metric of the parameter space w/o H?

# Metric in the parameter space w/o Hessian

In MCMC: from  $|\Psi(\vec{X}, \vec{\alpha})|^2$  sampling  $\vec{X} = (\vec{X}_1, \dots, \vec{X}_i, \dots, \vec{X}_M)$   
Can we estimate the metric of the parameter space  $\vec{\alpha}$  from  $\vec{X}$  ?

Yes. The so-called Fischer Information Matrix (FIM) can do it.

$$S_{k,k'} = \left[ \frac{1}{M} \sum_{i=1}^M \left( O_k(\vec{X}_i) - \bar{O}_k \right)^* \left( O_{k'}(\vec{X}_i) - \bar{O}_{k'} \right) \right]$$

where  $O_k(\vec{X}_i) \equiv \frac{\partial \ln |\Psi(\vec{X}_i)|}{\partial \alpha_k}$

The FIM can be interpreted as a measure of how curved a probability distribution is in Euclidean space.

# Stochastic reconfiguration (SR) method

Stochastic reconfiguration, Prof. Sandro Sorella proposed in 1998, computes

[S. Sorella *Phys. Rev. Lett.* 80, 4558 (1998)]

$$O_k(\vec{X}_i) \equiv \frac{\partial \ln |\Psi(\vec{X}_i)|}{\partial \alpha_k}$$

$$f_k = -\frac{\partial E}{\partial \alpha_k} = -2 \left[ \frac{1}{M} \sum_{i=1}^M e_L^*(\vec{X}_i) (O_k(\vec{X}_i) - \bar{O}_k) \right] \quad \mathcal{S}_{k,k'} = \left[ \frac{1}{M} \sum_{i=1}^M (O_k(\vec{X}_i) - \bar{O}_k)^* (O_{k'}(\vec{X}_i) - \bar{O}_{k'}) \right]$$

a.k.a. generalized forces (gradients)

The metric of the parameter space, a.k.a. Fisher information.

Then, update the variational parameters as  $\alpha_k \rightarrow \alpha_k + \Delta \cdot (\mathbf{S}^{-1} \mathbf{f})_k$

The same method was developed independently in different fields.

In the machine-learning context, this is called the Natural Gradient method.

Found by Prof. Amari in 1998 [*Neural Computation*, 10, 251-276 (1998)].

# Outline

- Basics of VMC and GFMC
  - Variational Monte Carlo (VMC)
  - Green Function Monte Carlo (GFMC)

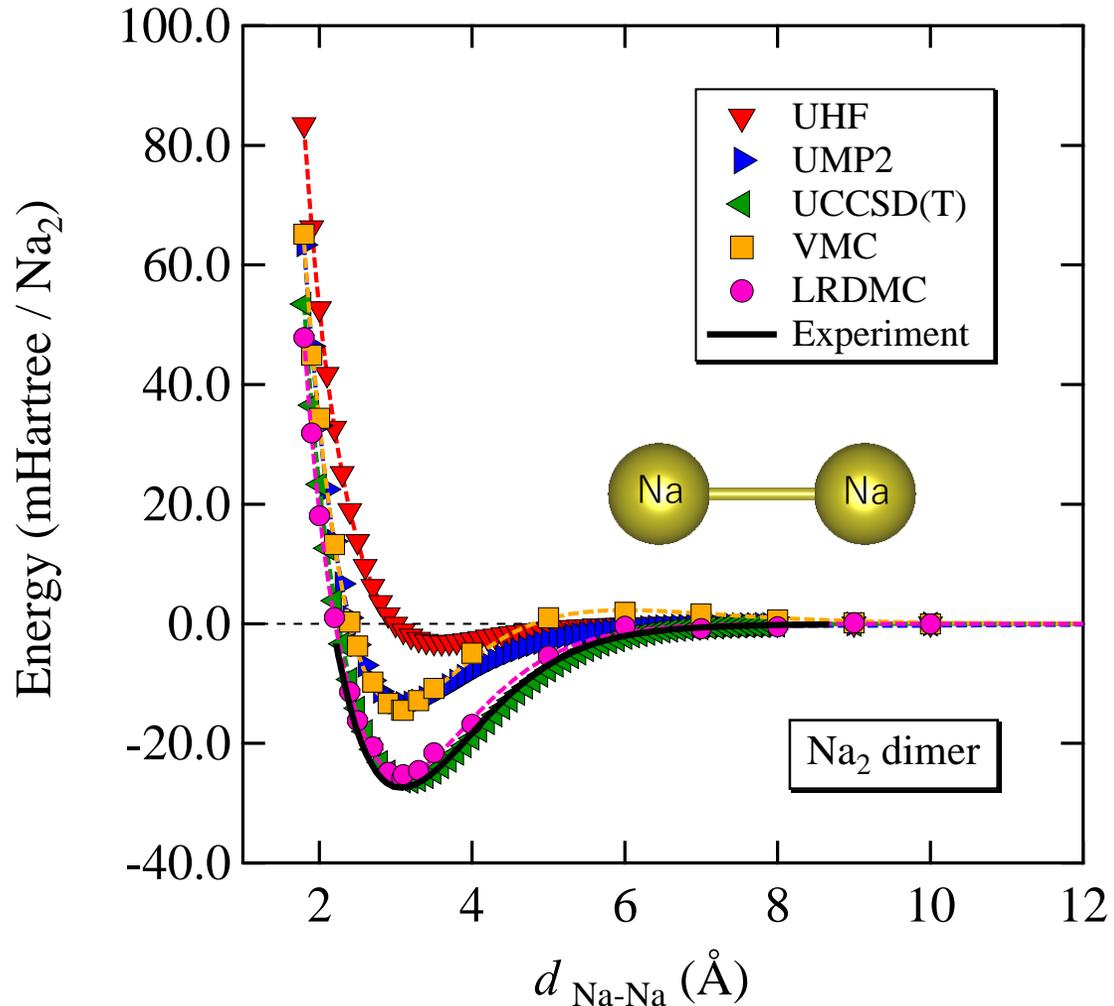
# What are the pains of VMC?

Since the VMC is a gradient-based optimization, it is sometimes unsatisfactory...

VMC cannot go beyond a given functional form. For instance, a Jastrow Slater Determinant ansatz cannot provide a correct answer to a problem in which the multi-configurational character should be considered.

VMC might reach the exact ground state if one can optimize an unlimitedly flexible WF (with infinite variational parameters), which is practically impossible. There is a tradeoff between the flexibility of ansatz and the difficulty of optimization.

# Example: Binding energy of Na<sub>2</sub> dimer



The binding energy curve of Na<sub>2</sub> dimer.

— Experimental curve.

◀ Obtained by CCSD(T)

▶ Obtained by MP2

■ Obtained by VMC with JAGP ansatz

# Green Function Monte Carlo (GFMC)

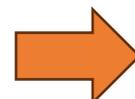
Let's go from Optimization (VMC) to Projection (GFMC).

Given  $|\Psi_T\rangle$ , and any state is expanded by the eigenstates  $|\Psi_T\rangle = \sum_n a_n |\Psi_n\rangle$   
(complete basis)

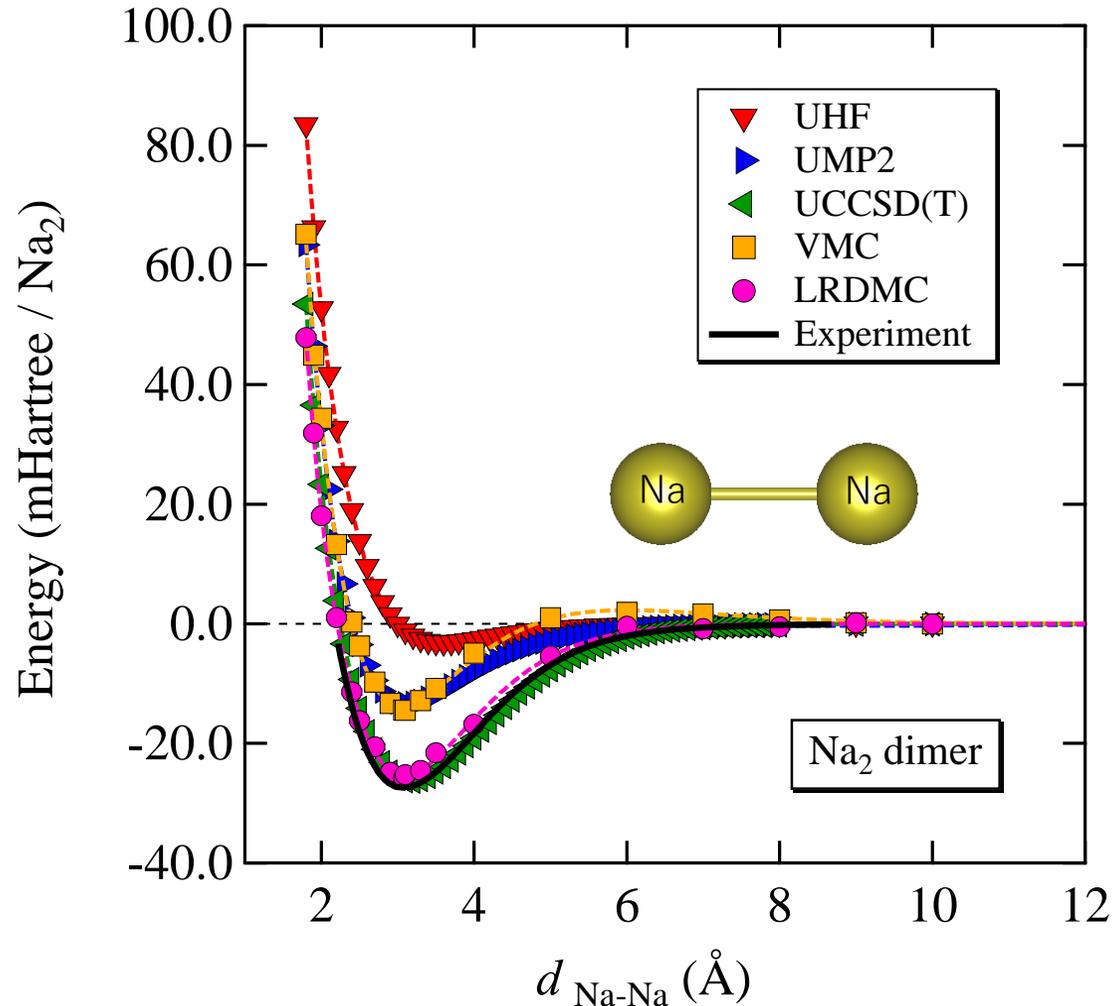
$$\lim_{M \rightarrow \infty} (\Lambda - \hat{\mathcal{H}})^M |\Psi_T\rangle = \lim_{M \rightarrow \infty} (\Lambda - E)^M \left[ a_0 |\Psi_0\rangle + \sum_{n \neq 0} \left( \frac{\lambda - E_n}{\lambda - E_0} \right)^M a_n |\Psi_n\rangle \right] \propto a_0 |\Psi_0\rangle$$

$\because \left( \frac{\lambda - E_n}{\lambda - E_0} \right) < 1$

By applying the projections  $(\Lambda - \hat{\mathcal{H}})^M$ , the ground state  $|\Psi_0\rangle$  can be projected out from  $|\Psi_T\rangle$

 We can go beyond the VMC limits!

# Example: Binding energy of Na<sub>2</sub> dimer



The binding energy curve of Na<sub>2</sub> dimer.

— Experimental curve.

◀ Obtained by CCSD(T)

▶ Obtained by MP2

● Obtained by GFMC with JAGP ansatz (LRDMC)

# Green Function Monte Carlo (GFMC)

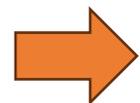
Let's go from Optimization (VMC) to Projection (GFMC).

Given  $|\Psi_T\rangle$ , and any state is expanded by the eigenstates  $|\Psi_T\rangle = \sum_n a_n |\Psi_n\rangle$   
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$$\lim_{M \rightarrow \infty} (\Lambda - \hat{\mathcal{H}})^M |\Psi_T\rangle = \lim_{M \rightarrow \infty} (\Lambda - E)^M \left[ a_0 |\Psi_0\rangle + \sum_{n \neq 0} \left( \frac{\lambda - E_n}{\lambda - E_0} \right)^M a_n |\Psi_n\rangle \right] \propto a_0 |\Psi_0\rangle$$

$\because \left( \frac{\lambda - E_n}{\lambda - E_0} \right) < 1$

By applying the projections  $(\Lambda - \hat{\mathcal{H}})^M$ , the ground state  $|\Psi_0\rangle$  can be projected out from  $|\Psi_T\rangle$



How to perform the projections in practice??

Interpreted as a probability density equation

Let's focus on a single projection:  $|\Psi_{k+1}\rangle = (\Lambda - \hat{\mathcal{H}}) |\Psi_k\rangle$

$$\Psi_{k+1}(x') = \sum_x \mathcal{G}_{x',x} \Psi_k(x) \quad \text{where} \quad \begin{aligned} \Psi_k(x) &= \langle x' | \Psi_k \rangle \\ \mathcal{G}_{x',x} &= \langle x' | \Lambda - \hat{\mathcal{H}} | x \rangle \end{aligned}$$

Let's interpret this as **a probability density equation** for

A stochastic variable:  $x$

Its probability density at k-th iteration:  $\Psi_k(x)$

Its transition probability:  $\mathcal{G}_{x',x}$  for  $x \rightarrow x'$

# Particle diffusion by Brownian motion

Langevin equation (Brownian motion)

$$\frac{dx}{dt} = f(x, t) + g(x, t)\eta(t)$$

where  $\eta(t)$  is the white Gaussian noise

Fokker–Planck equation

$$\frac{\partial \rho(x, t)}{\partial t} = -\frac{\partial}{\partial x} [f(x, t) \rho(x, t)] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [g^2(x, t) \rho(x, t)].$$

where  $\rho(x, t)$  is the probability density of  $x$

e.g., A Brownian motion in a harmonic potential

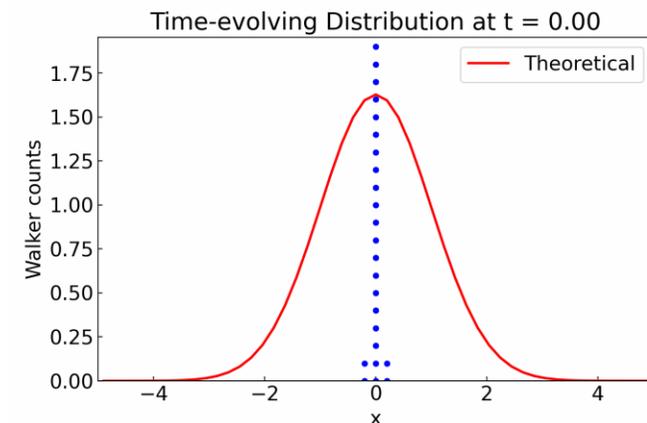
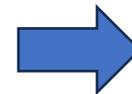
$$dx = -kx dt + \sqrt{2D} dt \xi$$

$k$  the spring constant

$D$  the diffusion coefficient

$\xi \sim \mathcal{N}(0, 1)$  the white Gaussian noise

We can estimate  $\rho(x, t)$



The random walk simulation can stochastically estimate the probability density.

# Analogy to the classical simulation

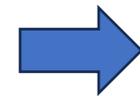
Since  $\sum_x \mathcal{G}_{x',x} \neq 1$  it cannot be interpreted as a transition probability.

The transition matrix  $p_{x',x}$  is obtained by  $p_{x',x} = \frac{\mathcal{G}_{x',x}}{b_x}$  where  $b_x = \sum_{x'} \mathcal{G}_{x',x}$

Driving equations (with weights)

The projection of WF

1) Generate  $x_{n+1} = x'$  with probability  $p_{x',x}$



$$\Psi_{k+1}(x') = \sum_x \mathcal{G}_{x',x} \Psi_k(x)$$

2) Update the weight with  $w_{n+1} = w_n b_x$

The random walk simulation can stochastically estimate the ground state

$$|\Psi_0\rangle$$

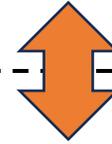
# Tip: Diffusion Monte Carlo

Langevin equation

$$\vec{x}_j(\tau + \delta\tau) = \vec{x}_j(\tau) + D\vec{F}(\vec{x})\delta\tau + \vec{N}(0, 2D\delta\tau)$$

Fokker–Planck equation

$$\frac{\partial \rho(\vec{x}, t)}{\partial t} = \sum_j D \vec{\nabla}_j \left[ \vec{\nabla}_j - \vec{F}_j(\vec{x}) \right] \rho(\vec{x}, t)$$



Corresponding random walks

$$\vec{X}_j(\tau + \delta\tau) = \vec{X}_j(\tau) + D\vec{F}(\vec{X})\delta\tau + \vec{N}(0, 2D\delta\tau)$$

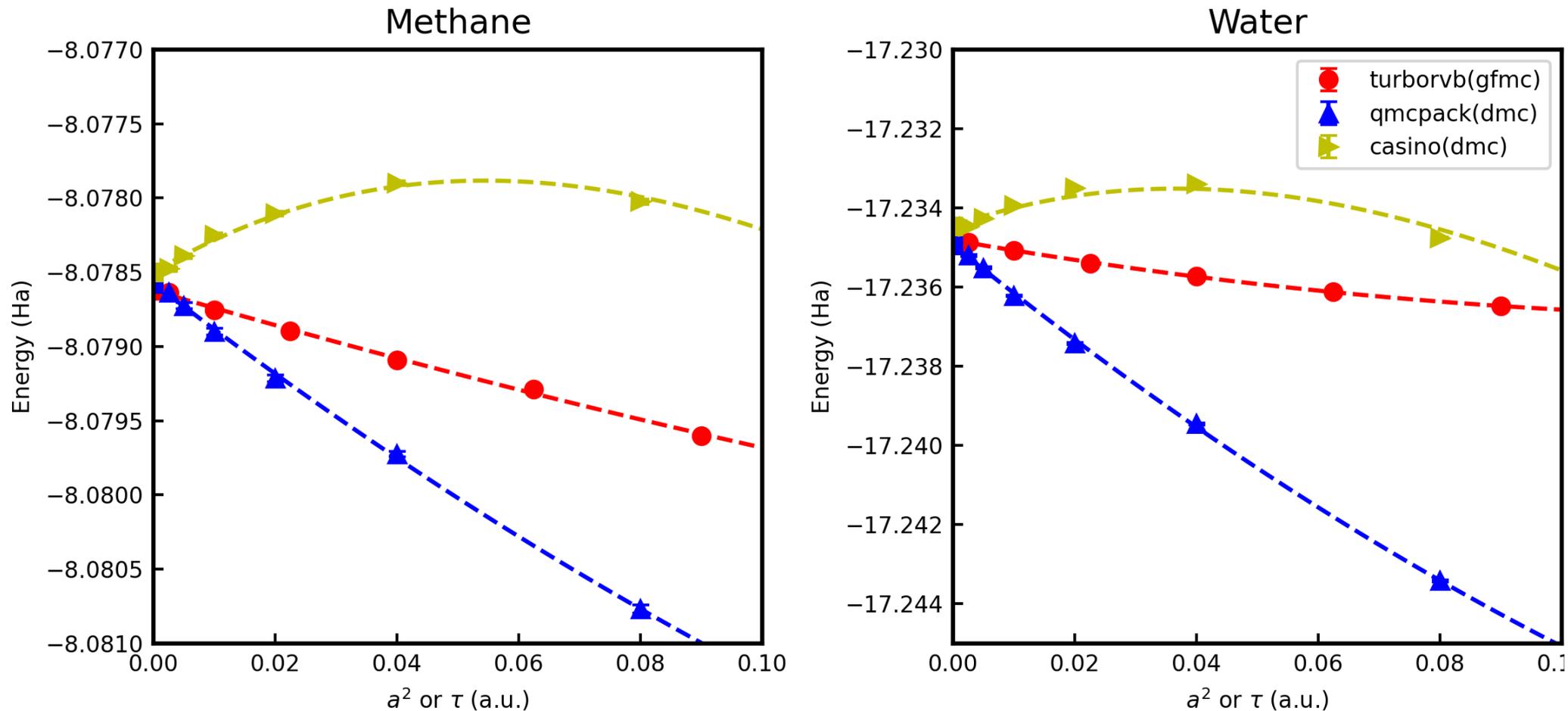
Schrödinger equation

$$-\frac{\partial \Psi(\vec{X}, \tau)}{\partial \tau} = \left( -\frac{1}{2} \sum_j \nabla_j^2 + \hat{V}(\vec{X}) - E_T \right) \Psi(\vec{X}, \tau)$$

Another implementation of the projection. DMC and GFMC give the same result.

# DMC v.s. GFMC

CH<sub>4</sub> and H<sub>2</sub>O molecules with cc-pVTZ basis and ccECP.

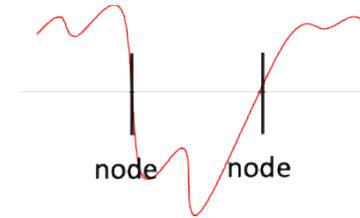


The data is taken from F.D. Pia et al., [arXiv:2501.12950](https://arxiv.org/abs/2501.12950) (2025).

# Importance sampling for Fermionic systems

To apply the GFMC for fermionic systems, a **guiding function** is needed to provide the nodal surface. Otherwise, the ground state is always bosonic.

(nodal surface: where the sign of a WF changes)



Modified projection

$$\Psi_{k+1}(x')\Psi_G(x') = \sum_x \mathcal{G}'_{x',x} \Psi_k(x)\Psi_G(x) \quad \mathcal{G}'_{x',x} = \mathcal{G}_{x',x} \frac{\Psi_G(x')}{\Psi_G(x)}$$

Remember that  $\mathcal{G}'_{x',x} > 0$  ( $\forall x, x'$ ) because it is interpreted as a probability.

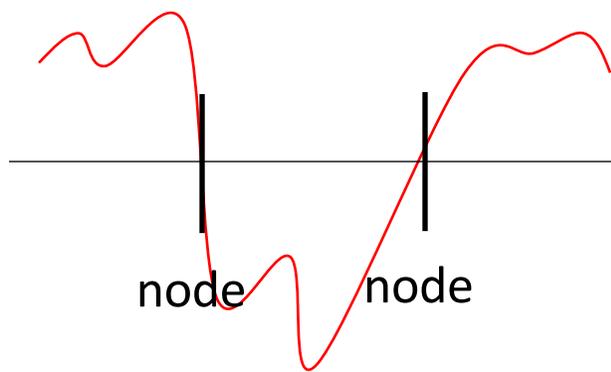
$$\mathcal{G}'_{x',x} \equiv \mathcal{G}_{x',x} \frac{\Psi_G(x')}{\Psi_G(x)} < 0 \text{ are neglected.} \quad \text{Notice } (\mathcal{G}_{x',x} \geq 0)$$

Walkers do not cross the nodal surface  $\rightarrow$  Sign problem!!

# The uncontrollable bias: Fixed-node approximation

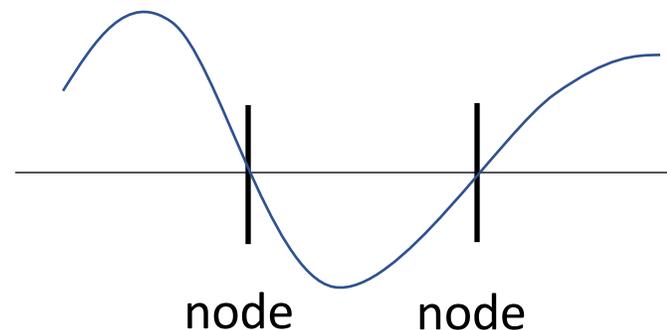
Ab initio Diffusion Monte Carlo (**DMC**): Given a nodal surface, provides the best wavefunction.  
(where the sign of a many-body WF changes.)

Trial WF (DFT or VMC)



Projection.

Fixed-node WF



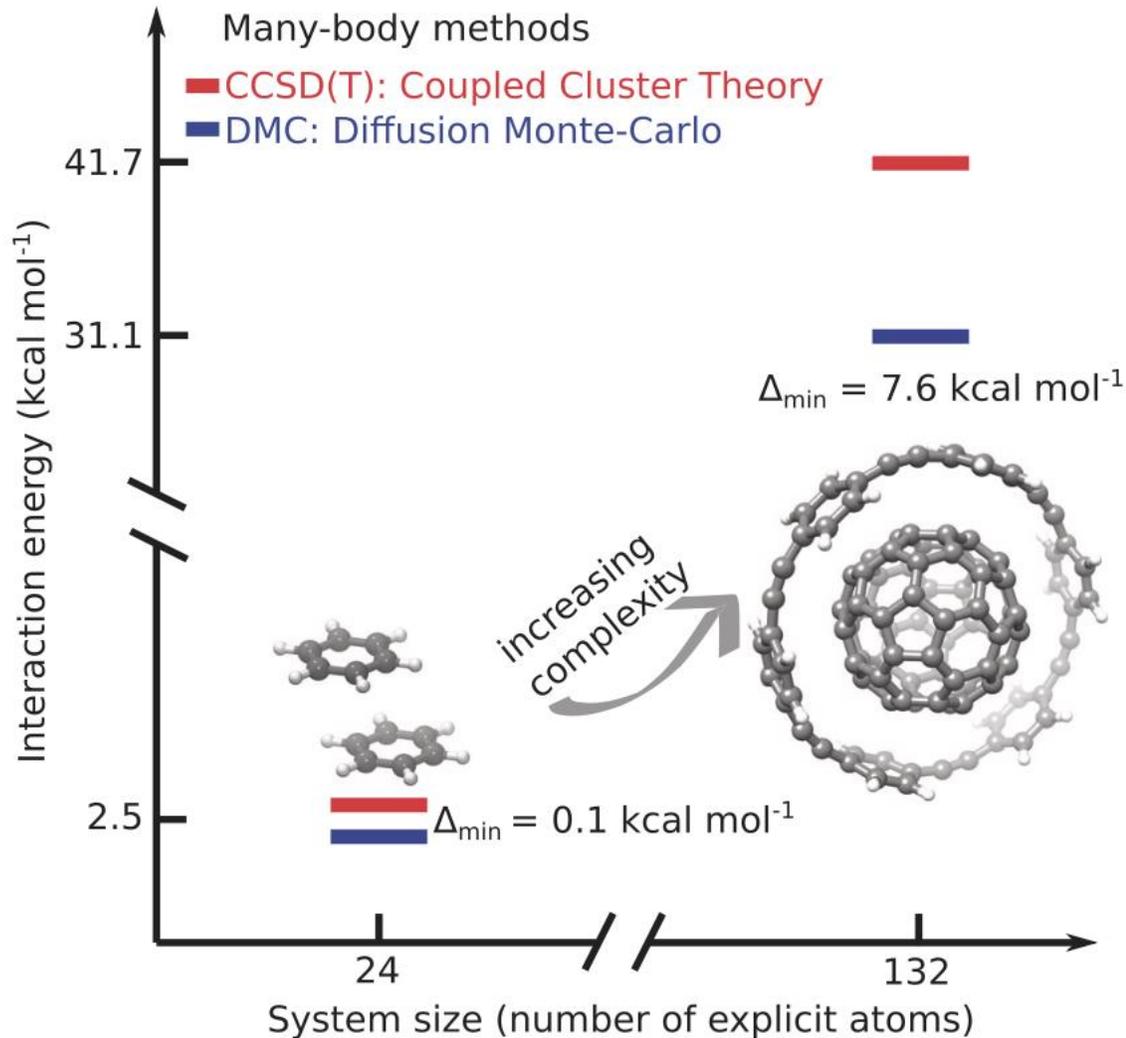
Relaxing the amplitude with the given Nodes.

W.M.C. Foulkes, et al. *Rev. Mod. Phys.* 73 33-83 (2001)

Since electrons are fermion, the nodal surface should be kept during DMC (the so-called sign-problem.).

The nodal surface is obtained by a mean-field approach such as DFT, introducing the uncontrollable bias.

# Advanced topic: DMC v.s. CCSD(T)



CCSD(T):

Gold standard in quantum chemistry

DMC (with DFT nodal surface):

Gold standard in condensed matter physics.

(exploiting nodal surfaces obtained by DFT)



- Binding energy calculations for large mol.-

Y.S. Al-Hamdani, et. al., *Nat. Commun.* 12, 3927 (2021)

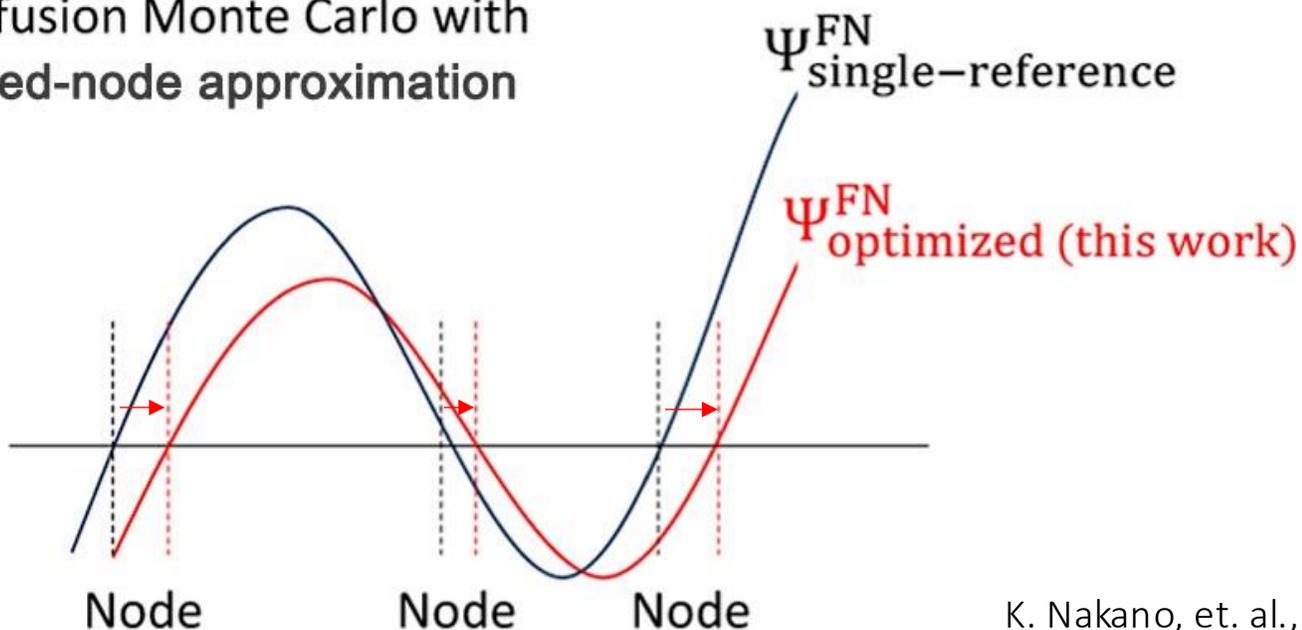
- Discrepancy for large mol. (~ 8kcal/mol).
- Under debate!! Which is correct?

# A possible remedy for the FN approximation

$$E(\vec{\alpha}) = \frac{\int d\vec{X} \Psi^*(\vec{X}, \vec{\alpha}) \hat{H} \Psi(\vec{X}, \vec{\alpha})}{\int d\vec{X} |\Psi(\vec{X}, \vec{\alpha})|^2} \geq E_0 \quad \text{Variational principle}$$

This also holds for GFMC, not only for MCMC.

Diffusion Monte Carlo with  
fixed-node approximation



1. GFMC

2. Compute  $\vec{f} = -\frac{\partial E}{\partial \vec{\alpha}}$

3. Update the nodal surface

# Nodal surface optimization by GFMC

## Beyond Single-Reference Fixed-Node Approximation in *Ab Initio* Diffusion Monte Carlo Using Antisymmetrized Geminal Power Applied to Systems with Hundreds of Electrons

Kousuke Nakano,\* Sandro Sorella, Dario Alf e, and Andrea Zen\*

Cite This: *J. Chem. Theory Comput.* 2024, 20, 4591–4604

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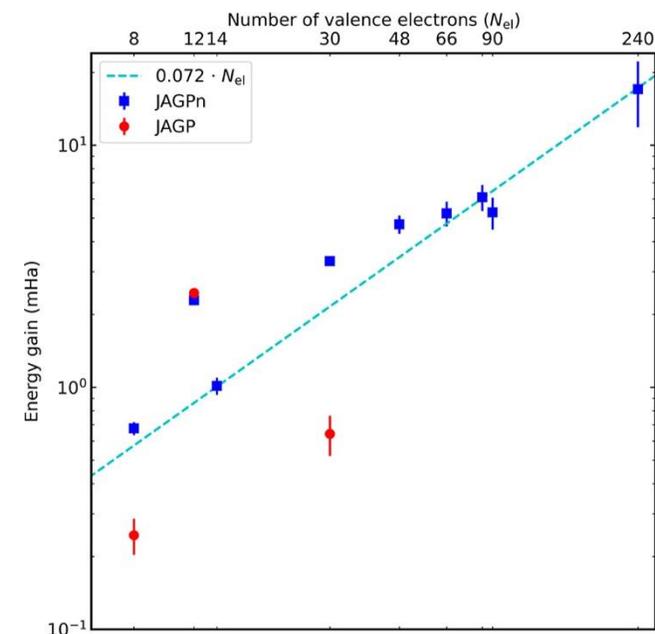
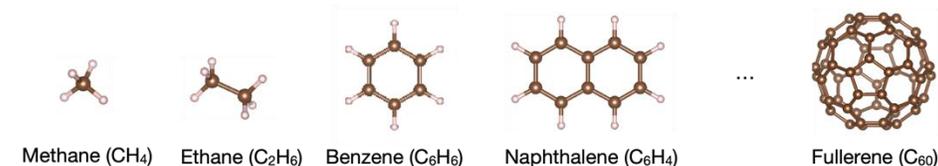
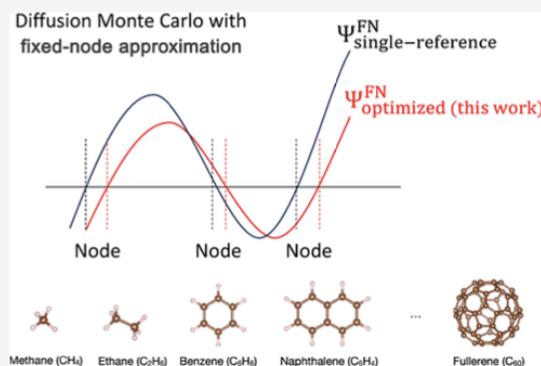
ACCESS |

Metrics & More

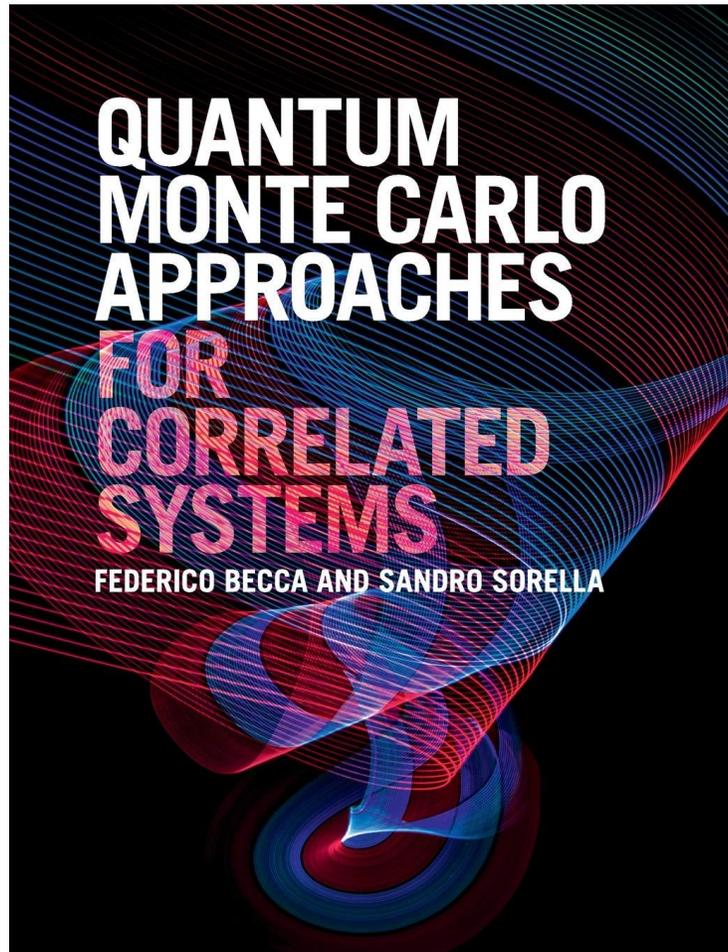
Article Recommendations

Supporting Information

**ABSTRACT:** Diffusion Monte Carlo (DMC) is an exact technique to project out the ground state (GS) of a Hamiltonian. Since the GS is always bosonic, in Fermionic systems, the projection needs to be carried out while imposing antisymmetric constraints, which is a nondeterministic polynomial hard problem. In practice, therefore, the application of DMC on electronic structure problems is made by employing the fixed-node (FN) approximation, consisting of performing DMC with the constraint of having a fixed, predefined nodal surface. How do we get the nodal surface? The typical approach, applied in systems having up to hundreds or even thousands of electrons, is to obtain the nodal surface from a preliminary mean-field approach (typically, a density functional theory calculation) used to obtain a single Slater determinant. This is known as single reference. In this paper, we propose a new approach, applicable to systems as large as the  $C_{60}$  fullerene,



# Textbook and Review papers



F. Becca and S. Sorella, Cambridge University Press (2017)

RESEARCH ARTICLE | MAY 29 2020

**TURBORVB: A many-body toolkit for *ab initio* electronic simulations by quantum Monte Carlo**

Special Collection: [Chemical Physics Software Collection](#), [Electronic Structure Software](#)

Kousuke Nakano ; Claudio Attaccalite ; Matteo Barborini ; Luca Capriotti ; Michele Casula ; Emanuele Coccia ; Mario Dagrada; Claudio Genovese ; Ye Luo ; Guglielmo Mazzola ; Andrea Zen ; Sandro Sorella

[Check for updates](#)

*J. Chem. Phys.* 152, 204121 (2020)  
<https://doi.org/10.1063/5.0005037>

K. Nakano\*, et al. *J. Chem. Phys.* 152, 204121 (2020)

特集 計算材料設計最前線 2024

## 第一原理量子 モンテカルロ法の 現状と物質科学分野 での応用展望

—原子に働く力の計算—

Current Status and Perspectives of *ab initio* Quantum Monte Carlo Methods in Materials Science

**Key-words**: *ab initio* calculation, Quantum Monte Carlo, Atomic force

中野 晃佑

Kosuke NAKANO (National Institute for Materials Science (NIMS))

### 2. 第一原理量子モンテカルロ法の概要

QMCは、多体シュレーディンガー方程式を、モンテカルロ法を使って解く手法であり、原理的には、XCのようなパラメタが必要ない理論的形式になっている。QMCの実装のうち、最も利用されている実空間のQMCとして、変分量子モンテカルロ法 (Variational Monte Carlo: VMC) と拡散量子モンテカルロ法 (Diffusion Monte Carlo: DMC) が挙げられる<sup>1)</sup>。

VMCが依拠する原理は、変分原理である。すなわち、所与の多体波動関数とそのエネルギーを  $\Psi(\vec{r}_1 \cdots \vec{r}_N)$ 、および  $E$ 、真の基底状態の多体波動関数とそのエネルギーを、 $\Psi_0(\vec{r}_1 \cdots \vec{r}_N)$ 、および  $E_0$ 、系のハミルトニアンを  $\hat{H}$  と表した時、

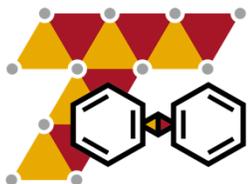
$$E = \frac{\int d\vec{r}_1 \cdots d\vec{r}_N \Psi^* (\vec{r}_1 \cdots \vec{r}_N) \hat{H} \Psi (\vec{r}_1 \cdots \vec{r}_N)}{\int d\vec{r}_1 \cdots d\vec{r}_N |\Psi (\vec{r}_1 \cdots \vec{r}_N)|^2} \geq E_0$$

中野晃佑, セラミックス, 11, 59 (2024)

# Outline

- Practical Tips for QMC calculations (software etc...)

# Our Quantum Monte Carlo packages



## TurboRVB

Quantum Monte Carlo Package 

QMC package (DFT, VMC/DMC-optimization, VMC, 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)



## TurboGenius

Python wrappers and command-line interfaces.

K. Nakano\*, et al., *J. Chem. Phys.* 159, 224801 (2023)

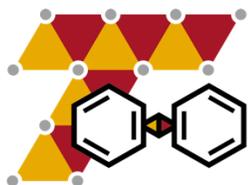


## TurboWorkflows

Workflow package realizing high-throughput calculations.

K. Nakano\*, et al., *J. Chem. Phys.* 159, 224801 (2023)

# Several features of TurboRVB



**TurboRVB**  
Quantum Monte Carlo Package 

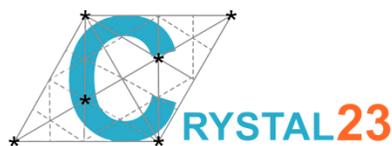
QMC package (DFT, VMC/DMC-optimization, VMC, DMC).

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)

- Open-source QMC package under GPLv3 license, available from GitHub.
- Written by Fortran90. Parallelized MPI and OPENMP.
- Ported to GPUs, by cuBLAS (cuLAPACK) and OpenACC.
- Localized orbitals (e.g. , GTOs) are employed both for molecules and crystals.
- Beyond the Slater-determinant ansatz, AGP and Pfaffian.

Refactoring and documenting the code is in progress (in FY2025).

# High-throughput QMC calculations



Any DFT codes employing localized AOs can be used.



**TurboRVB**  
Quantum Monte Carlo Package SISSA

VMCopt → VMC → DMC

Submit



Collect

by paramiko



Fugaku (RIKEN)



Leonardo (CINECA)

K. Nakano\*, et al., *J. Chem. Phys.* 159, 224801 (2023)

Routine QMC calculations are automatized! Make the most of our human resources!!

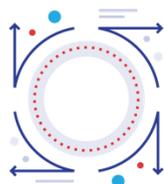
# Community efforts: Common WF format

The Journal  
of Chemical Physics

ARTICLE

scitation.org/journal/jcp

## TREXIO: A file format and library for quantum chemistry



Cite as: *J. Chem. Phys.* **158**, 174801 (2023); doi: [10.1063/5.0148161](https://doi.org/10.1063/5.0148161)  
Submitted: 28 February 2023 • Accepted: 4 April 2023 •  
Published Online: 5 May 2023



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Kosuke Nakano,<sup>7,8</sup> Otto Kohulák,<sup>1,8,a)</sup> Sandro Sorella,<sup>8</sup> Pablo de Oliveira Castro,<sup>9</sup>   
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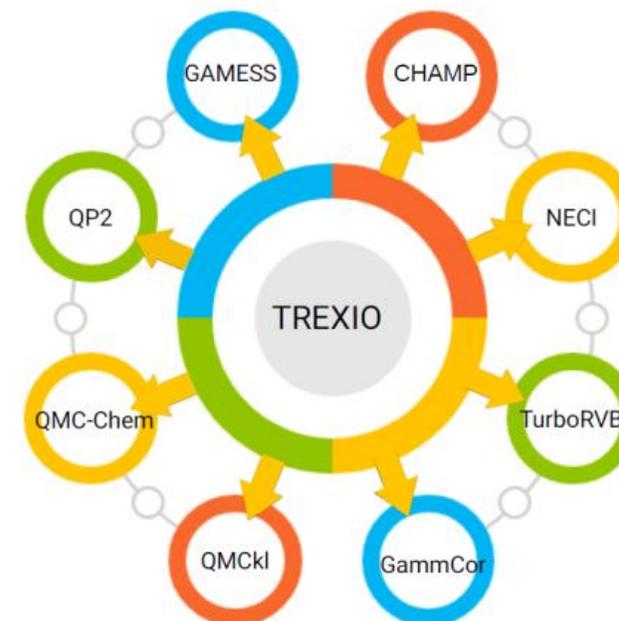
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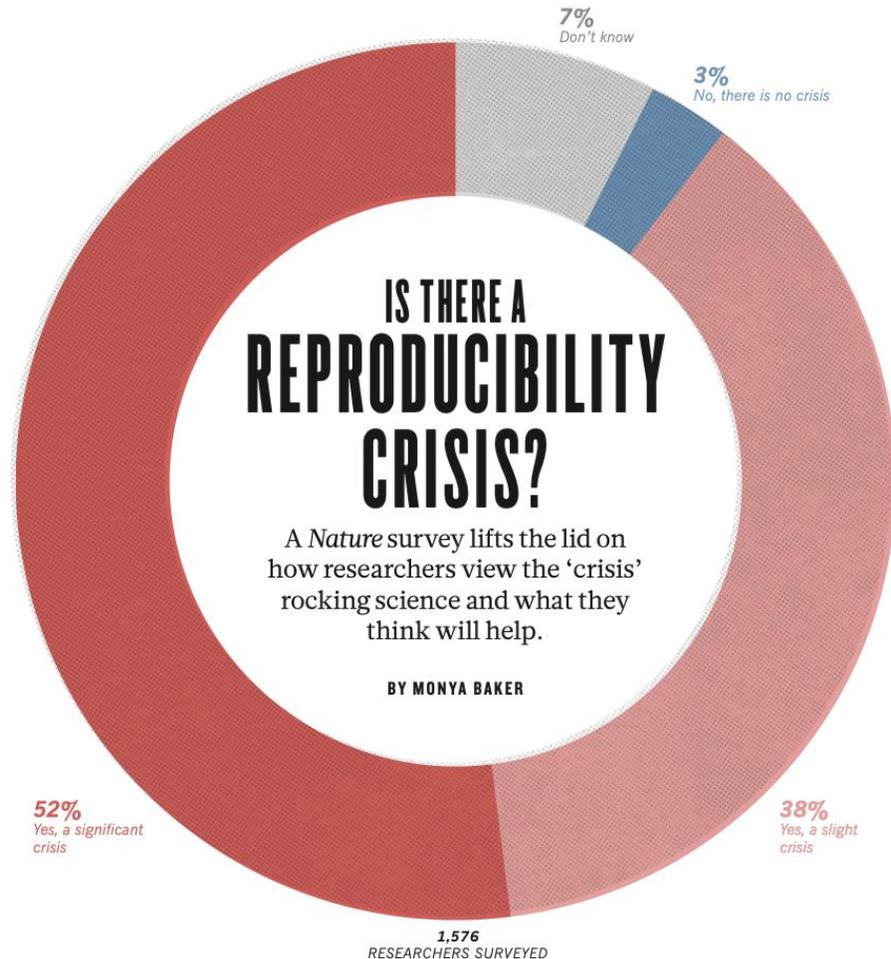
- I/O for the common WF format

<https://github.com/TREX-CoE/trexio>

- Converters are available from

[https://github.com/TREX-CoE/trexio\\_tools](https://github.com/TREX-CoE/trexio_tools)

# Reproducibility crisis in Science ...



## Report on Reproducibility in Condensed Matter Physics

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Dated: January 27, 2025

# Reproducibility among community DFT codes

## RESEARCH ARTICLE SUMMARY

### DFT METHODS

## Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,\* Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dułak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iuşan, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepernik, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt I. J. Probert, Keith Refson, Manuel Richter, Gian-Marco Rignanese, Santanu Saha, Matthias Scheffler, Martin Schlipf, Karlheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier\*

DFT codes. The essential part of this assessment is a pairwise comparison of a wide range of methods with respect to their predictions of the equations of state of the elemental crystals. This effort required the combined expertise of a large group of code developers and expert users.

**RESULTS:** We calculated equation-of-state data for four classes of DFT implementations, totaling 40 methods. Most codes agree very well, with pairwise differences that are comparable to those between different high-precision experiments.

### ON OUR WEB SITE

Read the full article at <http://dx.doi.org/10.1126/science.aad3000>

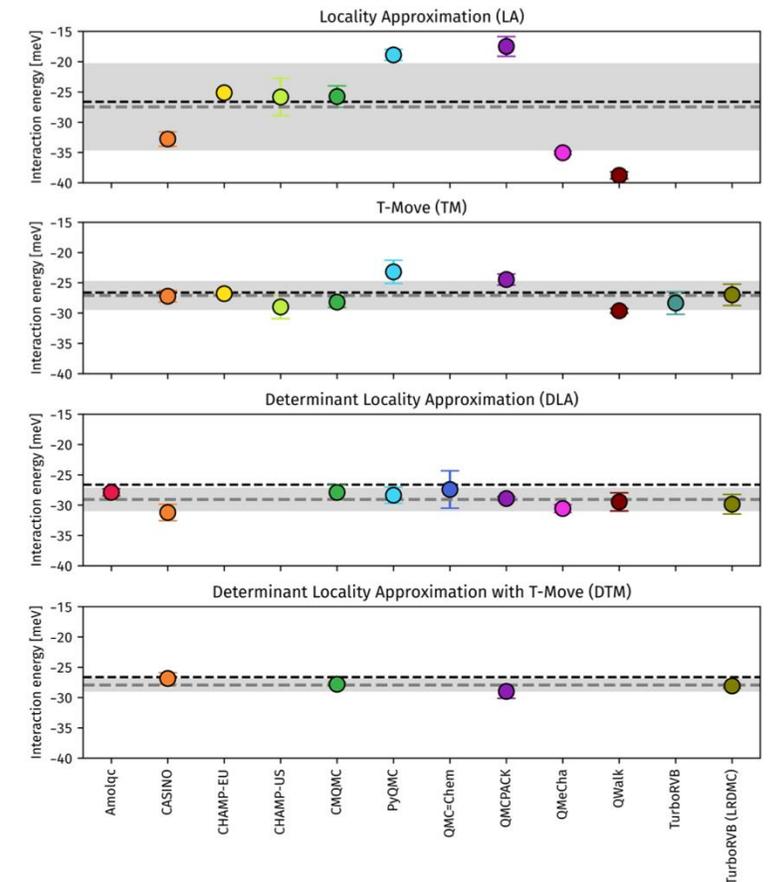
Even in the case of pseudization approaches, which largely depend on the atomic potentials used, a similar precision can be obtained as when using the full potential. The remaining deviations are due to subtle effects, such as specific numerical implementations or the treatment of relativistic terms.

**CONCLUSION:** Our work demonstrates that the precision of DFT implementations can be determined, even in the absence of one absolute

# Reproducibility among community QMC codes

Is fixed-node diffusion quantum Monte Carlo reproducible?

Flaviano Della Pia<sup>\*1</sup>, Benjamin X. Shi<sup>\*1</sup>, Yasmine S. Al-Hamdani<sup>2</sup>, Dario Alfè<sup>2,3</sup>, Tyler A. Anderson<sup>4</sup>, Matteo Barborini<sup>5</sup>, Anouar Benali<sup>6</sup>, Michele Casula<sup>7</sup>, Neil Drummond<sup>8</sup>, Matúš Dubecký<sup>9</sup>, Claudia Filippi<sup>10</sup>, Paul R. C. Kent<sup>11</sup>, Jaron T. Krogel<sup>12</sup>, Pablo López Ríos<sup>13</sup>, Arne Lüchow<sup>14</sup>, Ye Luo<sup>6</sup>, Angelos Michaelides<sup>1</sup>, Lubos Mitas<sup>15</sup>, Kousuke Nakano<sup>16</sup>, Richard Needs<sup>17</sup>, Manolo C. Per<sup>18</sup>, Anthony Scemama<sup>19</sup>, Jil Schultze<sup>14</sup>, Ravindra Shinde<sup>10</sup>, Emiel Sloutman<sup>10</sup>, Sandro Sorella<sup>20</sup>, Alexandre Tkatchenko<sup>21</sup>, Mike Towler<sup>22</sup>, C. J. Umrigar<sup>4</sup>, Lucas K. Wagner<sup>23</sup>, William A. Wheeler<sup>24</sup>, Haihan Zhou<sup>25</sup>, and Andrea Zen<sup>†2,3</sup>



F.D. Pia et al., *arXiv*:2501.12950 (2025).

We did a similar verification among 11 QMC community codes!!

# Acknowledgements



**EOF**